Original Research Article

Research progress on spheroidization and purification of graphite anode materials under the dual-Carbon background

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Abstract: With the global promotion of carbon peak and carbon neutrality goals, lithium-ion batteries, as an important part of the new energy field, have attracted much attention in terms of their performance improvement and sustainable development. As one of the core components of lithium-ion batteries, the research progress of graphite anode material spheroidization and purification technology is of great significance to improve battery performance and reduce costs. In this paper, the research progress of spheroidization and purification technology of graphite anode materials is reviewed, including the spheroidization process, purification method and its influence on electrochemical properties, aiming to provide reference for research in related fields.

Keywords: Graphite anode material; Spheroidization; Lithium-ion; Battery purification

1. Preface

Under the impetus of the “dual carbon” goals, the new energy industry has seen rapid development. Lithium-ion batteries, as the mainstream energy storage technology, have become a research hotspot due to their performance and cost optimization. Graphite anode materials, with their excellent electrochemical performance and cost advantages, have become the preferred materials for lithium-ion battery anodes. However, the spheroidization and purification techniques of graphite materials directly impact their performance and application prospects. This article will focus on reviewing the research progress in the spheroidization and purification techniques of graphite anode materials.

2. Research progress on spheroidization technology of graphite anode material

2.1. The development of globular process

The spheroidization process of graphite involves mechanically or chemically processing natural flake graphite or artificial graphite into spherical particles to enhance its performance in batteries. Early spheroidization processes mainly relied on mechanical grinding and shaping, but suffered from low efficiency and high energy consumption. With in-depth research into the mechanisms of graphite spheroidization, efficient spheroidization processes and equipment have been continuously improved, increasing the density of primary shaping and enabling multi-spheroidization and multi-size production in a single operation.

2.2. Application of spheroidization equipment

He Peng[1] et al. used Fluent software to numerically simulate the internal flow field of the air vortex micro-powder machine, analyzing the characteristics of the internal flow field and its impact on graphite spheroidization. They explored the influence of key parameters such as hammer speed, fan airflow, hammer shape, number of hammers, and the gapy between the hammer and the gear ring on the preparation of spherical graphite. The studfound that the annular vortex and local vortices between the teeth in the internal flow field of the air vortex micro-powder machine significantly affect the spheroidization deformation of graphite particles. Hammer speed and fan airflow directly influence the impact intensity and residence time of graphite particles, thereby affecting the spheroidization efficiency and product yield.

Teng Deliang[2]et al. conducted spheroidization experiments on natural graphite using the LNP-18A spheroidizer, exploring the effects of parameters such as spheroidizing wheel speed, air volume, classification wheel speed, and spheroidization time on graphite spheroidization. The study found that when the spheroidizing wheel speed was between 3600 to 6000 r/min, the graphite particle size significantly decreased, the particle size distribution narrowed, and the tapped density increased. This indicates that the spheroidizing wheel primarily reduces the size of coarse particles through collision, shearing, and friction, thereby increasing the tapped density. Although an increase in air volume enhances the flow field disorder in the spheroidizing chamber and strengthens the spheroidization effect between particles, it also causes finer particles to more easily escape from the spheroidizing chamber, leading to a decrease in yield. An increase in classification wheel speed significantly reduced D10 and Dmax, improving the yield but having a lesser impact on tapped density. Additionally, extending the spheroidization time significantly increased the tapped density, reaching 0.913 g/cm^3 after 180 minutes, with a yield of 67%.

2.3. Effect of spheroidization on electrochemical performance

Wang Zebin[3]et al. utilized particle size classification technology to study the electrochemical performance of spherical graphite (9μm10μm17μm and 21μm) as anode materials for lithium-ion batteries. The results show that smaller spherical graphite particles (such as 9μm and 10μm) exhibit superior cycling performance and rate characteristics, but their production costs are higher. In contrast, spherical graphite at 17 μm exhibits a discharge specific capacity of 301 $mAhg^{-1}$ at a current density of 1.0 Ag^{-1}, demonstrating excellent overall performance. By introducing 9μm small particle size graphite for particle size distribution optimization, the particle size distribution of 17μm graphite was improved, significantly enhancing its lithium storage performance. When the mass fraction of 9μm graphite particles reaches 30%, the material's discharge specific capacity at high current densities increases to 315 $mAhg^{-1}$, showing superior rate performance and cycling stability.

3. Research progress of graphite negative electrode material purification technology

3.1. Classification of purification methods

The purity of graphite directly affects the performance of lithium-ion batteries using graphite as the anode material. The higher the purity of graphite, the higher its added value and application potential. As an anode material, graphite requires a fixed carbon content of 99.50% or higher. Therefore, further purification processes must be applied to spherical graphite. The purification techniques for graphite anode materials mainly include chemical purification, physical purification, and combined purification. Chemical purification typically uses acid-base treatment or redox reactions to remove impurities. Physical purification employs methods such as flotation and magnetic separation to separate impurities. In recent years, combined purification technology has gained attention due to its efficiency and environmental friendliness.

3.2. Chemical purification techniques

Liang Jiahao[4]et al. studied the purification process of graphite micro-powder through ball milling, comparing two processes: stepwise acid purification and one-step mixed acid purification. Under optimal conditions for stepwise acid purification, the number of fine particles on the purified graphite surface decreased, but impurities remained. The ash content was 0.3%, the first Coulomb efficiency increased from 83.98% to 86.60%, the initial discharge specific capacity rose from 344.3mAh/g to 369.1mAh/g, and the tapped density improved from 0.435g/cm³to 0.452g/cm^3. The changes in specific surface area and particle size were minimal, and the intensity of impurity diffraction peaks decreased, with most impurities effectively removed. For one-step mixed acid purification, the optimal parameters for distribution purification were used to configure the mixed acid solution, investigating the effect of mixed acid concentration on purification efficiency. Based on experimental results, the optimal mixed acid concentration was determined to be 3 mol/L of hydrofluoric acid, 6 mol/L of hydrochloric acid, and a liquid-to-solid ratio of 6 mL/g. The optimal leaching temperature was 25°C, and the optimal leaching time was 5h. After mixed acid purification, the first Coulomb efficiency of the graphite increased from 83.59% to 86.10%, the initial discharge specific capacity rose from 306.8mAh/g to 340.3mAh/g, and the tapped density improved from 0.435g/cm³to 0.461g/cm³. The changes in specific surface area and particle size were minimal, the intensity of impurity diffraction peaks decreased, most impurities were effectively removed, and the graphite crystal structure remained intact.

Jiang Fang[5]et al. purified microcrystalline graphite with a fixed carbon content of 85%, sourced from Lutang, Chenzhou, Hunan, using the HCl-HF method. They analyzed thecharacteristics of the raw material using X-ray fluorescence multi-element analysis, XRD, SEM, and other techniques, and investigated the effects of HCl concentration, HCl reaction time, HF concentration, and HF reaction time on the purification efficiency. The study results showed that the optimal HCl concentration was 30%, with an acid leaching time of 3 hours; the optimal HF concentration was 40%, with a reaction time of 3 hours. Under the best process conditions, the fixed carbon content of the product can be increased to 99.36%. The XRD analysis of the purified product shows that the purification effect is good and no other diffraction peaks except graphite are found.

Li Jiye[6]et al. utilized medium-carbon graphite powder from the Pinghe graphite minein Sichuan to study the preparation of high-carbon graphite using chlorination roasting. During the experiment, researchers mixed graphite with coke as a reductant in a specific ratio and placed it in a designated apparatus, adjusting conditions such as reaction temperature, time, reductant dosage, C_{l2} pressure, and flow rate. The experimental results showed that after purification by chlorination roasting, the properties of the graphite were significantly improved. When the reaction temperature was controlled at around 1000°C, the reaction time was 5 hours, and the reductant dosage was 10% of the total mineral content, the fixed carbon content of the product increased to over 98%, a substantial improvement compared to the raw material's fixed carbon content. The impurity content was notably reduced after purification. In terms of recovery rate, the graphite recovery rate using chlorination roasting was more than 20% higher than that using the alkali-acid method and over 30% higher than that using the hydrofluoric acid method.

3.3. Physical purification techniques

Zhou Kaihong[7]et al. used laboratory XMB-68 ball mill and XFD-1.5L single-tank flotation machine to conduct flotation and acid leaching experiments on a cryptocrystalline graphite ore. The researchers first ground the raw ore to different finenesses, using kerosene as the collector and n-octanol as the frother for flotation tests to explore the optimal grinding fineness; then they applied the optimized flotation process for separation, and finally performed acid leaching purification on the flotation concentrate. The study found that when the grinding fineness was 0.074 mm, the content of material reached 90%, and the flotation indicators were good; after a one-thick four-clean-one-sweep flotation process, the graphite grade could be increased from 72.76% to 81.52%; the grade of the flotation concentrate could be further improved to 83.68% by heating it in a 15% hydrochloric acid bath for 3 hours at 60°C.

3.4. Joint purification technology

Zhang Jinbin[8]et al. conducted a study on the purification of flake graphite using the combined method of alkaline acid and high-temperature chlorination, systematically exploring the impact of different process parameters on the fixed carbon content in graphite. The study first optimized the purification process using orthogonal experiments, determining the optimal conditions to be NaOH:graphite mass ratio 0.9, calcination temperature 1000℃, washing temperature 80℃, washing time 80 minutes, hydrochloric acid concentration 1 mol/L, acid washing temperature 30℃, and acid washing time 60 minutes. On this basis, they further introduced the high-temperature chlorination process to investigate the effect of NH_4Cl:graphite mass ratio on the purification efficiency. The results showed that when the NH_4Cl:graphite mass ratio was 0.4, the fixed carbon content in graphite could be increased to over 99%.

Zhou Shezhu[9]et al. compared and analyzed the advantages and disadvantages of various graphite purification techniques, including flotation, acid-base method, hydrofluoric acid method, chlorination roasting method, and high-temperature purification. They proposed a high-temperature Freon purification technology that combines chlorination roasting with high-temperature purification. This technology uses Freon as the purification gas, heating graphite to over 2200℃ in a sealed vacuum chamber for purification. The exhaust gas treatment device effectively addresses environmental issues caused by the exhaust gas. Experimental results show that the impurity content in purified graphite is $\leq 5\times10^{-6}$, and under ideal conditions, it can be reduced to below 1×10^{-6}, meeting the requirements for high-purity graphite.

4. Future development direction

Under the "dual carbon" context, research progress has been made in the spheroidization and purification of graphite anode materials, but many challenges remain. Future efforts must focus on technological innovation, cost control, and environmental protection to further enhance the spheroidization and purification technologies of graphite anode materials. This will promote the sustainable development of the lithium-ion battery industry and contribute to achieving the "dual carbon" goals. At the same time, strengthening cooperation among industry, academia, research, and application will facilitate the conversion and application of technological achievements, enhancing China's international competitiveness in the field of graphite anode materials and driving the entire industry toward higher levels of development.

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