

# Research on Resource Recycling and Reuse of Battery Negative Electrode Materials

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## Abstract

With the continuous increase in demand for lithium batteries in the market, the number of discarded lithium-ion batteries (LiBs) is also rapidly rising. Recycling and reusing these eliminated negative electrode materials can effectively alleviate the environmental impact of waste LiBs and reduce resource waste. This paper focuses on the reaction mechanism of commonly used negative electrode materials in LiBs, summarizes the latest scientific research achievements in the recycling and reuse of negative electrode materials from waste LiBs, and explores the specific application conditions of different recycling technologies. At the same time, this paper also summarizes the application pathways of LiBs negative electrode materials in multiple industries, points out the technical difficulties and challenges encountered in the process of negative electrode material recycling, and predicts the future trends of negative electrode material recycling and regeneration.

## Keywords

Battery; Negative electrode material; Resource utilization; Recycling and reusing.

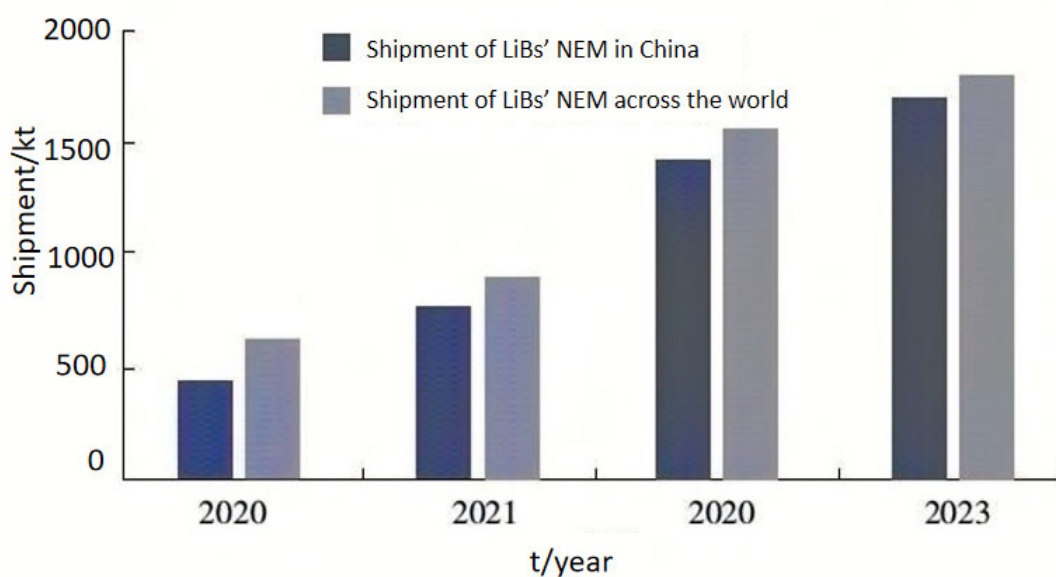
## 1. INTRODUCTION

LiBs have the advantages of high specific energy, strong charging and discharging capabilities, and long lifespan, making them an important research direction in the field of new energy. From a global perspective, the demand for lithium secondary batteries is increasing at a rate of several million kilowatts per year. It is expected that the global market size of LiBs will reach 92 billion by 2026. With the acceleration of China's consumption upgrade and the rapid development of the new energy vehicle industry, the production of discarded LiBs is showing a rapid growth trend. It is expected that by 2030, the global production capacity of discarded lithium batteries will reach 3.7 million tons, with China accounting for 57%. This type of discarded battery contains a large amount of recyclable components (such as carbon, lithium, manganese, cobalt, etc.), and effectively recycling it can not only reduce environmental pollution, but also generate considerable economic benefits. The research on the resource utilization of LiBs mainly focuses on the extraction and refining of elements such as lithium, cobalt, and precious metals, while the research on the recycling of positive electrode materials for LiBs is still relatively weak. Lithium ion are currently the most important positive electrode material for commercial LiBs. In recent years, the LiB industry has developed rapidly, and the demand for LiBs has increased sharply. How to improve its recycling performance is an important means to enhance its comprehensive utilization rate and a key factor in promoting the sustainable development of the industry.

## 2. OVERVIEW OF BATTERY NEGATIVE ELECTRODE MATERIALS

### 2.1. Composition of Negative Electrode Materials for Lithium ion Batteries

The core components of the negative electrode of LiBs include conductive substrates, functional active materials, and adhesive media. Copper foil is generally used as the conductive substrate. During the charging and discharging reactions of the battery, its properties and structure remain stable, making it easy to separate from the active substance and achieve recycling. As shown in Figure 1, the supply of negative electrode materials (NEM) for LiBs has shown a steady upward trend from 2020 to 2023. Negative electrode materials include carbon based materials, lithium titanate, silicon-based materials, and metallic lithium materials. Among various materials, graphite is the most promising negative electrode material for LiBs. By 2023, global graphite production will reach about 1.3 million tons, of which graphite accounts for 91%. There are two main types of graphite raw materials, one is natural graphite prepared from natural graphite ore, and the other is artificial graphite formed by high-temperature pyrolysis of petroleum coke, needle coke, and asphalt at 2500 °C. At present, the requirement for negative electrode materials of LiBs is above 99.5%, and the purification methods mainly include chemical purification, high-temperature heat treatment, etc.



**Figure 1.** Shipment of LiBs negative electrode materials from 2020 to 2023

### 2.2. Composition and structural changes of waste carbon negative electrode materials

The negative electrode material of discarded LiBs is composed of graphite, copper metal, organic electrolyte, and metal doped metal elements such as cobalt and manganese. At high temperatures, residual organic substances such as electrolytes and adhesives will evaporate as the temperature increases. The lithium ion content in waste graphite is 30 mg/g, and its lithium element comes from the solid-state interface of lithium ions in LiBs and the deintercalation of lithium ions on their surfaces. The raw materials of discarded carbon electrodes contain copper, with a copper content of about 35%, which can be recycled and reused. During the cycling process of LiBs, lithium ions will produce crystal like crystals in the LiB. The negative electrode material of LiBs undergoes microstructural and morphological changes such as volume expansion and particle breakage during charging and discharging. Physical, wet, and high-temperature methods are required to remove it, followed by deep purification. Finally, structural repair is carried out to achieve the goal of recyclability.

### 3. RECYCLING OF NEGATIVE ELECTRODE MATERIALS FOR LIBS

#### 3.1. Pretreatment of anode materials for lithium ion batteries

Mechanical crushing technology is a method of effectively separating LiB shells by mechanically breaking them and combining gravity and electromagnetic sorting to achieve resource recycling. Three mechanical methods, namely hammer vibration crushing, vibration screening, and air flow sorting, are used to directly recover elements such as Cu and carbon powder from the negative electrode material of discarded LiBs. At the same time, air flow sorting technology is used to separate and recover 0.125-0.25mm raw materials from the metal. By using mechanical crushing and sorting techniques, the various components in discarded lithium-ion power batteries are effectively separated. However, during processing, there is mutual interference between the units, resulting in low separation efficiency between the units.

Based on the significant difference in hydrophilicity/hydrophobicity between electrodes, flotation method is used for the separation of negative electrode materials. Flotation is a method of using the different physical and chemical properties of mineral surfaces to float solid minerals from water. Firstly, Fenton assisted flotation was used to modify its surface under  $H_2O_2/Fe^{2+}(40/280)$  and liquid-solid phase (25/100) conditions. Then, flotation was used for sorting, resulting in a recovery rate of 98.99% for  $LiCoO_2$ . Secondly, by ball milling flotation, the wettability between  $CoO_2$  and graphite was changed to achieve a difference in the wettability between  $CoO_2$  and graphite. After flotation, the  $CoO_2$  grade was 97.13%, the graphite content was 73.56%, and the recovery rates were 49.32% and 73.56%, respectively. The organic compounds were removed by a combination of ultrasound and pyrolysis. In addition, the recovery rate of lithium cobalt oxide on the prepared graphite electrode increased from 74.62% to 93.89%. Although flotation technology can simultaneously recover lithium cobalt oxide electrodes and graphite electrodes, making their recycling simpler, less efficient, easier to operate, and more efficient, the impurity content in the separated graphite is high, and the purity of the separated graphite needs to be further improved.

#### 3.2. Metal material recycling technology

##### 3.2.1 Pyrometallurgy by pyrometallurgy

The metal raw materials smelted by pyrometallurgy are mainly melted and reduced at high temperatures. On this basis, by high-temperature oxidation of discarded lithium batteries, they can be transformed into a new alloy, and LiBs that have not undergone any processing can be directly sent to smelting facilities. When the metal components are reduced and transformed into alloys, the plastic and organic solvents inside generate heat energy during combustion. Purify the obtained metal through methods such as sulfuric acid extraction and solvent extraction to obtain  $CoO$  and  $Ni(OH)_2$ . Although the process is simple, it is prone to lithium loss. Reduce lithium loss through reduction smelting of iron, cobalt, and nickel; After adding manganese and other metals, the lithium mixed into the slag or dust is leached to obtain purified lithium. This project plans to use a high-temperature argon atmosphere of  $650\text{ }^\circ\text{C}$  to calcine waste lithium batteries, extract  $LiCO_3$  with water, dissolve it in  $CO_2$  solution in water to convert insoluble lithium  $CO_3$  into  $LiHCO_3$ , and then vaporize and crystallize to obtain  $CO_2$ . The use of pyrometallurgical technology to extract valuable metals from discarded lithium batteries has problems such as high energy consumption and environmental pollution. At the same time, the problem of lithium cycling loss urgently needs to be effectively solved.

##### 3.2.2 Wet metallurgy

According to the metal elements in the waste negative electrode material, different acid-base agents can be selected and recovered through wet smelting methods. The synchronous removal of cobalt oxalate was achieved through methods such as reducing acid leaching, alkali leaching,

and chemical plating. In this project, citric acid will be used as the sol gel agent to prepare Co<sub>3</sub>O<sub>4</sub> by the Sol gel method, and its electrochemical performance will be tested, and the coulomb efficiency of 442.3 mAh/g and 99.7% will be obtained. Using the classic acid leaching method to recover lithium, 30.07 mg/g of negative electrode active material was obtained. On this basis, a series of graphene based composite materials with large specific surface area, good stability, and large specific surface area were prepared, and porous carrier materials with good high temperature resistance were prepared on this basis.

Some people also use a two-stage calcination process with 1.5mol/L hydrochloric acid to acid leach waste graphite, which can achieve 100% copper, lithium, and aluminum content in graphite. When the pH value is between 7 and 9, the copper and aluminum content in the leaching solution can reach 99.9%. Adding Na<sub>2</sub>CO<sub>3</sub> to the leaching solution resulted in the recovery of over 99% of lithium in the form of Li<sub>2</sub>CO<sub>3</sub>.

### 3.2.3 Biohydrometallurgy

The use of ferrous sulfide bacteria method to extract cobalt and lithium from discarded lithium batteries is a green and environmentally friendly approach. Research has found that the leaching rate of cobalt is faster than that of lithium, but the leaching rates of cobalt and lithium are very slow. Currently, it is feasible to extract cobalt and lithium from discarded lithium batteries using copper catalysis. Using copper ions as a catalyst and acidophilic sulfur bacteria as the main active ingredient. Under the conditions of copper ion content of 0.75g/L and 6-day leaching, the leaching rate of cobalt can reach 99%. Compared to pyrometallurgy, hydrometallurgy, and bio metallurgy, thermal metallurgy technology has problems such as high energy consumption and severe pollution. Microbial hydrometallurgy process has the advantages of simple process, low investment, environmental protection, etc., but the process flow is relatively long; Meanwhile, the high concentration of toxic substances generated by the reaction between heavy metals and bacteria severely restricts the resource utilization of heavy metals. The use of wet metallurgical methods for effective separation and recovery is of great significance for improving resource utilization, energy conservation, and emission reduction.

### 3.3. Carbon based material recycling technology

Waste LiBs containing composite components are a representative type of hazardous waste, and their high-value treatment has important practical significance for environmental protection. However, during the charging and discharging of LiBs, their graphite structure is severely damaged and contains a large amount of impurities, making it difficult to recycle. During the continuous alkaline acid removal process, not only can the microstructure of graphite be reconstructed, but also harmful components can be removed due to the expansion of its lattice, resulting in a carbon content of up to 99.9%. By subsequent heat treatment, its structure has been well restored, and its carbon emissions can be reduced by 37.0%. This project plans to use sulfate solution below 250 °C as an auxiliary agent, utilizing the electronegativity of NaF itself to reduce the generation of active groups on graphite materials, thereby achieving effective control of material morphology and structure. The graphite prepared by the present invention has a purity of 99.55% and a specific capacity of 286 mAh/g. Waste lithium battery negative electrode material charcoal can also be used as a raw material for graphene. The project adopts an improved Hummers method to produce graphene oxide from discarded LiB negative electrode carbon powder, and adds reducing agents such as vitamin C on this basis to achieve the reduction of graphene oxide. Research has found that graphene flakes produced by the oxidation-reduction method have a good layer structure and contain a small amount of impurities and oxygen atoms; The results indicate that the larger the interlayer spacing of the layered structure, the lower the resistivity.

## 4. RECYCLING AND REUSE OF NEGATIVE ELECTRODE MATERIALS

### 4.1. Compound material

By recycling LiBs, the comprehensive utilization rate of LiBs can be further improved, achieving high value-added utilization of LiBs. On the basis of recycling graphite, it is combined with polymers (PP, PE) to prepare "polymer/graphite nanofilms". Previous research has found that the tensile strength of PP/GRx and PE/GRx composite films is 33.9 MPa, with excellent mechanical properties and a tensile strength increase of about 10 times. The use of regenerated graphite to prepare graphene oxide Cu composite electrodes can effectively compensate for the defects in graphite electrodes and exhibit excellent catalytic activity. The main steps of this process are: first purify the graphite of the negative electrode, then calcine it to remove organic impurities, and finally remove lithium. This study used graphene oxide as the raw material and prepared graphene oxide (GO) by ultrasonic exfoliation method. Then, under the conditions of pH 5.3 and Cu<sup>2+</sup> mass concentration of 1.0 mg/L, surface modification was carried out to obtain graphene oxide Cu composite material. As the reaction time prolongs, the catalytic activity of copper oxide gradually increases, reaching around 33% after 300 minutes. After 120 minutes of treatment, the photocatalytic degradation rate of the material reached 55% and remained at 91% thereafter. The results showed that compared with CuO, the photocatalytic degradation effect of graphene oxide Cu composite on methylene blue was significantly better.

### 4.2. Battery materials

Adopting appropriate processes can achieve the recycling of waste LiB cathode materials. At present, research has extracted graphene metal compounds containing carbon from lithium batteries and modified them through various mechanical, chemical, and other methods to obtain high-capacity lithium batteries with a specific capacity of up to 112 Wh/kg, laying the foundation for the recycling of waste lithium batteries. Some people have also proposed using hydrothermal methods to recycle discarded LiBs, selecting the optimal proportion of recyclable graphene and combining it with recyclable graphite. By improving the lithium storage capacity of lithium ions in negative electrode materials, the specific capacity can reach 368 mAh/g. Meanwhile, graphene oxide with excellent performance can also be prepared using graphite from discarded LiBs, which can be used to prepare high-performance electrodes in areas such as dyes and catalysis.

## 5. CASE STUDY

### 5.1. Material

This study takes the ternary NCM523 soft and hard ternary LiB as the research object. Firstly, the positive electrode active material is obtained by manual disassembly. Then, using the previous research results of the research group, the positive electrode active material is separated from the copper foil and ball milled to obtain the negative electrode active powder for testing. The main composition of metal elements in the powder was determined by ICP-OES method. The reagents used in this experiment are sulfuric acid, sodium carbonate, oxalic acid, and ethylenediaminetetraacetic acid.

**Table 1.** Content of valuable metal elements in negative electrode powder

Li	Cu	Ni	Mn	Co
27.4	0.45	0.04	0.06	0.03

## 5.2. Leaching experiment

Weigh an appropriate amount of powder in a beaker, leach with sulfuric acid as the solvent, and stir at a speed of 300 r/min. Study the sulfuric acid concentration, solid-liquid ratio, and leaching time; And the reaction temperature related to the dissolution process. After completing the reaction, filter out the reaction solution, digest the filtered liquid, and then measure the Li using ICP-OES. The lithium leaching rate ( $\alpha$ ) is calculated by formula (1).

$$\alpha = \frac{CV}{m\omega} \times 100\% \quad (1)$$

Among them, C is the lithium content in the extraction solution, measured in mg/mL. V is the volume of the extract, expressed in mL. Where m is the weight of the powder material, measured in grams.  $\omega$  represents the lithium content in the powder, measured in milligrams.

## 5.3. Recycling of graphite and lithium

Separate the extract from graphite by filtration. After multiple washes, drying, and sieving, regenerated graphite was obtained. After evaporation concentration and pH adjustment of the extraction solution, impurities are removed using methods such as oxalic acid and ethylenediaminetetraacetic acid. After removing impurities, slowly introduce 3 mol/L Na<sub>2</sub>CO<sub>3</sub> solution into the leachate, water bath at 95 °C for 30 minutes, and then rinse with hot water to obtain lithium carbonate again.

## 5.4. Test characterization

The XRD-6000 X-ray diffractometer (X-ray diffractometer, Cu target, wavelength of 0.154056 nm) from Shimadzu Laboratory in Japan was used to measure the negative electrode powder and regenerated Li<sub>2</sub>CO<sub>3</sub> powder before and after acid immersion. Using the PHILIPS XL30 (SEM) technique from the Netherlands, combined with AME-TEK EDAX energy spectrum analysis technology, the microstructure of the samples under different process conditions was characterized. The various components in the sample were determined using the Agilent 700 series plasma emission spectroscopy method from Germany. The button type half cell was used for acid treatment and its electrochemical properties were studied. Firstly, a carbon: conductive agent (super P): adhesive (CMC/PAA/styrene butadiene rubber (SBR) ratio of 4.0:0.5:5.5)=86:6:8 (weight ratio) was used to coat the slurry on copper foil. It was dried in a vacuum drying oven at 80 °C for 4 hours, then cut, weighed, rolled, and dried to obtain negative electrode flakes. Using the collected negative electrode plate as the active electrode, a lithium metal sheet as the reference electrode, and a Celgard 2300 polyethylene porous membrane as the separator medium, a 1mol/L concentration of lithium hexafluorophosphate (LiPF<sub>6</sub>) dissolved in a mixed solution of ethylene carbonate (EC), diethyl carbonate (DEC), and methyl ethyl carbonate (EMC) was prepared as the electrolyte. Then, the CR2032 battery clip was combined and assembled in a dry glove box filled with argon gas atmosphere. The blue electron microscope (LAND-CT2001A) was used to conduct charge and discharge tests on it, and the charge and discharge tests were conducted at 25 °C and 0.005-1.5 V.

## 5.5. Discussion on Results

The positive electrode material of discarded LiBs is rich in metallic elemental lithium. The acid leaching method is used for recycling and regeneration, and the graphite in it is purified and recycled to achieve the recycling and reuse of discarded LiB positive electrode materials; The following conclusion can be drawn:

1. At a mass fraction of 1.5mol/L sulfuric acid, a solid-liquid ratio of 60g/L, a reaction time of 40 min, and a temperature of 45°C, the lithium leaching rate is 98.5%.

2. After concentrating and removing impurities from the acid leaching solution, the mass fraction of  $\text{Li}_2\text{CO}_3$  re prepared is 99.1%. Its composition meets the technical specifications of  $\text{Li}_2\text{CO}_3$  products in the national standard "Lithium Carbonate (GB/T 11075-2013)", and has higher purity and lower impurities, thus effectively utilizing the lithium resources in the waste electrode.

3. Through XRD, SEM-EDS and other analysis methods, the structure and morphology of the original and filtered electrode materials were analyzed, and it was found that they were flake graphite. Graphite prepared by acid leaching method has higher purity, lower impurities, and smoother surface.

4. The regenerated graphite has good electrochemical properties, with a reversible specific capacitance of 354 mAh/g at 0.1°C. After 30 weeks of cycling, its capacity remains at 97%. At 1.0°C and 2.0°C, the reversible specific capacitance reaches 345339 mAh/g, achieving the recyclability of discarded graphite electrodes.

5. The recycling and recovery of discarded negative electrode materials have significant practical significance for achieving the recycling of lithium and graphite. However, in the disposal of discarded LiBs, efficient separation of positive and negative electrode materials must be achieved to provide a good environment for subsequent separation, recovery, and recycling.

## 6. CONCLUSION

With the widespread use of discarded LiBs and the innovation of regeneration processes, discarded lithium-ion secondary LiBs are considered an ideal type of lithium-ion secondary battery. At present, the recycling and reuse of negative electrode materials for lithium-ion capacitors have achieved preliminary results. With the rapid development of energy storage technology, various types of LiBs have emerged one after another, and the demand for LiBs worldwide is also increasing; How to improve the recycling rate of waste materials and enhance material quality is an urgent problem that needs to be solved. At present, China's environmental protection policies for discarded lithium batteries are not yet perfect, and an efficient circular economy strategy urgently needs to be established. The expected benefits of renewable resources in the LiB industry chain urgently need to be improved. Provide the necessary resources for the current and future overall supply chain.

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