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Graphite Recovery from Retired Lithium-ion Batteries

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Executive Summary

As the most widely used anode material in lithium-ion batteries, graphite has an increasing demand and scrap volume year by year, which brings serious resource and environmental problems. Directly recovering graphite from lithium-ion batteries has been proven to be feasible, but it has not been implemented in industry on a large scale due to cost issues. This paper provides a brief introduction to the recovery of anode graphite in lithium-ion batteries and presents a method adopted by Botree suitable for industrial application. The method involves deep impurity removal of graphite using a combination of heat treatment and leaching, followed by carbon coating through calcination to restore the graphite structure. The regenerated graphite exhibits performance close to that of commercial-grade graphite.

1 Introduction

Lithium-ion batteries (LIBs) are currently widely used in many fields such as new energy vehicles, portable electronic products and energy storage power stations. Graphite is widely regarded as an ideal anode material for LIBs owing to its excellent cycling stability and rate capability [1]. In general, graphite accounts for 12~21% of the weight of LIBs, the price of battery graphite is around \$8,000~13,000 per tonne, and the cost of graphite accounts for 8%~15% of the cost of LIBs [2]. According to the 2021 survey, nearly 83% of battery grade graphite belongs to man-made graphite and the demand for battery grade graphite is expected to reach an estimated 285 million tonnes by 2035. Graphite market was valued at \$14.3 billion in 2019 and is expected to reach \$21.6 billion by 2027 [3]. Graphite has been classified as a critical/strategic mineral by the US and European governments because it is used in many energy-related applications [4]. With the rapid growth in the number of LIBs produced or discarded each year for hybrid and electric vehicles, this could pose a risk to the supply lines of limited resources [5]. In addition, the production of large quantities of artificial graphite consumes large amounts of petroleum resources, which undoubtedly exacerbates energy and environmental problems. Therefore, from an economic and environmental point of view, it is important to recover and recycle graphite from LIBs, especially for countries that still rely on imported graphite.

However, at present, industrial recycling for LIBs mainly focuses on valuable metals, such as nickel, cobalt, copper and aluminium, so in the recycling process, enterprises will give priority to the recycling of cathode materials and collectors with higher economic value, while less attention is paid to graphite anode materials. With the importance of graphite materials gradually appearing, more and more researchers are committed to the recycling of graphite. This paper briefly introduces the method for recovering anode graphite from used LIBs, and provides an attempt of Botree, which is hoped to provide inspiration for the industrial application of used graphite recycling. The regenerated graphite achieved an impressive graphitization degree of 97.28% and exhibited excellent electrochemical performance. It demonstrated a reversible specific capacity of over 350 $mAh \cdot g^{-1}$ at 0.1C cycling and showed significant improvements in cycling stability and capacity retention at 1C cycling.

2 Graphite recycling

To recycle used graphite from LIBs, it is first necessary to understand the failure modes of the graphite anode. The failure of the graphite anode is primarily due to the formation of the SEI film, the formation of lithium dendrites, and the disordering of the graphite structure caused by the lithium intercalation process [6]. From existing research, there are two main directions for recycling graphite: (1) regenerating graphite for reuse in LIBs; (2) synthesizing graphite-based functional materials for environmental and energy applications [7]. For graphite regeneration, the primary methods involve hydrometallurgy [8], pyrometallurgy [9], and the integration of both methods [10] to remove metal and organic impurities while repairing structural defects that occur during the graphite cycling process. Additionally, scholars have also modified graphite through methods such as doping [11] and carbon coating [12] to enhance its electrochemical performance. Thanks to structural defects in waste graphite, surface functional units and mixture of metal impurities are conducive to the synthesis and performance improvement of graphite-based functional materials, in addition to the recovery of waste graphites, the use of waste graphites to synthesize new functional material is also a mainstream in other energy environmental related fields. The overall process chart for waste graphics recovery is shown in Figure 1.

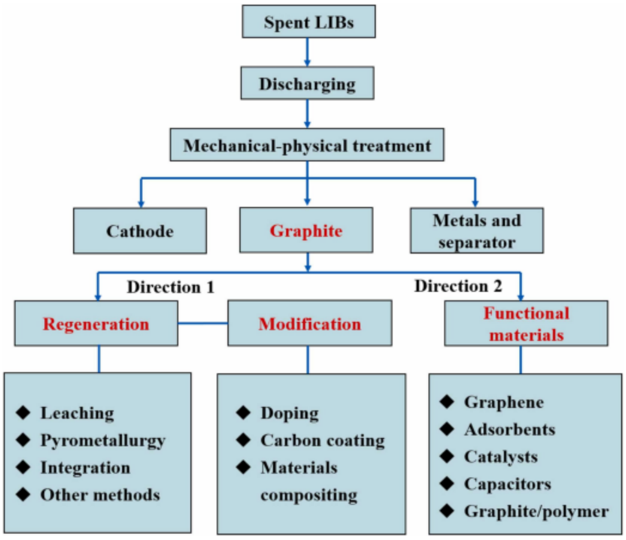

Fig. 1. The overall flow chart of spent graphite recycling [13].

2.1 Graphite impurity removal

The introduction of magnetic impurity particles into the graphite anode material of LIBs can severely impact the safety and reliability of the batteries. High levels of metal impurities (such as Fe and Cu) can pierce the separator, causing self-discharge of the battery, while organic impurities (such as electrolytes and binders) can lead to material agglomeration, affecting granulation and subsequent electrode sheet fabrication. Removing impurities and the surface SEI film from graphite is currently the main challenge hindering the recycling of used graphite. Common impurities in waste graphite are shown in Table 1.

Table 1 Impurities of spent graphite.

Species	Impurities
Metal impurities	Ni, Co, Mn, Li_2CO_3, LiF, CuO, Fe, Al_2O_3, Na
Organic impurities	Organic binder, Electrolyte
SEI	Li_2CO_3, LiF, Li_2O, LiOH, $ROCO_2Li$, ROLi , $(ROCO_2Li)_2$

2.1.1 Heat treatment

The presence of organic binders will cause the agglomeration of graphite particles, increase the internal resistance of the material, hinder the transmission of ions, and result in poor rate performance and cycle capacity. At present, chemical dissolution and heat treatment are mainly used to remove organic binders. The chemical dissolution method mainly uses the principle of like dissolves like to dissolve the organic binder in the material. In this process, a large number of toxic chemical reagents are used, which is not only costly, but also pollutes the environment greatly, which hinders the practical application of this method. High temperature heat treatment is an effective method for removing binders [14]. It can effectively remove binders by utilizing the principle that organic binders will decompose into gases at high temperatures (usually above 400°C).

It is worth noting that controlling the temperature and atmosphere of the heat treatment process is essential to avoid affecting and damaging the material itself. Additionally, high-temperature heat treatment can remove residual electrolyte and conductive agents from the waste graphite. The organic solvents in the electrolyte will volatilize at high temperatures, and $LiPF_6$ will decompose into LiF at high temperatures, which can be removed in subsequent hydrometallurgical leaching. The conductive agents in the graphite can be calcined in the air to become gaseous CO_2 and CO. However, it is important to note that calcining in the air may result in carbon loss from the graphite.

2.1.2 Leaching

The leaching method is to extract metals through suitable solvents such as water, acid, alkali or organic solvents [15]. In the process of waste graphite recovery, the leaching method is often used to remove most impurities in graphite, such as soluble lithium compounds, metal impurities and solid electrolytes. Water leaching not only removes some water-based binders and water-soluble lithium compounds but also reacts with the residual lithium in the waste graphite to produce hydrogen, thereby separating the SEI film from the graphite [16]. Acid leaching can remove most metal impurities, compared to untreated waste graphite, the electrochemical performance of graphite treated by leaching is improved. However, since strong oxidative solvents expand the interlayer spacing of the graphite and do not improve the surface defects of the waste graphite, the leached graphite still does not meet the requirements for commercial-grade graphite. Therefore, subsequent structural repair of the graphite is also a very important step in the graphite regeneration process.

2.2 Structural repair of graphite

Structural repair of recycled graphite after impurities removal will restore the original properties of graphite to the greatest extent. Currently, the commonly used methods for structural repair of graphite are graphitization and coating.

2.2.1 Graphitization

High-temperature graphitization can effectively restore the crystal lattice of waste graphite and improve the crystallinity and graphitization degree of graphite. In industry, graphitization furnaces are commonly used to perform graphitization within the temperature range of 2000-3000°C. This graphitization process restores the ordered layered structure and porous characteristics of graphite, while also enhancing its conductivity [17]. As a result, the graphitized graphite demonstrates higher specific capacity and good cycling stability in electrochemical tests. Extremely high temperatures can also deeply remove any residual fluorine impurities. However, re-graphitizing waste graphite significantly increases energy consumption and the cost of graphite recycling, which is a major factor hindering the industrial application of regenerated graphite.

2.2.2 Coating

Compared with fresh graphite, spent graphite exhibits higher irreversibility in LIBs, mainly due to the growth of surface films and structural destruction [18]. Carbon coating has been proven to be an efficient and low-cost method to enhance the electrochemical performance of graphite. By coating the surface of waste graphite with an isotropic amorphous carbon layer, the decomposition of the electrolyte can be suppressed, allowing for the random transport of Li^+ to eliminate some irreversible capacity and improve the rate performance of the graphite. Common coating materials include pitch, glucose, polyethylene glycol, and phenolic resin [19,20], which are sintered at temperatures of 800-1100°C to obtain carbon-coated graphite. Compared to waste graphite, carbon-coated graphite has higher specific capacity and cycling stability, mainly due to the carbon coating layer's improvement of the surface morphology, which reduces pore defects.

3 Botree's solution

After investigating a large number of scholars and the market on the methods of recycling waste graphite in LIBs, Botree combined heat treatment, leaching and coating methods to summarize a set of waste graphite recycling processes suitable for industrial production, and verified the feasibility of the process through a large number of experiments and pilot production.

3.1 Process Introduction

First, the graphite anode from used batteries is obtained through careful disassembly. Then, the anode is mixed with pure water at a solid-liquid ratio of 1:10 and stirred for 1 hour. After stirring, the copper foil is filtered out to obtain a mixture of graphite and water. This mixture is then pressure-filtered to obtain waste graphite cakes. The waste graphite cakes are calcined at 500°C in an air atmosphere for 1 hour to obtain waste graphite powder. Add 0.1 mol of sulfuric acid and hydrogen peroxide at a solid-liquid ratio of 1:4, stir at room temperature for 2 hours, then wash and dry to obtain impurity-free graphite. Then, 3wt% pitch is added to the graphite and mixed evenly. Finally, the mixture is calcined at 900°C for 2 hours in a nitrogen atmosphere to obtain carbon-coated regenerated graphite.

3.2 Regenerated graphite effect

3.2.1 Impurity removal results

For the regenerated graphite samples, ICP was used to analyze the removal efficiency of metal impurities in the graphite before and after regeneration. Table 2 shows the element content in the waste graphite obtained by pure water separation and the regenerated graphite obtained by the regeneration process in Section 3.1. Table 3 shows the content of magnetic substances (Fe, Cr, Ni, Zn, Co) in the graphite before and after regeneration.

Table 2 Element content in graphite before and after regeneration.

Graphite samples	Fe	Na	Cr	Cu	Ni	Al	Mo
GB/T 24533-2019	≤50 ppm	≤5 ppm	≤5 ppm	≤5 ppm	≤5 ppm	≤5 ppm	≤5 ppm
before regeneration/ppm	310.48	1031.15	20.62	2626.73	150.84	1124.39	20.78
after regeneration/ppm	/	3.64	/	/	/	/	/

Table 3 Magnetic substance content in graphite before and after regeneration.

Graphite samples	Magnetic materials
GB/T 24533-2019	≤0.5 ppm
before regeneration/ppm	4.59
after regeneration/ppm	0.32

From the results in Tables 2 and 3, it can be seen that the levels of impurity metal elements and magnetic substances in the graphite before regeneration do not meet the national standard GB/T 24533-2019 of the People's Republic of China. Specifically, Na primarily originates from the binder sodium carboxymethyl cellulose (CMC) used in the graphite anode, while other metal elements mainly come from the current collector, cathode materials, and external sources. However, after applying the regeneration process of hydrometallurgical leaching followed by calcination and carbon coating, the levels of impurity metals and magnetic substances in the graphite meet the standard requirements, demonstrating that this regeneration process can deeply purify the graphite samples.

3.2.2 XRD test

Figure 2 shows the XRD spectrum of the regenerated graphite, which has a strong diffraction peak of $d002$ at a diffraction angle of θ=26.536°, indicating that the regenerated graphite still maintains a complete graphite structure. No impurity phase that does not belong to graphite is found in the figure.

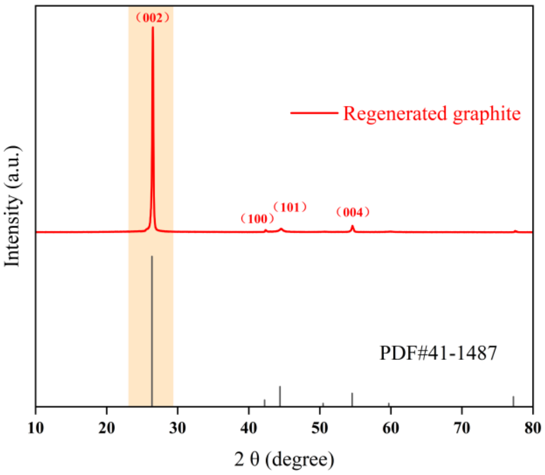

Fig. 2. XRD spectrum of regenerated graphite.

The degree of graphitization is an important indicator that determines whether graphite meets the standards for graphite negative electrode materials for LIBs. By analyzing this indicator, it can be determined whether the graphite layered structure is damaged. According to the requirements of the national standard GB/T 24533-2019, the degree of graphitization of graphite needs to be ≥90%. The degree of graphitization is calculated based on the inter-layer spacing *d*002 of graphite, and *d*002 is calculated based on the (002) diffraction angle θ of carbon recorded in the XRD spectrum. The calculation formulas (1) and (2) are as follows:

$$2d_{(002)}\sin\theta=\lambda \tag{1}$$

$$\text{Graphitization degree}=\left(\frac{0.344-d_{(002)}}{0.344-0.3354}\right)\times 100\% \tag{2}$$

In the formula: λ is the wavelength of the beam, $d_{(002)}$ is the spacing of the graphite, θ is the angle of diffraction.

By Rietveld analysis, the interlayer spacing *d*002 of the regenerated graphite is found to be 0.33563 nm, with a graphitization degree of 97.28%, whichw ell meets the national standard (≥90%) requirements. This indicates that the layered structure of the regenerated graphite has not been severely damaged and meets the requirements for commercial graphite. This proves that the recycling and regeneration method used in this study yields high-purity graphite.

3.2.3 SEM test

SEM tests were performed on the graphite before and after regeneration. Figure 3 (a, b) shows the SEM images of the graphite before regeneration. It can be observed that there are obvious impurities on the graphite surface. These impurities come from the binder and conductive agent in the pole piece. In addition to the presence of impurities, there are a large number of defects on the graphite surface due to damage during the battery cycle. It can also be observed from Figure 3 (a) that the graphite has a large-scale agglomeration phenomenon and the particle size distribution is uneven, which is mainly caused by the presence of the binder. In contrast, the SEM images of the regenerated graphite (c, d) show that the graphite particles are uniformly distributed, surface impurities are completely removed, and the surface becomes smoother, exhibiting a distinct layered structure. This indicates that the hydrometallurgical leaching followed by calcination and carbon coating has a significant restorative effect on waste graphite, maximizing the restoration of the original morphology of the graphite. For a graphite surface with uniform particle distribution, intact layered structure and smooth surface, it is beneficial to the penetration between electrolyte and graphite particles, which can promote the lithium-ion decomposition and improve the electrochemical properties.

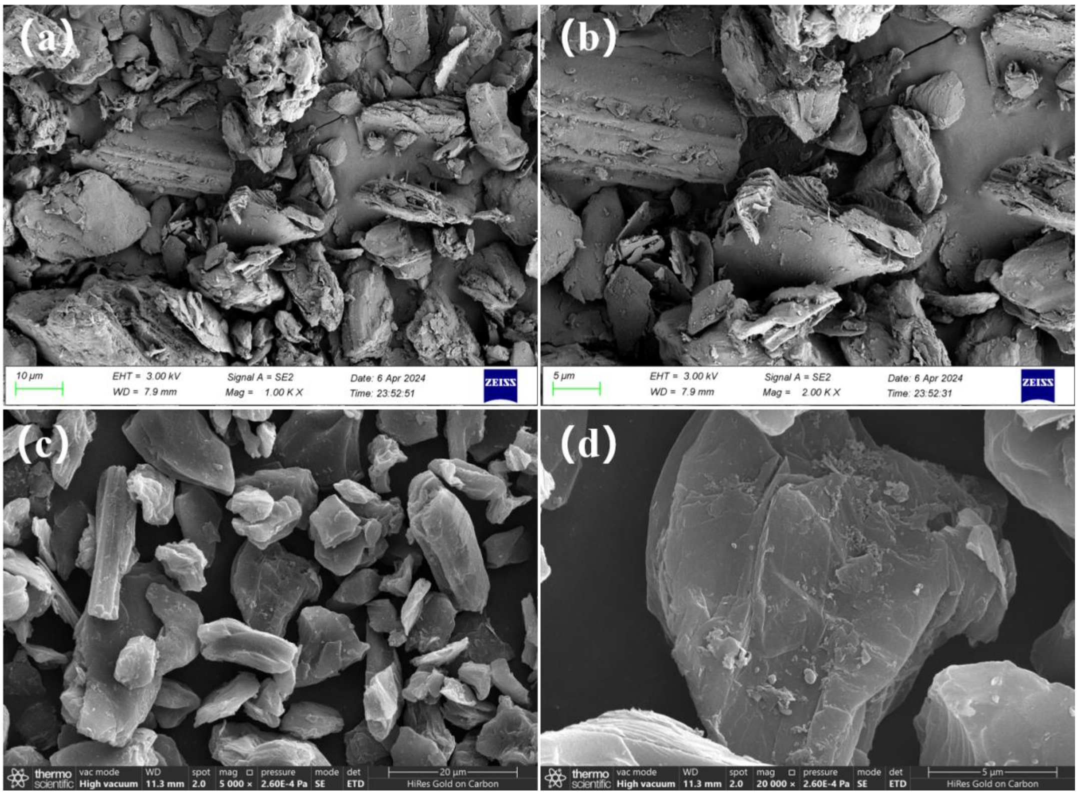

Fig. 3. SEM images of graphite powder obtained before and after regeneration: (a, b) before regeneration; (c, d) after regeneration.

3.2.4 Electrochemical performance analysis

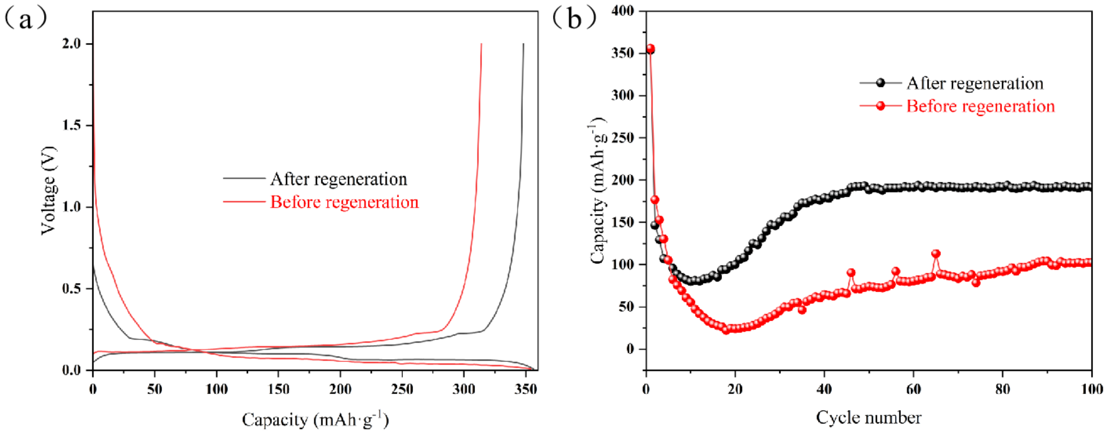

Fig. 4. Half-cell performance of graphite before and after regeneration (a) First charge and discharge curve at 0.1C and (b) Cyclic performance at 1C.

The graphite powders obtained before and after regeneration were made into half-cells for electrochemical performance analysis. Figure 4(a) shows the first charge and discharge curves of graphite powder before and after regeneration at 0.1C. Both samples exhibited a stable voltage plateau, among which the graphite before regeneration showed a larger voltage polarization than the graphite after regeneration, which was attributed to the poor conductivity of the untreated graphite before regeneration. From the figure, it can be seen that the initial discharge capacity of the graphite before and after regeneration both reached 350 mAh·g^{-1}, indicating that the lithium storage performance of the material itself has not been significantly lost. However, the initial charge capacity of the graphite before regeneration is significantly lower than that after regeneration, resulting in a large difference in the initial charge-discharge efficiency between the two. The initial efficiency of the regenerated graphite reached 97.76%, while the initial efficiency of the graphite before regeneration was only 88.93%. This is also due to the difference in material conductivity. Combined with the SEM image analysis in Section 3.2.3, there are a lot of impurities in the graphite before regeneration, and large-scale agglomeration occurs, which greatly increases the material resistance and is not conducive to the transmission of lithium ions. Additionally, the surface morphology of the graphite before regeneration is damaged, creating numerous defects. This results in the consumption of more electrolyte and lithium ions during the first charge-discharge cycle, which is one reason for its lower initial efficiency. Furthermore, the presence of impurities reduces the content of active material in the anode, leading to a lower specific capacity under the same ratio. The cycling performance of graphite before and after regeneration at 1C is shown in Figure 4 (b). Due to the direct transition from 0.1C formation to 1C cycling, resulting in a rapid decrease and then slow increase in the circulation capacity of both materials at the beginning. However, by comparison, it is found that the cycling stability and capacity retention of the regenerated graphite at 1C is significantly higher than that of the graphite before regeneration. This is likely because the combined method of hydrometallurgical leaching and heat treatment deeply removed impurities from the graphite, and the carbon coating maximally restored the original morphology of the graphite, enhancing its conductivity. This improvement aids in the formation of a stable SEI film on the graphite surface. In general, Botree's recycled graphite process has a significant repair effect on waste graphite in used LIBs, which is beneficial to restoring the electrochemical properties of graphite.

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Presenter Biography

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Zhu Liang holds a PhD in Materials Engineering from KU Leuven, Belgium. After PhD, he has been engaged in the R&D of cathode materials used in lithium-ion battery for over 11 years in Umicore. He possesses extensive industry experience in cathode materials for lithium-ion batteries and in-depth insights in the new energy and sustainability sector. During his studies, he published 5 first author academic papers as well as several second author papers.