

Recycling Technology of Waste Lithium Batteries

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Abstract. Lithium-ion batteries (LIBs) are key components in new energy vehicles, portable electronic devices, energy storage systems, and other fields due to their advantages of high energy density, long cycle life, and no memory effect. However, the wide application of Li-ion batteries has also brought about a problem that cannot be ignored. The number of used lithium-ion batteries has increased dramatically. Globally, the number of lithium-ion batteries scrapped each year has reached a staggering scale, which is still growing at an alarming rate. At the same time, with the popularity of smartphones, tablet PCs, laptops, and other electronic products and the speed of replacement, the lithium-ion batteries used in these devices are also facing the problem of decommissioning and disposal. The accumulation and improper disposal of used lithium-ion batteries not only occupy a large amount of land resources, exacerbate the pressure of municipal waste disposal, but also pose a potential threat to the ecological environment. Therefore, this paper summarises the current recycling technologies of used lithium-ion batteries, mainly involving the recovery of positive and negative materials, aiming to solve the occurrence of these problems.

Keywords: LIBs, waste, recycling, electrode material.

1. Introduction

In today's wave of global energy transition and sustainable development, LIBs are leading a profound energy revolution as the core of new energy technologies. From the powerful drive of electric vehicles to the continuous power supply of portable electronic devices, from the construction of large-scale energy storage systems to the flexible scheduling of smart grids, lithium-ion batteries, with their high energy density, long cycle life, fast charging and discharging capabilities, and environmental friendliness, have become a key cornerstone to support the green, low-carbon, and high-efficiency operation of modern society. However, with the wide popularity of lithium-ion battery applications, the disposal problem at the end of its life cycle has become increasingly prominent, and the recycling and reuse of used lithium-ion batteries has become a global environmental challenge that needs to be solved urgently, as well as a significant issue of resource recycling [1]. In recent years, with the booming development of the new energy vehicle industry, especially the rapid growth of the electric vehicle market, the number of used lithium-ion batteries has shown explosive growth. The International Energy Agency and other institutions predict that in the next few years, the world will have millions of tonnes of lithium-ion batteries to reach the retirement period. Suppose these used batteries are not properly disposed of. In that case, they will not only occupy a large amount of land resources but also may leak heavy metals, organic solvents, and other harmful substances, causing long-term and severe pollution of soil, water, and even the entire ecosystem [2]. At the same time, cobalt, nickel, manganese, lithium, and other rare metal resources contained in used batteries, if effectively recovered, will significantly ease the global resource constraints and promote the recycling of resources. Currently, the recycling technology of used lithium-ion batteries mainly includes three categories: physical, chemical, and biological. Physical recycling is primarily through crushing, sorting, and other means, directly recovering valuable materials in the battery; chemical recycling uses chemical reactions to extract the metal elements in the battery; biological recycling is an emerging technology, using microorganisms or the role of enzymes to achieve biodegradation of battery materials and metal recovery. Although these technologies have made some progress in the laboratory stage, they still face many challenges in practical application [3].

Therefore, this paper focuses on recovering electrode materials from used LIBs, summarises the current research progress, and analyses future development direction.

2. Pre-treatment of Waste Lithium-ion Batteries

2.1. Dismantling

Disassembly is the first and critical step in the recycling process of waste LIBs. It is a process that intends to mechanically disassemble items present in batteries, such as casing electrodes and electrolytes. Relaxation is necessary to simplify the structure of the batteries and decrease the energy consumption required to recycle and the costs for each step. These include shredding and crushing, mainly used in industries that use this type of separation. These methods are not only efficient in the disintegration of the physical structure of the batteries but also assist in the separation of risky elements from feasible recyclable materials [4]. Primary demineralization is essential as it sets a base on which the integrates may undergo one or more treatments, like solubilization or direct extraction, by properly managing their physical state.

Further, dismantling a battery's structure is contrived to avoid valuable materials and effectless contact between the structures of batteries. For example, it is easier to extract the active materials – lithium and cobalt- when separating electrodes from the casing without contaminating other materials [5]. Subsequent mechanical methods of dismantling have also adopted automation and high-precision tools that have not only improved the recoveries but also cut the cost of person-hour in dismantling. As such, the last step of this process aims at creating a homogenous and pure material feed for following recycling operations while at the same time achieving the highest material recovery and potential for a profitable recycling process at hand [6].

2.2. Dissolution

Dissolution, a technique used in LIB recycling before other processes, uses chemical reactions to disintegrate certain parts of the battery, especially the active electrode materials. This method is ideal for recovering precious metals to develop new batteries, such as lithium, cobalt, and nickel. During the dissolution process, solvents or acids dissolve the active materials from the electrode to isolate them from all other materials, such as the shell, usually made of metallic or plastic material, and the separators [7]. The selection of the chemical agents is essential as it impacts the dissolution process effectiveness and the quality of the separated materials. Once disintegrated, it is possible to recover the valuable metals from the solution and purify them for appropriate recycling; hence, dissolution forms part of the LIB recycling process.

This is mainly because dissolution is another process that enables the recovery of metals in a handy form, requiring minimal purification. Nevertheless, the process must involve the precise control of chemical reactions to minimize the generation of undesired side products, which might affect the quality of the reprocessed materials [8]. The new development has centered on the factors that control solubility, time, temperature, and solvent concentration to enhance the recovery efficiency with the least environmental harm. Moreover, new solvents and acids that are more environmentally friendly are also being investigated to replace traditional ones with the view of advancing green dissolution processes that can be scaled up as well [9]. In totality, dissolution continues to be one of the core processes of recycling LIBs to enable the recovery and reuse of valuable metals.

3. Cathode Material Recovery Technology

3.1. Wet Recovery

Wet methods are essential in recycling LIBs, especially in recovering valuable metals from cathodes. These techniques mainly encompass the application of liquid solvents that selectively dissolve such active metals as lithium, cobalt, and nickel from the cathode. First, the extraction

encompasses leaching under which the metals are dissolved with an effective solvent, usually an acid. This step is crucial because it defines how effective the metal recovery process will be; the solvent and conditions for leaching, such as temperature, pH, and concentration of the solution, are essential factors that must be considered for maximum dissolution of the metal ions. Afterward, leaching allows the separation of the valuable metals from the other constituent of the cathode that is less valuable or useful.

After leaching, the dissolved metals are precipitated by making the solution condition so that the metals precipitate out of the solution. Precipitation is another differentiation process that enables the collection of individual metals due to their chemical behavior differences. For instance, a change in pH level or the introduction of some specific chemicals causes the sedimentation of cobalt. At the same time, lithium and nickel remain dissolved in solution. This selective recovery is handy since it makes further processing and refining processes less complex. Following the precipitation process, the metals are often purified additionally, for example, by solvent extraction where bulk impurities remain, thus yielding high-purity metals that can be used to fabricate new batteries.

The main advantage of wet recovery techniques is that they yield higher recovery rates while requiring less energy than other methods. It can be done at relatively lower temperatures, lowering the energy needed and, hence, the pollution level [9]. Moreover, compared to other recycling techniques, wet recovery is compatible with numerous types of cathode materials, thus allowing the recycling of many LIB chemistries with its help. However, applying solvents and acids in its processing incurs problems in waste liquid disposal, which is an environmental nuisance. There have been advancements in the works to identify less hazardous solvents and more effective methods to reduce these impacts while achieving a very high recovery rate, such as the wet type of recovery [10].

3.2. Dry Recovery

The dry recovery entails using thermal and mechanical approaches to extract preferable metals from the cathode of the obsolete Li-ion batteries. The pyrometallurgical process is one of the common dry methods of recovering battery materials, where the materials are exposed to heat to melt the metals and then/or separate them. In this case, lithium and cobalt, alloys that melt at low temperatures, are first separated, while other constituents that may be found to melt at high temperatures are left behind. Depending on what is being produced, the molten metals can then be cooled and solidified, and this way, it becomes easy to separate the metals and package them for the following process or reuse. Pyrometallurgy is most commendable given that it deals with large quantities of battery waste and makes it possible to recover the metals in record time.

The other significant step in dry recovery is sorting, which involves physical techniques like grinding the batteries, sifting, and using a magnet to segregate the cathode components from the other battery materials. The grinding process makes the battery materials in fine powder so the particles can be sorted using a sieve based on size. These may include further processing through one or more techniques, such as magnetic separation, which is used to sort out ferromagnetic materials from non-ferromagnetic ones [4]. Mechanical separation is also recommended because it does not involve using chemicals and solvents and, hence, is environmentally friendly. Nonetheless, it has relatively low efficiency in making high-purity recoveries of the types of metals compared to the wet approaches to recovery. It may, therefore, require further processing to attain the needed levels of purity.

By comparison, dry recovery processes generally tend to be less complex and are often less hazardous regarding their environmental impact, given that they do not utilize chemical solvents; they are usually more energy-intensive than wet recovery processes. For instance, the high temperatures used in pyrometallurgy can lead to high energy costs, thus being a disadvantage compared to chemical avoidance. Further, the fixed expenses for the equipment required to perform the high-temperature process and mechanical separation are also relatively high. However, dry recovery continues to be an essential part of the overall LIB recycling picture, where wet recovery is not possible or where the rules regarding using solvents are stringent. More efforts have been and will continue to be put into improving these processes to increase efficiency and decrease energy usage in dry recovery methods.

4. Negative Electrode Material Recovery Technology

4.1. Heat Treatment

Thermal recycling is a heat treatment process to recover valuable metals from lithium battery negative electrode materials. This method involves exposing the battery assembly to high temperatures, which causes the active materials, including graphite and lithium, to decompose or melt, making it easier to separate them from other minor and unwanted materials. Heat treatment by sintering breaks down the complex compounds in the negative electrode material to collect the desired metals. This process is particularly beneficial as it can be applied to a wide range of materials in batteries; this demonstrates the capability of the process in the recycling industry [10].

Thermal processing does not involve using any chemical materials or adding chemicals, which is an essential advantage as it eliminates the problem of secondary contamination that is always present in chemical recycling methods. Although this process is environmentally friendly due to the lack of direct use of chemicals, the high temperatures used in the process increase energy consumption, which may offset the environmental benefits achieved [8]. However, current research continues to explore ways to fine-tune these heat treatment parameters (e.g., temperature and time) to improve recovery and energy utilization.

In addition, thermal treatment is also very effective for the recovery of graphite, which is one of the most critical components in the negative electrodes of lithium batteries and lithium. Graphite is a substance with a very stable lattice, and high temperatures apply to this material. Therefore, heat treatment is the most suitable technology to recover this material.

4.2. Leaching Recovery

Another chemical treatment process for recycling negative electrode materials of LIBs is leaching recovery; this is a process used to dissolve metals with the help of an acid or any other solution. This process starts with a process referred to as leaching, where battery materials are subjected to a leaching solution that only dissolves some metals, such as lithium and graphite, which constitute the battery's negative electrode. Leaching is far more sensitive to the kind of acid used, the concentration of the reagents involved, the operating conditions of temperature, and the speed of mixing. Sulfuric and hydrochloric are generally utilized as extracting agents due to their high solubility of lithium and other valuable metals. The outcome solution or leachate, which contains an appreciable amount of dissolved metal, is then subjected to another process to recover such metal in a helpful form.

The resultant metal-rich solution is then taken through the purification and metal recovery steps, which can be either Precipitation or Solvent extraction depending on the types of metal ions present. Precipitation is usually done under a pH change or by adding a precipitating agent where the metals enter a solid residue from the liquid phase. This step is necessary to ensure that metals with very high purity are obtained to enable the direct reuse of the metals to create new LIBs. Solvent extraction is applied after leaching to selectively engineer the metals since the impurities are washed away to improve the quality of the metals extracted from that place [4]. This demonstrates that leaching should be combined with the recovery mentioned above steps to achieve a high metal recovery rate from LIBs.

Leaching recovery is higher ranked due to its versatility in the case of bearing several types of metals and the advantage of integration with other procedures. For instance, leaching is combined with heat treatment or mechanical to improve the extracting process. However, of significant importance while employing the method of leaching itself is the environmental consideration that may be involved in using the leaching agents and the secondary waste products as they may result from the leaching process.

5. Conclusion

This paper mainly summarises the recycling methods of cathode and anode materials and discusses the pre-treatment process before recycling.

Currently, the recycling technology of cathode materials mainly separates the cathode materials utilizing crushing and screening first. Then, it extracts the metal elements therein by acid leaching, dissolution, and electrochemical treatment. However, some recycling technologies are still in the research and development or demonstration stage, and the maturity of the technology is not high, making it difficult to achieve large-scale commercial applications. In particular, the reagent consumption and wastewater treatment costs involved in the chemical method recovery process are high. In addition, the recycling process may include safety and environmental risks such as flammability and explosiveness, as well as wastewater and exhaust gas emissions. In the future, the research and development and optimization of positive electrode material recycling technology should be strengthened to improve recycling efficiency and reduce costs. At the same time, the intelligent and automated development of the recycling process should be promoted to improve recycling efficiency and safety.

Anode recovery technology mainly focuses on the recovery of copper foil and the reuse of anode-active substances. Copper foil can be separated from the negative electrode material by physical or chemical methods. In contrast, high-temperature pyrolysis, chemical treatment, and other techniques can convert the negative electrode active substance into reusable material. However, there is still room for improvement in the recovery efficiency of the current negative electrode recycling technology, especially in the reuse of active substances. Future research should explore the application possibilities of negative electrode recycling materials in more fields, such as energy storage systems and supercapacitors. In addition, researchers should develop comprehensive recycling technologies that organically combine the positive and negative electrode recycling processes to achieve comprehensive recycling and utilization of used Li-ion batteries.

With the continuous progress of technology and market expansion, the waste lithium-ion battery recycling industry is expected to usher in a broader development prospect in the future.

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