

Lithium-Ion Battery Recycling: Challenges and Opportunities

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Abstract. The handling of lithium-ion batteries (LIBs) has emerged as a critical environmental concern as more and more people select electric automobiles and electric cars are seen on the road more regularly. If the spent LIBs are not recovered in time, they will cause serious damage both ecologically and socially harmful. Through recycling, the environmental impact of LIBs can be greatly reduced, and valuable materials can be recovered. In this research, the current situation of LIBs recycling methods, including pyrometallurgy, direct recycling methods and hydrometallurgy are reviewed. Pyrometallurgical recycling is a widely used method which can use little pretreatment. It uses high temperature reaction to reduce the and recover valuable metals. In the hydrometallurgy, chemical leaching of LIBs enables the extraction of several different metals, including lithium, cobalt, manganese, nickel, and aluminum. It is more efficient to refine and separate metals using hydrometallurgy. Direct recycling is a promising approach that recycles valuable metals directly rather than transforming them into raw materials through the application of physical and chemical processes. In conclusion, recycling lithium-ion batteries is a crucial industry that may help address environmental issues and offer a reliable source of valuable resources. The development of LIBs recycling has great prospects and can aid in the sustainable exploitation of resources.

Keywords: Recycling, Lithium-ion battery, Pyrometallurgy, Hydrometallurgy, Direct recycling.

1. Introduction

The vehicle which uses an internal combustion engine is the main type of vehicles that most people used in the past. It consumes fossil fuels and produce toxic gases. It is estimated that nearly thirty percent of all emissions of greenhouse gases and a quarter of worldwide carbon dioxide emissions related to energy come from the transportation sector. In order to reduce emissions and save conventional automotive fuels, many vehicle manufacturers start to develop electric vehicles vigorously. Electrolyte in a LIB is a mixture of organic solvents and Li salts, while the battery itself consists of an anode, a cathode, current collectors, and the electrolyte itself. Co, Li, and Ni are frequently sought for for recycling because they are found in LIBs. The number of electric vehicles has been rising rapidly in recent years due to their rapid development so lithium-ion batteries which mainly used in EVs cause a recycling problem. One reason is that LIBs have a high concentration of harmful electrolyte and heavy metals. Their triggers can constitute a harm to the environment and to public health if they are disposed of improperly. The deposited lithium on the anode, which is formed during each consecutive cycle of discharge and recharge, has the potential to react vigorously with water, which could result in an unsafe situation. By recycling old LIBs, valuable metals like Co, Ni, and Li can be recovered, allowing for the establishment of a steady supply system for these elements. So, by limiting increased raw material consumption and environmental contamination, the effective recycling of wasted LIBs would have positive economic and environmental effects.

Currently, there are three main ways to recycle lithium batteries: pyrometallurgy, hydrometallurgy, and direct recycling. Before using these methods to recycle LIBs, pretreatments should be made. Pretreatments make it possible to sort metal components, materials, and scrap into distinct piles with equivalent physical qualities, resulting in increased recovery rates and less energy usage. In the discipline of pyrometallurgy, metals are extracted and purified from ores, concentrates, and recycled materials using high temperatures. Several different metals, including copper, lead, zinc, nickel, chromium, and iron, are extracted via pyrometallurgy. While pyrometallurgy offers numerous benefits, including its adaptability to many different materials, it also has several drawbacks. High energy use and environmental effects are two of these. Metals are dissolved, transported, and

separated while they are in a liquid form in the hydrometallurgy metallurgical process. It can handle a wider range of ore types and chemical composition; hydrometallurgy is more efficient at purifying and isolating metals. A promising approach to manufacturing sustainably is direct recycling. Recovering the active cathode particle without converting it to substitute components or dissolving and precipitating the entire thing makes it more effective than traditional approaches [1].

This article aims to review the previous studies on recycling of spent LIBs and summarize some recent ways of recycling, hoping to help future scholars reference.

2. Pretreatment

In the equivalent pyrometallurgical or hydrometallurgical processes, pretreatments allow metal components, materials, and scrap to be separated and provide identical physical qualities that lead to higher recovery rates and less energy consumption. Seo Kim et al. determined the extent and the order of the pre-treatment operations, which are broken down into the following categories: discharge, disassembly, comminution, classification, separation, dissolution, and thermal treatment [2]. A subsequent section provides more in-depth details on each pretreatment stage.

The pyrometallurgical process does not require a pretreatment. The pretreatment process differs significantly from hydrometallurgical or direct recycling. In certain situations, pretreatment phases can be exchanged the order or be omitted. This paper will introduce pretreatment from the above several pretreatment processes.

2.1. Discharge

When disassembling used LIBs, the anode and cathode frequently make contact, resulting in a short circuit and a loss of power. Inflammation of the batteries is caused by this current, which ignites the flammable solvent in the electrolyte. To be able to forestall any potential for a fire or electrical short, it is required to discharge the battery as a pretreatment step before disassembling the battery. In most cases, discharge can be accomplished through the use of salt solutions, or through ohmic discharge. The discharge process can be accomplished in a straightforward and effective manner by using salts, such as sodium chloride (NaCl). Yet, this procedure is not only costly but also time-consuming. Water and iron are used in the mechanical mixing process in ohmic discharge. It is highly effective despite having a greater degree of complexity [3].

2.2. Disassembly

Disassembly is used to describe the manual or automated operations required to remove cell packaging and gain access to the active components. Cutting tools are used to manually open the cells, releasing their contents, these are then separated by hand into anode, cathode, and separator, respectively. Due to the toxicity of chemical ingredients, disassembly by hand may bring about a number of health and safety hazards. This provides for the possibility of automating the process of disassembly. Also, automated disassembly should be very efficient and be able to meet the needs of an industrial scale.

2.3. Comminution

Crushing and grinding are needed to release the electrode material from the disassembled LIBs. Dismantling a LIB safely requires a lot of time and effort due to the complexity of the structure and the risks of electric shock and fire. Because of this, many existing methods begin with comminution, just like lead acid batteries do. However, this needs additional time, energy, and ancillary processing chemicals. Fairuz Alfalah Wibisono et al. used the ABAQUS/Explicit solver to run dynamic finite element simulations to see how well three models of battery materials respond to loads. The discovery can be used to figure out the right shapes for cutting tools, figure out how much energy the comminution process uses, and get an idea of how big the comminution product will be [4].

2.4. Classification

It is typically essential to separate batteries during the recycling process to ensure that lithium batteries can be disposed of and recycled in a proper manner. In most cases, the procedure for classifying LIBs entails conducting tests and analyses pertaining to the physicochemical qualities of those batteries. Recycling lithium batteries in a way that maximizes recovery, minimizes waste, and assures a safe and ecologically responsible process requires that the batteries be sorted. For instance, the experiment done by Zhan et al. reveal that in order to take into account the LIBs' direct recycling, the constituent components from the cathode composites were de-agglomerated utilizing a wet agitation technique in a blender. By employing the froth flotation method to separate the mixture according to the level of surface hydrophobicity, the performance of the process has been assessed [5].

2.5. Separation

Once the LIB comminution products have been initially separated, further refined methods such as magnetic, eddy current, electrostatic, separation by gravity, and flotation with froth are used. In the LIB recycling process, Fe-containing components are typically removed via magnetic separation. High induction magnetic separators are used on an industrial scale in the Recupyl process to effectively take apart the metal pieces. Densimetric tables are used to classify nonmagnetic materials based on their relative density differences [6]. Of course, there are many other methods of separation ways.

2.6. Dissolution

Dissolution is typically used to remove metal components from batteries, including cobalt, nickel, lithium, etc. Through the application of extraction and dissolution techniques, these metals can be salvaged and reused. The positive and negative electrodes in the battery must first be removed separately and treated in the appropriate acidic or alkaline solution before the dissolution process can begin. Solvents like sulfuric acid, sodium hydroxide, potassium hydroxide, and similar compounds are widely used. He et al. used a Na-salt-free aqueous exfoliating and extracting solution to make it easier to recycle LIBs that contained LFP and NMC [7]. Recent advances in solid-liquid extraction have looked into ionic liquids for the solubility of Li, Co, Ni, and Mn oxides, as well as solvent extraction for a selective separation, in order to achieve a high yield [8].

2.7. Thermal treatment

Used lithium-ion batteries have important materials recovered through mechanical separation and thermal treatment. Wang et al. designed a roasting and flotation technique that successfully recovered the metal values and graphite from crushed spent LIBs products. The recovery rate was 97.66% and the concentration of Co in the LiCoO_2 concentrate reached 40.12 weight percent [9].

3. Pyrometallurgy

The organic material is evaporated out during the pyrometallurgical process, and the cathode and anode react to make the lithium water soluble. Valuable metals are reduced during the pyrometallurgy process and subsequently recovered as alloys.

3.1. Roasting

In an oxidizing atmosphere, roasting removes undesirable sulfur and carbon from sulfide/carbonate ore, leaving an oxide behind. The extraction of cathode materials via a chemical reaction can also be accomplished through the roasting process. For instance, the sulfation roasting process is utilized in order to treat the LiCoO_2 compound [10].

3.2. Calcination

Broadly speaking, calcination refers to a class of thermal treatments for solid materials that take place in the absence of or with a very low supply of oxygen or air. Calcination is a common step in the metallurgical processing of minerals that can be further reduced to a useful chemical. It has been observed that the calcination process may result in the production of hazardous gases. Hence, it is recommended that an implementation of exhaust gas collection technology or following treatment to reduce pollution [11].

3.3. Reduction

The lithium metal oxides (LMOs) are left over after the metal scraps have been separated out during the pretreatment procedure. It is feasible to breakdown LMOs at high temperatures to produce lithium oxide and metal oxides, but this uses a lot more energy, and the subsequent extraction procedure makes it difficult to separate Li_2O and metal oxides [11].

Carbon vacuum pyrolysis was demonstrated by Xiao et al. to reduce LiCoO_2 . LiCoO_2 was reduced by carbothermic reaction to CoO or Co and Li_2CO_3 in a vacuum at high temperatures [12].

3.4. Methods of Pyrometallurgy

A study compared the Sc-1 and Sc-2 direct current plasma smelting systems and the ultrahigh temperature (UHT) furnace, two alternative pyrometallurgical methods for recovering precious metals from LIBs (Sc-3). The study demonstrated that switching from direct current plasma arc technology (Sc-1 and Sc-2) to UHT furnace technology (Sc-3) can lower the overall the possibility of global warming of the entire recycling process [13].

It was proposed that chlorination roasting may be used to recover lithium from pyro-slag through evaporation. Findings showed that most of the $\text{LiAl}(\text{SiO}_3)_2$ in the ash was converted to LiCl [14]. This research suggested that chlorination roasting, which occurs after thermal treatment of the used LIBs, could be an effective method.

The pyro-methods have the advantage of being simple to expand for use in large-scale industries, but they are also very energy-intensive, produce harmful byproducts, and have low extraction rates.

4. Hydrometallurgy

In the metallurgy process known as hydrometallurgy, metals are dissolved, transferred, and separated while they are in a liquid state. Leaching LIBs with chemicals allows for the extraction of a number of different metals, including cobalt, nickel and lithium, among others [15]. Hydrometallurgy is more effective in refining and separating metals because it can process a greater variety of ore types and chemical compositions. The recovery procedure often entails processes like leaching, extraction, distillation, and electrode positioning.

First of all, Leaching is the process of dissolving the lithium battery cathode substance containing metal ions that is obtained after it has been disassembled into a chemical solution. The following phase of processing is the leaching solution to remove metal ions. After that, the organic solvent is distilled away, leaving behind the metal-containing organic liquid phase and the inorganic phase. Ultimately, electrodeposition is used to transform pure metal salts into pure metals.

In one work, LiCoO_2 produced from LIBs was leached in a sulfuric acid solution using ethanol. The addition of 5% vol% ethanol to a 6 mol/L sulfuric acid solution at 90 °C resulted in an extraction efficiency of greater than 99% for both Co and Li, suggesting that the ethanol is capable of converting Co^{3+} to Co^{2+} while becoming acetic acid [16]. Using ethanol as a reducing agent broadens the pool of potential reagents for acid leaching methods.

Chen et al. employed nitric acid and ascorbic acid combinations to dissolve the positive electrode components. Furthermore, leaching reactions and solid characterization were also examined with XPS, XRF, XRD, and other techniques. The findings demonstrated that in the studies carried out

under the most favorable conditions, lithium, manganese, cobalt, and nickel all had near-perfect leaching efficiency within 10 minutes [17].

5. Direct Recycling

Direct recycling refers to directly recycling used lithium batteries after disassembling them instead of converting them into raw materials through physical and chemical methods. In the process of direct recycling, useful materials are extracted directly, and harmful substances are not discharged into the environment. The separation, extraction, regeneration, and refinement processes can all make use of the beneficial elements found in batteries. To extract valuable materials from spent batteries, these operations can be accomplished via mechanical separation, magnetic separation, physical separation, gravity separation, and other techniques. The higher purity metal materials created from these valuable elements can then be refined through metallurgy. Compared to recycling technologies based on metallurgy, direct recovery could be better for the environment and the economy, but only if it takes less energy and chemicals to recover electroactive materials with the same purity and performance as commercial ones than it does to make new ones [18].

a successful and environmentally responsible approach of LIB regeneration based on healing specific to defects was disclosed by Xu et al. This offered a paradigm-shifting approach to LIB recycling. Spent LiFePO_4 (LFP) cathodes were demonstrated to be quickly regenerable via cold conditions aqueous lithiation and fast post-annealing, making this material one of the most significant for electric vehicles and network storage applications [19].

In a study, an environmentally friendly method of making and recycling LIBs was outlined. In this process, water was used in place of N-methyl-2-pyrrolidone (NMP) when making electrodes, and a combination of active substance with carbon black was recovered by separating it from the current collector and dissolving the water-soluble binder in water. To create battery-grade material, the active component of carbon black was isolated and relitigated [20].

6. Conclusion

Used LIBs can be recycled to can increase the efficiency of natural materials and enhances human economic and environmental sustainability. This paper discusses the various recycling methods and review their physicochemical characteristics and mechanism. Direct recycling, hydrometallurgy, and pyrometallurgy are the three most common types of recycling processes.

Pretreatments are required before utilizing these techniques because they enable the separation of metal components, materials, and scrap and give identical physical qualities that increase recovery rates while using less energy. The selection and improvement of pretreatment technology for lithium battery recycling is very important to improve the recovery rate and resource utilization rate of LIBs. Pyrometallurgy has the following processes: roasting, calcination and reduction. Large amounts of waste and exhaust gases are produced during pyrometallurgy, which involves high temperature settings and complicated reaction processes that might result in energy consumption and pollution issues. Hydrometallurgy is a research hotspot in the field of lithium battery recycling. This paper describes three studies. By using ethanol as a reducing agent, there are more alternatives available when selecting reducing agents for acid leaching procedures. Leaching efficiencies of using nitric acid and ascorbic acid combinations are high. $\text{H}_2\text{C}_2\text{O}_4$ and H_2O_2 can be used in extract Li and Co. Hopefully, researchers can further improve the chemical reagents and leaching conditions to enhance metal recovery rate. Direct recycling has great potential in improving recovery efficiency and reducing cost. Defect-targeted healing is a relatively new technology, and it is effective and environmentally friendly. But further study is required to address the technical issues with direct recovery technology.

In conclusion, recycling lithium batteries presents both challenges and opportunities, but people are confident that through concerted work, better and more long-lasting recycling methods will be developed in the near future.

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