Recovery process of waste ternary battery cathode material

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Abstract. LIBs is a kind of energy storage device, which has the advantages of high energy density, no memory effect, good safety performance, and many cycles; It is widely used in many scientific and technological fields at home and abroad. With the large-scale increase in the use of lithium-ion batteries, the amount of scrap also increased. In order to better realize resource recovery, energy conservation and emission reduction, it is necessary to study a series of new technologies for waste battery recovery; This review mainly introduces the recovery process of the waste cathode material (LiNiCoMn1-x-yO2) of the ternary battery, and carries out the resource recovery. The content describes the three major links of the recycling process. The first link introduces the pretreatment of waste ternary batteries. The second link analyzes the current methods of recycling the cathode materials of waste ternary batteries. After analyzing the advantages and disadvantages of each method, the process of wet recycling is introduced in detail. It is also the most commonly used way of recycling waste batteries at this stage. The last link describes the regeneration process of cathode materials.

1. Introduction

With the rapid development of modern science and technology, the shadow of electronic products such as mobile phones, cameras, laptops and other electronic products can be seen everywhere in our life. As the main energy supply battery, the demand and output of lithium-ion battery are also increasing year by year, and its output once increased by eight times from 2000 to 2010[1], its lifespans is about 1 to 3 years, when the service life of a certain number of years will ushered in the wave of battery retirement, so we face the problem of how to deal with the waste battery, because lithium ion batteries are rich in precious metals, the content of these metals is even higher than the content of natural ores. For example, waste lithium batteries contain a large number of strategically scarce metals such as cobalt, whose content is almost 850 times of the average cobalt content of minerals in China. If discarded randomly, it will cause a great waste of resources. However, if handled improperly, it will also bring huge pollution to the environment, such as groundwater and soil pollution, and affect the health of people and animals in real life. Therefore, by recovering precious metals from these wastes, not only can environmental pollution be reduced, but also resource sustainable development can be achieved.

2. Pretreatment of waste ternary battery

2.1 Pretreatment

2.1.1 Discharge treatment.

The internal structure of lithium-ion battery can be divided into positive pole, negative pole, diaphragm, electrolyte and shell as shown in Figure 1. In order to obtain the cathode material powder, the waste lithium-ion batteries should be pretreated. The first step of pretreatment is to discharge the waste lithium-ion batteries. The recovered waste lithium-ion batteries generally contain electricity with a residual voltage of more than 2.0 V. If these residual electricity cannot be effectively treated, it will inevitably lead to a series of potential safety hazards, which makes it difficult to carry out the experiment normally; The methods of discharging waste batteries are generally divided into physical methods and chemical methods. The physical method is divided into external resistance method, short circuit method and low temperature environment treatment method. The external resistance method is to use a wire to connect the two poles of the waste battery with the resistance load for a period of time, and then use a multimeter to measure the open-circuit voltage. Generally, the residual voltage after discharge is less than 1V, which can be considered as complete discharge[2], This discharge mode is fast and thorough, but the disadvantage is that a lot of heat will accumulate in a short time, resulting in battery explosion; Short circuit
method usually refers to the use of metal powder or graphite to short circuit the waste battery discharge[3]. Compared with the discharge results of these two substances: Although the metal powder short circuit discharge speed, but the battery temperature rises rapidly, may lead to explosion; The graphite short-circuit discharge speed is moderate, will not cause the battery temperature rise too high, is a safe way of discharge[4]. Low-temperature environmental treatment usually refers to discharge in a low-temperature environment of liquid nitrogen. The specific operation method is to store waste batteries at a low temperature in the early stage, and then store them in a vacuum for 1 hour. The principle is to freeze the electrolyte inside the battery to make it lose its conductive property, so as to make the battery inert. Finally, the diaphragm and fluid collection are removed by mechanical shock. This method will not make the temperature of the experiment too high, the disadvantage is that the experimental equipment requirements are very high, the investment of capital is relatively larger.

Most chemical methods use Na₂SO₄ solution[5], NaCl solution[6]. MnSO₄ solution[7]. Soak the waste battery for several hours, and the residual electricity is released naturally by soaking in the solution. Although the cost of using this method is relatively low, but the experiment time is long, and the use of a large number of chemical solvents will bring certain pollution to the environment, but also corrosion of the experimental equipment; For example, in the electrolytic system of NaCl solution, the chlorine gas and hydrogen produced will bring certain pollution to the environment. The discharge process also causes the discharge solution to be more alkaline. Serious corrosion will be caused to waste lithium ion batteries, resulting in electrolyte leakage, a large number of alkanes, olefin and dimethyl carbonate and other organic gases and flocculation precipitation. This method is an open system, which poses a great threat to the safety of working environment and the health of operators in industrial production practice.

![Fig. 1 Internal structure of lithium battery](image)

**2.1.2 Disassembly processing.**

The purpose of disassembly of waste batteries is to realize the separation of components, the main component of the negative electrode is copper foil and carbon black, the adhesive relay between the two is very small, direct percussion shock can be separated and recycled, polymer diaphragm can be concentrated for recycling, metal shell can also be used for secondary recycling; For the most valuable recycling positive electrode material disassembly methods mainly include manual disassembly method, mechanical disassembly method, organic dissolution method, alkaline leaching method, high temperature decomposition method, etc. The following methods will be introduced.

Manual disassembly method: Manual disassembly method is generally suitable for waste batteries with small volume, and the quantity is generally only suitable for laboratory scale recycling. Although the materials obtained from the treated batteries are of high purity, the disassembly efficiency is not high, and the disassembly process is easy to cause some pollution to the environment, so the whole process also needs to wear a good mask and corrosion resistant gloves.

Mechanical disassembly method: Mechanical disassembly method is mainly used in the industrial field, through the crusher of waste battery crushing treatment, get different particle size powder, after the physical screening to screen out the positive electrode material required for the experiment. The advantage of this method is that it can realize continuous automated production, withstand more resistance and accumulate greater production effectiveness. The disadvantage is that HF gas produced in the disassembly process may pollute the environment, so it is necessary to add a gas treatment device to avoid this harmful phenomenon.

Organic dissolution method: Because the binder is mostly poly vinylidene fluoride (PVDF) and other organic matter, the use of organic solvent can be dissolved, so as to achieve the separation of positive electrode material and aluminum foil[9]. Commonly used organic solvents mainly include N-methyl-2-pyrrolidone (NMP), N,N-Dimethylformamide (DMF), Dimethylacetamide (DMAC), and sulfoxide (DMSO), etc[9]. Compared with the above organic solvents, DMSO dissolving binder with low toxicity and low cost was the most suitable. The experimental results showed that the positive electrode material and aluminum foil could be completely separated under the conditions of 60 ℃, 85 min and ultrasonic assistance. NMP organic solvent has the advantages of good effect, short time and no damage to aluminum foil. Under the condition of temperature 80 ℃, time 30 min and ultrasonic assistance, NMP can remove the binder quickly, but the disadvantages are volatile, high toxicity and high price.

Alkaline leaching method: Since the positive electrode material is metal oxide, which only reacts with acid instead of alkali, alkali solution can be used to separate the positive electrode material and aluminum foil. The positive electrode material can be separated by dissolving aluminum foil with NaOH. The effective separation between the positive electrode material and aluminum foil can be achieved by normal temperature and moderate stirring. 2Al +2NaOH+2H₂O→2NaAlO₂+ 3H₂↑. The experimental results show that the dissolution effect of aluminum foil is obvious when NaOH 3 mol/L, temperature 50 ℃, solid-liquid ratio 100 g/L, time 1 h. The method of alkali leaching is simple and easy to operate. The disadvantage is that strong alkali is easy to
corrode the equipment, and the \( \text{H}_2 \) gas produced by subsequent acid leaching process will be flammable and explosive, which will bring certain security risks. Therefore, ventilation treatment should be carried out. High temperature decomposition method: according to the carbon material, binder and aluminum foil melting boiling point of different can also use high temperature decomposition method to achieve separation[10]. It was found that the decomposition rate of PVDF gradually increased with the increase of temperature from 350℃, and reached 100% at 580℃. Therefore, in the process of the experiment, the mixture can be put in 700℃ and calcined in Muffle furnace for 2 h, then the binder can be removed, so that the positive electrode material and aluminum foil can be separated. In short, high-temperature decomposition method has the advantage of simple and efficient treatment, but the disadvantage is that the experimental process will consume huge energy, but also produce harmful gases such as HF, if not properly treated, it will bring secondary pollution to the environment.

To sum up, when testing in the laboratory, manual disassembly is often the first step in the experiment after the discharge of waste ternary battery. After that, alkaline leaching or organic dissolution method is often used to dissolve aluminum foil. In general, alkaline leaching method is generally used in the experiment in order to save costs without affecting the experimental results. Finally, in order to remove the high melting point binder and carbon black, high temperature decomposition method is often used to treat; In the industrial field, in order to improve production efficiency and reduce labor costs, mechanical disassembly has become the most widely applicable method in the first step after the discharge of waste ternary battery, and the subsequent treatment methods are roughly the same as those used in laboratory experiments. However, it should be noted that these treatment methods will produce a certain amount of harmful gases or liquids in the experimental process, which will cause secondary pollution to the environment, so it is necessary to install appropriate tail gas treatment devices and waste liquid discharge devices. At present, there is no relevant literature to report specific treatment devices.

3. Selective recovery of valuable metallic elements

Cathode material is an important part of ternary battery, and its recovery value is the highest relative to other components. Its cost accounts for about 1/3 of the total cost. There are many metal elements in cathode materials, and the metal elements with recycling value are usually selectively recycled. The common methods of recovering such metallic elements are pyrometallurgy, hydrometallurgy, biological metallurgy, etc.

3.1 Pyrometallurgy

The pyrometallurgy is mainly applied to the recovery and treatment of waste batteries in the industrial field. The main principle is to obtain metal oxides or compounds by melting the cathode materials at high temperature under the premise of adding reducing agents, and then conduct wet separation and recovery; The advantages of pyrometallurgy are that the process is relatively mature, the process flow is simple and clear, and this process does not require physical separation and mechanical treatment. The specific process is to put the cathode material, metal ore and reducing agent carbon powder of the three-element battery into the furnace and wash into the protective gas for heat treatment for 5 hours, during which the temperature is set at 1450 ℃. The experimental results make the binder and electrolyte achieve perfect decomposition, and also get the metal and metal compounds related to the cathode material. The defect of the experimental process is that it is easy to produce harmful gases and pollute the environment in the environment with high temperature greater than 1000 ℃, and the energy consumption is too high, and the requirements for the experimental equipment will also be higher. Therefore, the waste battery treatment often combines the pyrometallurgy and hydrometallurgy to achieve complementary advantages.

3.2 Hydrometallurgy

Among all the recycling methods of waste batteries, hydrometallurgy is the most widely used. Its principle is to transfer the active substances of positive electrode materials to the leaching solution in the form of ions, and finally realize the separation and recovery of valuable metals through precipitation, extraction or ion exchange. With low recovery cost, high recovery efficiency, low pollution and other advantages, hydrometallurgy can be divided into acid leaching treatment, alkali leaching treatment, biological treatment.

3.2.1 Acid leaching treatment.

Acid leaching treatment is divided into inorganic acid treatment and organic acid treatment[11]. Common inorganic acids include: Common inorganic acids include: HCL, \( \text{H}_2\text{SO}_4 \), HNO\(_3\), the results showed that hydrochloric acid had the best leaching efficiency and high leaching rate of valuable metal elements can be achieved without adding reducing agent. Factors affecting metal leaching rate include concentration of acid solution, time, temperature, amount of reducing agent, etc. Experimental results show that hydrochloric acid has the best leaching rate under optimal conditions. When the concentration of hydrochloric acid is 4mol·L\(^{-1}\), the ratio of solid to liquid is 1:20, and the reaction time is 18 h at 90℃, almost 100% of the metal elements including Li, Ni, Co and Al can be leach from the waste cathode material.

Although strong acid treatment makes the metal leaching rate relatively high, inorganic acid will generate many harmful gases during the experiment, which will bring secondary pollution to the environment. For example, chloric acid will generate chlorine gas in the process of acid leaching, sulfuric acid acid leaching will generate sulfide, nitric acid leaching will generate nitrogen oxide,
and the equipment will be corroded due to the strong acidity of inorganic acid.

Compared with inorganic acid treatment, organic acid leaching has the advantages of degradable, short time, low temperature, high leaching rate and less pollution [12]. The disadvantage is that the cost is high and proper methods should be adopted to realize the regeneration and recycling of organic acids[13]. The organic acids citric acid, malic acid, oxalic acid and trichloroacetic acid used in the experiment have good leaching effect on valuable metals from waste batteries. Chen et al.[14]As for the recovery process of the mixture, citric acid was used for acid leaching. The experimental results showed that when the concentration of citric acid was 1.5mol·L⁻¹, the ratio of solid to liquid was 1:20, the reduction dose was 0.5:1, and the temperature was 80°C for 2h, the leaching rates of Li,Ni,Co and Mn could reach 99%, 91%, 92% and 94%, respectively. X. H. Zhang[15]trichloroacetic acid was used as the leaching agent for acid leaching. The experimental conditions were as follows: the concentration of trichloroacetic acid was 3mol·L⁻¹, the ratio of solid to liquid was 50g·L⁻¹, the content of reducing agent was 4%, and the leaching rates of Li,Ni,Co and Mn were 99.7%, 93%, 91.8% and 89.8%, respectively, at 60°C for 30min. But the leaching rate of Al was 7%. Malic acid has certain reducibility due to its own hydroxy group, Zhou Tao et al [16]The acid leaching experiment shows that when malic acid is used as the leaching agent, under the conditions of malic acid concentration of 1.2mol·L⁻¹, volume fraction of H₂O₂ of 1.5%, solid-liquid ratio of 40g/L, reaction temperature of 80°C and reaction time of 30min, The leaching rates of Li, Co, Ni and Mn in malic acid extract reached 98.9%, 94.3%, 95.1% and 96.4%. Zhang et al[17]After oxalic acid leaching, Co³⁺,Ni²⁺ and Li²⁺ ions will react with oxalic acid and precipitate directly from the leaching solution in the form of co-precipitation. After filtration, the filtrate mainly contains metal ions Li²⁺ ions, which can be recovered as Li₂CO₃. The generated NCM can be regenerated into NCM by forging and burning in a high temperature environment according to a certain proportion. First, 0.6 mol·L⁻¹oxalic acid and waste positive electrode powder were put into the reactor, the solid-liquid ratio was 20g·L⁻¹, and the water bath temperature was kept at 70 °C. With the increase of reaction time, lithium was dissolved, and the transition metal was deposited on the surface of the material in the form of oxalate, thus achieving the separation of lithium and transition metal. Through the above comparison, we can see that the appropriate use of organic acids for selective leaching can greatly shorten the experimental process and save various human and material resources, which is one of the most important factors for future industrialization.

To sum up, pyrometallurgy and hydrometallurgy are two inexpensive processes commonly used in industrialization to recover lithium batteries. Pyrometallurgy can deal with large scale waste lithium ion batteries of different models, while hydrometallurgy can quickly and effectively deal with specific models of waste lithium ion batteries. Therefore, pyrometallurgy and hydrometallurgy can take a place in the field of lithium battery recycling by virtue of their unique advantages.

3.2.2 Alkaline leaching treatment.

Although the acid leaching treatment can make the metal ions have a high leaching rate, the acid leaching treatment is not selective for the leaching of metal ions, which makes the metal separation and purification more complex, which will lead to excessive discharge of wastewater. Therefore, the method of ammonia leaching to recover the cathode active substances in waste lithium ion batteries can prevent the occurrence of such drawbacks. Ammonia, ammonium sulfate and ammonium carbonate were used as the leaching system to explore their influence on the leaching efficiency of active substances of ternary lithium battery positive material. The results showed that When the molar ratio of ammonia, ammonium sulfate and ammonium carbonate in the leaching solution is 1:0.5:1, the leaching effect of Ni,Co and Mn was better at 80°C and 1 h, and the total selectivity of Ni,Co and Li was greater than 98.60%.

3.3 Combined pyro-wet process

Some defects existing in single pyrometallurgical or hydrom roasting is etallurgical process can be solved by using pyro-wet combined process. Sulfuric often used in the stage of fire pretreatment[18]Nitrification roasting[19]And carbon reduction roasting[20]The waste lithium battery is treated by the process to convert Li, Ni, Co, Mn and other metals into the corresponding metal sulfate, metal nitrate or metal carbonate. In contrast, carbon reduction roasting does not require the introduction of inorganic acid, which is relatively environmentally friendly, so it is also the most commonly used recovery process in the fire-wet process. Zhang et al[20]Under the optimal conditions of temperature 650 °C, time 3 h and carbon content 19.9%, the extraction rate of lithium can reach 84.7%, and the extracted slag can be recovered by H₂SO₄ acid leaching and extraction separation process with the recovery rate of Ni, Co and Mn above 90%.

3.4 Bio-metallurgy

Biometallurgy is a kind of mineral biooxidation process enhanced by microorganisms. In this process, insoluble metal oxides are converted into water-soluble metal sulfates, which can realize the leaching of waste battery materials. Common microbial leaching systems are eosinophilic sulfur oxidizing bacteria (SOB), iron oxidizing bacteria (IOB), mixed bacterial system (MS-MC), and for the passage of three, the MS-MC system can leach most metals from LiNiCoNiₓ-y-Mn₂O₄ with a leaching rate up to 95%. Although the bacterial leaching method has the advantages of high efficiency, low pollution and low cost, the culture conditions are strict and can only be realized in a specific environment, and the culture time period is long, which makes it difficult to implement in practical application. Compared with bacteria, fungi can survive in a wide range of PH without reducing metal
leaching rate. Aspergillus Niger strain MM1 can dissolve a large amount of Co and Li, and the leaching rates can reach 82% and nearly 100%, respectively. Therefore, fungal bioleachation may be an environmentally friendly method for dissolving and recovering large amounts of metals from waste LIBs[21].

4. Regeneration of positive electrode materials

The regeneration of cathode material refers to the direct use of waste lithium battery cathode material leaching solution as raw material, repreparation of new three the process of the cathode material. The leaching solution after acid leaching can be used to resynthesize cathode materials, including coprecipitation method, sol-gel and hydrothermal method. The resynthesis process can realize a closed waste lithium ion battery recovery process. Coprecipitation method: The most commonly used method for wet material regeneration is coprecipitation method. Precipitators include hydroxide, carbonate and oxalate precipitation. The main principle is that excessive metal ions such as Co, Ni and Mn are similar in nature and are not easy to separate[22]. Therefore, it is particularly important to control the pH value of the solution to precipitate Ni, Co and Mn at the same time to the maximum extent. Different precipitating salts (carbonate, hydroxide and ammonium bicarbonate) are used, the pH of the solution to be controlled is also different. NaOH is usually used as the precipitating agent, use ammonia to adjust the pH to 11. Yanko Marinov Todorov et al.[23]2 mol·L$^{-1}$ metal sulfate solution and 6 mol·L$^{-1}$ NaOH aqueous solution were prepared, and the pH value was adjusted to 11 by ammonia water to obtain Li(NiCoMn)$_{1/3}$(OH)$_2$ precursor, which was mixed with Li$_2$CO$_3$ and then ball milling. Calcined at 900 °C for 20 h, Li(NiCoMn)$_{1/3}$(OH)$_2$ was obtained.

Compared with coprecipitation method, sol-gel method and hydrothermal method are less used in practical industrial applications because of their high cost and complex experimental instruments. The following is a brief introduction to their methods.

Sol-gel method: sol-gel method[24,25,26]It refers to a synthesis method in which part of the product prepared by metal carboxylate in water or non-water solvent or solution is completely hydrolyzed is evaporated at high pressure. The other part of the product prepared by metal carboxylate in water or non-water solvent or solution formed by complete hydrolysis is evaporated at high temperature to remove the solvent and finally form a gel, and then the gel formed is solidified and dried after heat treatment to prepare the product. The advantages of this method are: small product size, narrow particle size distribution, large specific surface area, easy to control the form, low heat treatment temperature and time. However, due to the relatively complex synthesis process, it is not suitable for industrial production.

Hydrothermal method: hydrothermal method[27]The synthesis of cathode material is to place the material and water into a hydrothermal reactor in a closed environment at a certain temperature and pressure. Considering the effect of synthesis temperature on the electrochemical properties of products, hydrothermal synthesis method has its unique advantages: the temperature of hydrothermal method is low, which avoids volatilization of lithium ions at high temperature and causes lithium deficiency compounds. In addition, hydrothermal method also has the advantages of homogeneous product, no inert gas protection, simple process, etc. However, this method has some difficulties in the synthesis of complex materials.

5. Conclusion

Compared with some foreign developed countries, our country's research on the new technology of waste battery recycling is still in the initial stage. Although the country has mentioned some treatment methods for some pollution sources in the environmental protection Law, there are also some recyclable metal elements in lithium ion batteries. At present, the country does not have a complete treatment system for the recycling and treatment of these metal elements. Most of the enterprises still have poor technology and imperfect system, and some illegal operators even take the immoral way of deliberately raising the recycling cost and earning profits.

Looking into the new era, some big cities, such as Shenzhen and Shanghai, have gradually implemented the industrial chain model of waste battery recycling, and the system is constantly improving. From the perspective of the future, the battery recycling industry is optimistic.

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