Recovery of cathode material of abandoned lithium-ion battery: Comparison of methods and the recent situation of utilization of Chinese factories

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Abstract. Lithium-ion batteries were successfully brought to the forefront of various industries more than 30 years ago, and today they play an important role in the portable power and electric vehicle industries. In the context of expanding markets and increasing industrial and domestic demand, the recycling of materials from batteries after their disposal has received some attention. However, lithium-ion batteries contain inactive chemical components that make recycling complex and expensive. Existing technologies, therefore, need to be analyzed and improved. This paper uses thesis research to summarize, compare, and critique the current methods of recycling batteries to recover valuable cathode metals and the utilization of these methods in factories across China. It was found that the current plants usually use hydrometallurgy, pyrometallurgy, and combinations thereof, and that the plants utilize bioleaching, although it is more environmentally friendly. In the end, a conclusion about the current situation and a prediction for future challenges are made.

Keywords: lithium batteries, cathode material recycling, hydrometallurgy, pyrometallurgy, bioleaching

1. Introduction

In recent years, China's battery industry has been developing rapidly, and the use of lithium-ion batteries is one of the key drivers in this trend. As a low-carbon, clean and safe energy storage device compared to batteries that were used before LIBs came out. This battery is widely used in electric vehicles, energy storage, power grids and other important industries [1]. Currently, lithium-ion batteries are classified into four main categories according to different cathode materials: lithium ternary, lithium iron phosphate, lithium cobalt, and lithium manganate. Nowadays, lithium ternary batteries dominate in lithium-ion battery applications. The dramatic increase in demand has led to a dramatic increase in production; however, as lithium-ion batteries undergo a number of charging and discharging cycles, the electrode material will gradually deteriorate, which leads to a decline in battery capacity. Batteries need to be replaced when their capacity drops to approximately 70% to 80% of the initial capacity, which directly leads to a significant rise in the number of discarded lithium batteries [2]. From 2018 to 2022, the theoretical recycling volume of waste lithium-ion batteries has increased rapidly from 259,000 tons to 762,000 tons, but the proportion of the actual recycling volume has only increased from 34.7% to

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53.8%, which indicates that there is still a large amount of spare capacity [3]. The recovery of valuable metals from the cathode of waste lithium-ion batteries is the most important part of the lithium battery recycling process, because the cathode material accounts for about 30% of the cost of lithium batteries and nearly 90% of environmental impact [4] and contains a large number of valuable metal elements such as Ni, Co, Mn, Li, etc. Moreover, the extraction of these metals from waste lithium-ion batteries has obvious advantages over the direct extraction from ores, such as short process, high efficiency, low environmental pollution and low energy consumption as well as human cost [5]. It is of great significance to study the efficient and green recycling technology of waste lithium battery cathode materials. This paper will analyze the recycling process of lithium batteries and the application of these technologies in Chinese factories.

2. Methods of recovery

Because of the complex structure and large number of cathode materials in lithium-ion batteries, various pre-treatment methods are required before they can be recycled. Lithium-ion batteries must first be sorted and then pre-treated by chemical treatment methods or physical treatment methods, as shown in Figure 1 [6].

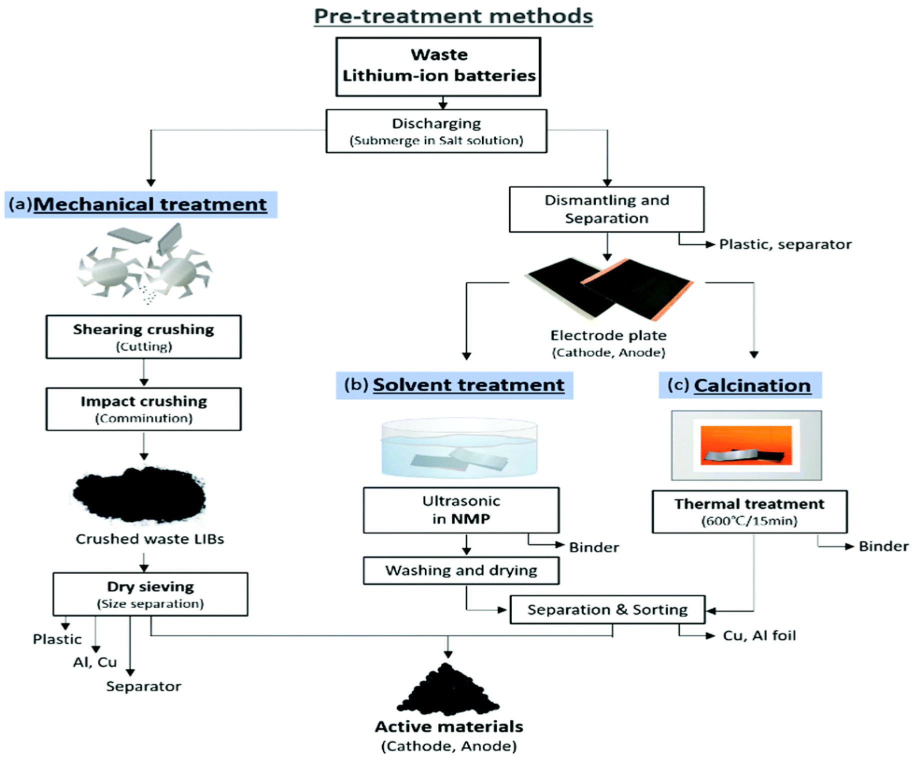

Figure 1. Example of pre-treatment technology and processes of waste LIBs; (a) mechanical (b) solvent treat and (c) calcination [6].

The main objective is to remove organic binders, flammable electrolytes, aluminum collectors, etc. from the cathode materials of used lithium-ion batteries [7]. This is followed by direct recycling, pyrometallurgy, hydrometallurgy or a combination of methods, as shown in Figure 2 [8].

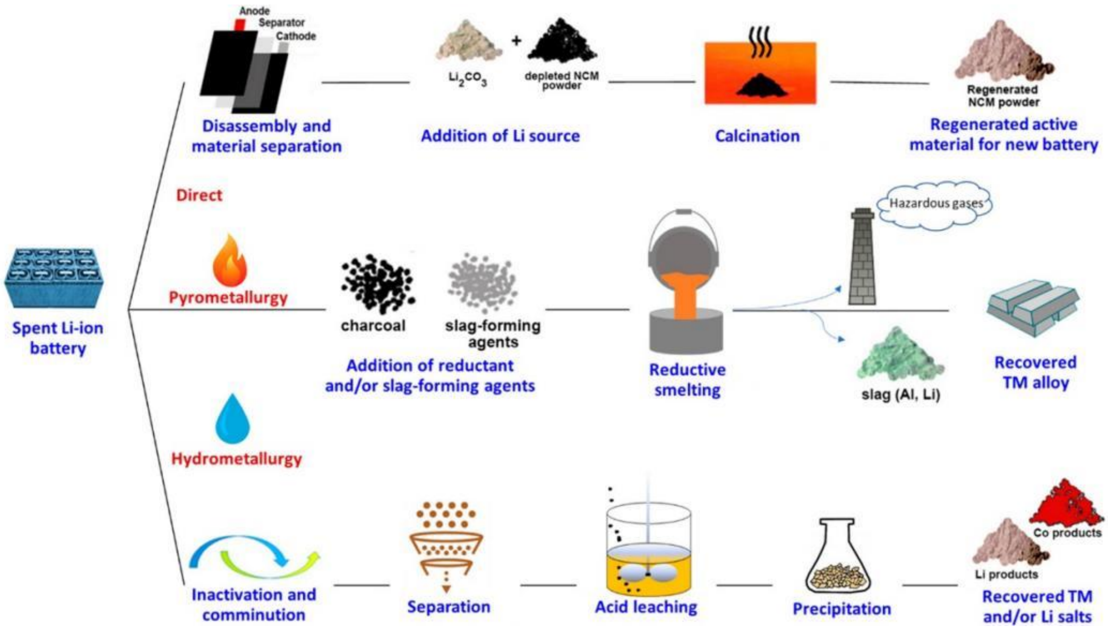

Figure 2. Typical direct, pyrometallurgical, and hydrometallurgical recycling methods for recovery of Li-ion battery active materials [8].

2.1. Pyrometallurgy

Pyrometallurgy uses heat to convert metal oxides used in battery materials to metals or metal compounds [9]. This method has the advantages of high chemical reaction rate, large capacity, relatively flexible feeding and simple operation [10]. In reduction roasting, the battery material is heated under a vacuum or inert atmosphere to convert the metal oxides into mixed metal alloys containing cobalt, nickel, copper, iron, and lithium and aluminum residues (depending on the battery composition). Pyrometallurgical methods require simpler pre-processing methods (usually shredding or crushing) to prepare the batteries for recycling and fewer different methods to recover lithium-ion batteries of different compositions, shapes and sizes [8]. However, the pyrometallurgical process, with its high temperature treatment leads to loss of Li and Al, does not allow for the complete recovery of all components of spent LIBs, and only a few companies are able to profitably recycle lithium-ion batteries using this method [11]. Meanwhile, during the decomposition process the batteries are usually evaporated or decomposed, and then toxic gases are formed, which will increase the cost of exhaust gas treatment in the factory.

2.2. Hydrometallurgy

In hydrometallurgical process, the pretreated battery materials (with Al and Cu current collectors previously removed) are most often extracted with H_2SO_4 and H_2O_2, although HCl, HNO_3, and organic acids including citric and oxalic acids are commonly used. Once metals have been extracted into solution, they are precipitated selectively as salts using pH variation or extracted using organic solvents containing extractants such as diallyl phosphates or phosphonates [9]. Compared with pyrometallurgical processes, hydrometallurgical processes have many advantages, such as high extraction efficiency, low energy consumption, low hazardous emissions and low capital costs [10]. However, the low adaptability of the raw materials to be processed and the problem of corrosion of the equipment by the acids commonly used in the leaching stage are also great challenges [11]. However, inorganic acids produce acidic wastewater and harmful exhaust gases (Cl_2, SO_2, NOx, etc.). These acidic wastewater and exhaust gases can cause environmental pollution, and the further corrosion of equipment is also a problem that cannot be ignored [12]. Therefore, many scholars have focused their research on the use of organic acids because they reduce the corrosion of equipment and increase the environmental characteristics, while organic acids are biodegradable and easy to recycle [10]. Leaching temperature, acid and reductant

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concentrations, reaction time, and solid-liquid ratio are process parameters often measured by researchers [12].

2.3. Combination of Pyrometallurgy and Hydrometallurgy

Combining pyrometallurgical process and hydrometallurgical process has certain advantages over either method. Fire roasting treatment of anode active material, changes the composition of anode active material to make it more conducive to the subsequent treatment of the wet process as well as reduces energy consumption and at the same time, enhances the leaching capacity of the hydrometallurgical process of valuable metals [10]. This method also overcomes the disadvantages of the complexity and high cost of the hydrometallurgical process, and can achieve the preferential extraction of individual valuable metals (e.g., Li), which reduces the difficulty of the subsequent extraction and separation of metals [13]. However, the combination of these two methods, which are not very environmentally friendly, does not solve the problem of pollution, and it is hoped that the combination of other methods will be greener in the future.

2.4. Bio-hydrometallurgy

Bioleaching is a natural chemical process based on microorganisms in which insoluble solids are converted to soluble and extractable forms [19-20]. Multiple microbial-driven reactions in the bioleaching process help to extract metals from the complex solid matrix of the waste LIB and convert the hazardous portion of the waste LIB into non-hazardous forms [21]. Thus, the bioleached medium is usually highly rich in diverse valuable metals including Co and Li, but they are mainly in the dissolved form. In recent years, bio-hydrometallurgical (bioleaching) methods which use acid producing microorganisms (bacteria or fungi) for the recovery of valuable metals from spent LIB have received some attention, mostly because the bioleaching process is cost-effective, environmentally friendly, less energy intensive, and has low emissions of GHGs as well as highly efficient [14-16]. Other potential advantages include the minimal chemical and water requirements of the bioleaching process, simplicity of operation, less needs for highly skilled workers, selectivity for metals, growth of most microorganisms under ambient conditions, and sustained reuse of microorganisms [15,17-18]. Xin et al. [22] showed that the average leaching rate of Li, Co, Mn and Ni from three typical waste LIBs cathodes was over 95%. However, the microorganisms used for bioleaching have a slow leaching rate and the required microorganisms are difficult to incubate efficiently, which means that bioleaching takes a relatively long time. On the other hand, bioleaching can only produce solutions with low concentrations of metal ions, since higher metal concentration will destroy the activity of microorganisms and make it difficult for them to rapidly extract valuable metals from them [23]. Table 1 compares the differences between methods discussed above.

Table 1. Comparison of different metallurgical processes

Methods	Traits	Merits	Demerits
1.Pyrometallurgy	High-temperature melting treatment for batteries	Wide range of raw materials to be processed, large processing capacity, easy flow and simple process	High process energy consumption, low metal recovery rate, high equipment requirements, high requirements for equipment, high environmental impact
2.Hydrometallurgy	Leaching of cathode materials with acid, followed by selective separation and purification of valuable metals	High recovery rate, high purity, product flexibility strong, low energy consumption	Battery cells must be pre-treated, reagent consumption High volume, large amount of salt-

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Table 1. (continued).

			containing wastewater to be treated
3.Combination of 1 and 2	Fire treatment changes the composition of the positive electrode active material, making it more favorable for subsequent wet treatment	Low energy consumption and high leaching rate	emissions of waste acids and gases
4.Bio-hydrometallurgy	Leaching of metals from minerals using acids generated during microbial growth and reproduction	Environmentally friendly, low operation costs and less energy requirement, high efficiency at low metal concentration.	Long process time, no feasible in high toxic environment, hard process control measures

3. Methods used in China

In many cases, a combination of hydrometallurgical and pyrometallurgical methods are used to process today's lithium-ion batteries. Pyrometallurgy is likely to be used because of the fixed investment in exciting equipment and the flexibility of the battery feedstock. On the other hand, the methods being developed rely to a greater extent on hydrometallurgy, at least in part because of the smaller cost of facilities to implement them. East Asia has nearly two-thirds of the current lithium-ion battery recycling capacity of 207,500 tons of battery recycling capacity, with nine completed facilities and two planned facilities. Five of the completed capacities are located in China, with a total capacity of 188,000 tons; one facility is planned in Hubei Province (capacity unknown). In China, the recycling status of several factories related to lithium battery recycling is shown in Table 2 [7].

Table 2. Companies Involved in LIB Recycling and Volumes Processed by Technique

Company	Location	volume(tons/year)	Method	Status
Brunp Recycling Technologies	Hunan, CN	100,000	Pyro/hydro combo	Established
Taisen	Hunan, CN	6,000	Hydro	Established
GEM	Jingmen, CN	30,000	Hydro	Established
Guanghua Sci-Tech	Guangdong,CN	12,000	Preprocessing	Established
Gotion High-Tech	Hefei, CN	Unknown	Unknown	Planned
Quzhou Huayou	Quzhou, CN	40,000	Pyro	Established

4. Discussion

In this table, we can see that one plant uses pyrometallurgy and recovers about 40,000 tons per year, and two plants use hydrometallurgy with a total recovery of about 36,000 tons per year. One plant uses a combination of pyrometallurgy and hydrometallurgy, and has the highest total amount of recycling of any other plant, with about 100,000 tons per year, due to the large size of the company and the high recycling rate of the method used. There is also a plant that specializes in the pre-treatment of waste lithium batteries for recycling, processing around 12,000 tons per year. In Hefei, Gotion High-Tech was planning to set up a battery recycling facility, but since there has been no definite news in three years, this plan was probably cancelled or delayed indefinitely. Moreover, it is noticeable that there are no plants using the bioleaching method and no planned bioleaching facilities. There is a lack of examples

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to prove the suitability of this method for industrialization, but as bio-metallurgy is the best method found to recycle used batteries, it has environmental advantages, at least at the reaction level, but there is no guarantee that no negative externalities will occur in the plants where it is applied. This requires the company to make a preliminary judgement before applying it. Another reason why there are no plants using bioleaching is that existing plants do not want to replace equipment or establish new departments because of the high cost, so new plants are needed. Governments should pay attention to the development of green engineering such as bio-metallurgy and make appropriate investments and subsidies.

5. Conclusion

This paper mainly outlines the various methods of recycling waste lithium-ion battery cathode materials, as well as the characteristics and advantages and disadvantages of these methods, and also collates the recycling situation of factories with existing recycling technologies in China. Overall, today's recycling rate of waste lithium-ion battery cathode materials is very insufficient, with only five recycling companies in China recycling about 60% of the world's total tonnage. Not only that, most companies tend to use a combination of pyrometallurgy and hydrometallurgy, which is relatively convenient, but from an environmental point of view, it doesn't work. With the rapid development of the electric vehicle industry, the market share of lithium-ion batteries is gradually expanding, because the manufacturing of lithium-ion batteries depends largely on limited natural resources, such as Li and Co, which can cause a serious shortage of these valuable metals, and the toxic components and heavy metals in spent lithium-ion batteries are eco-toxic, which will seriously endanger human health. Therefore, the recycling of waste lithium-ion batteries is crucial for resource sustainability and human health. Biological hydrometallurgy (bioleaching), also mentioned in this paper, is a promising new technology that currently exists only in laboratories due to long processing times and limitations. This would be more promising if traditional metallurgical processes could be integrated with environmentally sound bioprocesses.

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