Research Progress in Modified Graphite Negative Electrode Materials for Lithium-Ion Batteries

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Abstract. As manufacturing and technology advance quickly, more and more energy is utilized, creating a number of issues with resource scarcity and environmental damage. Electric chemistry technology has advanced quickly in recent years, with lithium-ion batteries (LIBs) standing out due to their higher working potential, high energy density, and low pollution levels. These batteries are now widely employed in industrial sectors including electronics and electric cars. Carbon-based materials are frequently employed as negative electrode materials for LIBs because of their benefits of having a large specific surface area, strong conductivity, and affordability. However, untreated graphite has drawbacks such as low capacity, unstable layered structure, and low charging and discharging platform, which can have a significant impact on the performance of batteries. By modifying graphite materials differently, these problems can be effectively solved. Therefore, this paper faced by LIBs and potential future developments is summarized in this study, along with certain modification techniques and research advancements of graphite anode materials in recent years.

Keywords: Lithium-ion battery, negative electrode, graphite, modified.

1. Introduction

High specific capacity, high operational voltage, and superior safety performance are benefits of LIBs. Since its introduction to the market in 1991, lithium-ion batteries have established themselves as one of the most efficient methods for storing energy and are compatible with a variety of portable gadgets, including laptops and cell phones. Lithium-ion batteries have increasingly been used in large-scale energy storage businesses like electric automobiles as research into them has continued to advance [1]. Numerous positive electrode material systems have been researched since the invention of lithium-ion batteries, but graphite negative electrode material systems are still in use today. The layered structure of graphite materials and their low lithium intercalation potential make them good candidates for lithium-ion insertion and extraction. Graphitized carbon (natural flake graphite, graphitized mesophase carbon microspheres, synthetic graphite, etc.) and non-graphitized carbon (soft carbon, hard carbon, etc.) are the subjects of study at the moment. The development of synthetic graphite and natural graphite negative electrode materials has long since established itself as the industry standard, accounting for over 90% of the market share within the dual market context of power-type lithium batteries and consumer-type lithium batteries. Flake graphite is the primary raw material used in natural graphite negative electrode materials, although there are a number of disadvantages: The first charge-discharge efficiency of flake graphite is low due to its low specific surface area; anisotropy hinders Li^+ diffusion within it; and cracks may form between layers as a result of the insertion and removal of lithium ions, which increases Li^+ diffusion resistance. Since conventional graphite negative electrodes can no longer satisfy the rising high-performance standards, several researchers both domestically and internationally have been actively investigating modification technologies. This article discusses the most recent developments in coating, surface, element doping, and other modification methods used to modify graphite negative electrode materials.

2. Structure and Principle of Lithium-ion Batteries

An example of a lithium-ion concentration difference battery is a LIB, which is primarily made up of an electrolyte, separator, positive electrode, and negative electrode. Figure 1 illustrates the analysis of the lithium-ion battery's operation utilizing graphite as the negative electrode and $LiCoO_2$ as the positive electrode [2]. During charging, lithium ions separate from the positive $LiCoO_2$'s lattice, diffuse into the electrolyte, and then gradually insert themselves through the separator into the interlayer of the graphite negative electrode. The positive electrode will simultaneously release an equivalent number of electrons that will travel via the external circuit to the graphite negative electrode, completing the circuit, to maintain charge balance. Lithium ions will separate from the graphite interlayer of the negative electrode during discharge, return via the electrolyte, and embed in the $LiCoO_2$ lattice, concluding a charge-discharge cycle. Electrons will then be transported to the positive electrode through the external circuit [3].

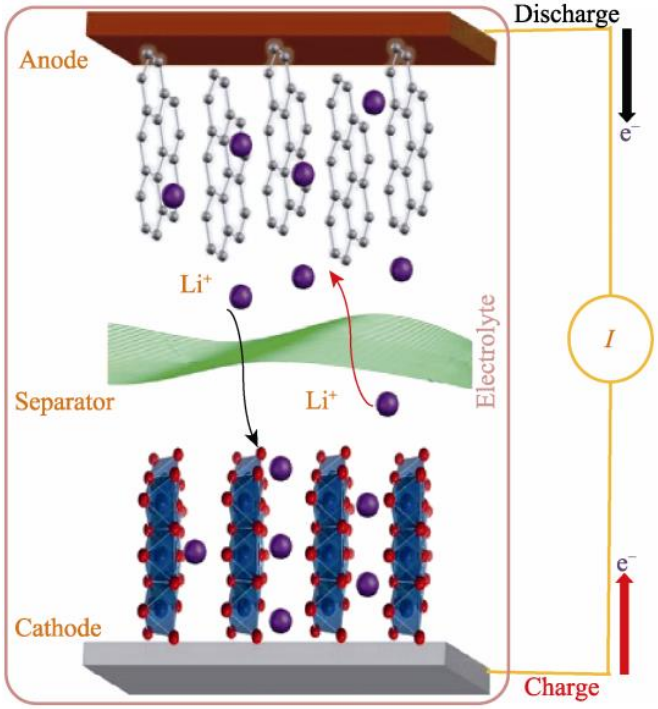

Figure 1. Schematic diagrams of working principle for LIBs

3. Modification of Graphite Anode Materials

According to the energy storage mechanism, the fast-charging lithium-ion anode materials are divided into three types: intercalation materials, conversion materials, and alloy materials. As shown in Figure 2, intercalation materials mainly include carbon materials (such as graphite) and intercalation transition metal oxides [4].

Lithium ions are extracted from the positive electrode during the charging process and subsequently incorporated into the negative graphite to create graphite-embedded lithium-ion compounds. The process of lithium ions continually embedding and extracting active components and passing through oxidation-reduction processes is what makes LIBs work. Lithium ions are embedded in the layered graphite structure of the negative electrode during discharge and are removed from the graphite during the charging of LIBs. During charging, lithium ions are detached from the lithium-containing material in the positive electrode, passed through the separator by the electrolyte, and then reached the negative electrode. Generally speaking, the optimum graphite anode material needs to include the following benefits: (1) It has strong chemical and structural stability, which increases battery cycle life. (2) The discharge process results in modest, reversible specific

capacity variations in electrode potential. (3) Excellent electrical and ionic conductivity, which increases the battery's power density. (4) Concerns about environmental safety and preservation [5].

However, the commonly used graphite continues to have the drawbacks of low working potential, poor rate performance, low specific capacity, and poor stability, which will lead to a decrease in the performance of LIBs and also face security issues, making it unable to meet the requirements of their current development status. The alteration of graphite, the component of the negative electrode in lithium-ion batteries, must thus be studied [5].

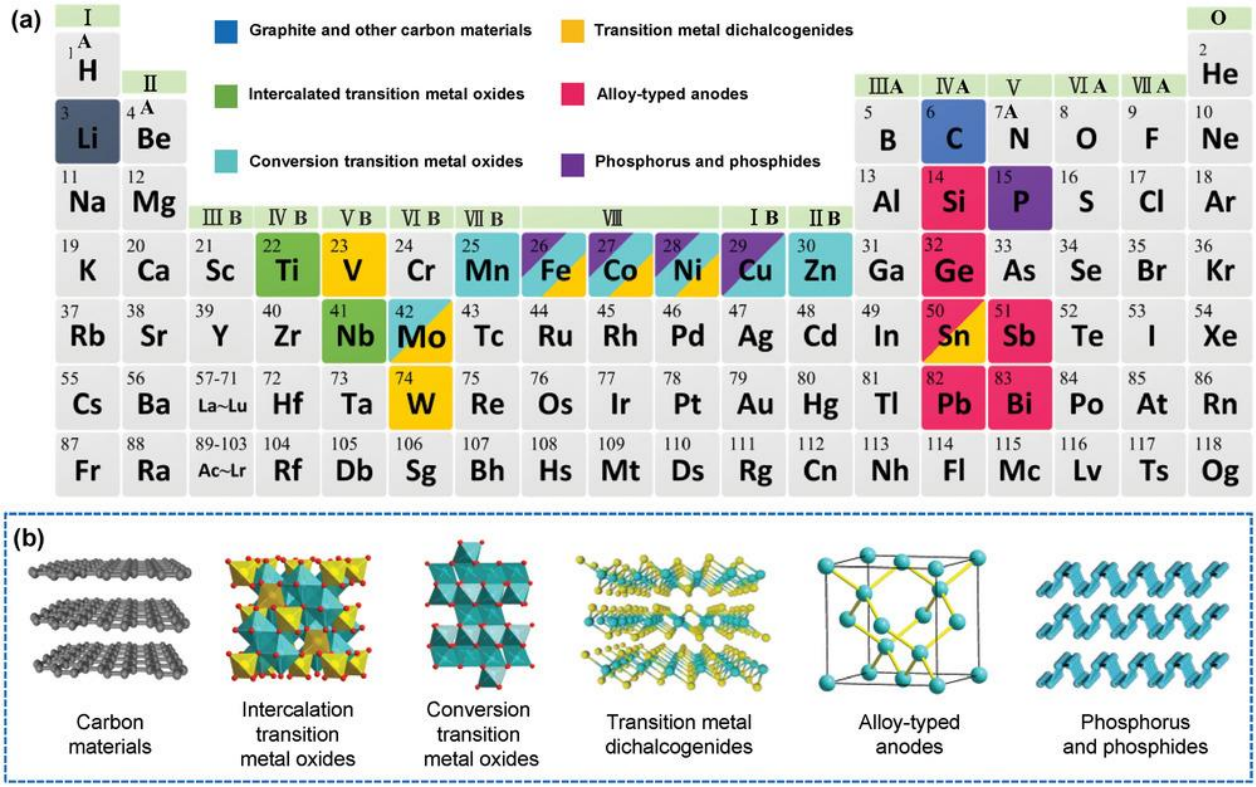

Figure 2. Intercalation materials for graphite modification [4]

3.1. Surface Modification

3.1.1. Carbon coating

Due to the change in graphite layer spacing during charge and discharge, the graphite flakes flake off and are crushed, which results in poor electrocyclic performance. The surface of graphite is saturated with embedded ions, and solid diffusion of lithium ions in graphite is slower than embedding. The performance of the battery amplification is further impacted by lithium deposition, which results from the restriction of additional lithium-ion embedding. Higher capacity, more stable cycling, and better rate performance may all be attained with LIBs by using high-performance carbon negative electrode PTCDA strong carbon coated graphite material [6].

3.1.2. Hydrothermal modification

Due to the unstable structure, poor rate performance, and poor cycling of the solid electrolyte interface (SEI) layer formed by graphite anode material, it is necessary to improve it. The melamine hydrothermal method can effectively enhance graphite and significantly improve its electrochemical performance. Because melamine and graphite can form a dense melamine coating on the surface of graphite particles under hydrothermal conditions. The ionic conductivity of Li^+ is improved by producing Li3N during the lithium process, and this improves the poor structural stability and magnification performance of the graphite negative electrode. This is accomplished by altering the mass ratio of melamine to graphite to improve the graphite magnification and cycling performance [7].

3.1.3. Double layer coating modification

Graphite is the most used anode material for lithium-ion batteries. The graphite anode's speed performance, however, has not been enough for the commercial development of electric cars. As a result, the double-coated artificial graphite particles (AG@HC@Al_2O_3) generated by hard carbon and alumina coating enhance the graphite anode material. The AG@HC@Al_2O_3 synthesis process schematic diagram is shown in Figure 3. The outer alumina coating can enhance the interface wettability, that is, by increasing the degree of wetting of the electrolyte to the graphite negative electrode, it is easier for lithium ions to enter, further improving the high current charging ability. The inner hard carbon layer offers more insertion sites for lithium ions by increasing the layer spacing, thus improving rate performance. Additionally, the loss of coulomb efficiency brought on by single-layer hard carbon coating can be lessened by double-layer coating utilized as a synthetic solid electrolyte interphase film. After 150 cycles, AG@HC@Al_2O_3 showed a remarkable capacity retention rate of 94.4% at 1C (1C = 372 mAh g-1). The double-layer coating approach was effective in producing AG@HC@Al_2O_3 with high speed and rate performance, which was superior to untreated graphite. Graphite materials will be employed more frequently in the field of high-speed lithium-ion batteries after being upgraded using this technique [8].

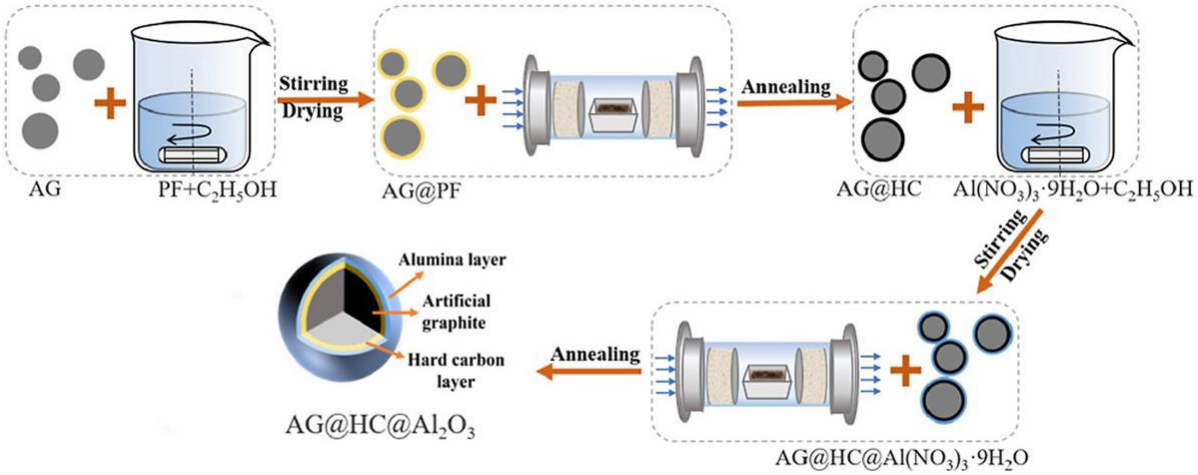

Figure 3. Preparation of AG@HC@Al_2O_3 [8]

3.1.4. Oxidation/reduction treatment

To modify the chemical characteristics of the graphite surface and produce EG powder, the graphite powder is first peeled off using the Li^+/Na^+ intercalation process, and then the surface of the peeled graphite is oxidized using oxygen plasma etching. Electrostatic adsorption was used to cover the crystal SnO_2 particles with amorphous FeO (OH), creating a finely structured SnO_2 FeO (OH) coating. Electrochemical experiments revealed that surface-modified graphite performs better than untreated graphite in terms of capacity and rate, and the discharge capacity is also enhanced [9].

3.2. Alkali Roasting

Due to its high graphitization, purity, and crystallinity, pulse graphite has been studied as a negative electrode material for LIBs, which can significantly increase the cycle life and capacity of LIBs. However, the original vein graphite cannot be utilized directly as a negative electrode material since it becomes unstable during the battery cycle. To improve the chemical characteristics of the raw vein graphite, alkali roasting and acid leaching were applied. By comparing various NaOH solution concentrations, the acid leaching with HCl purification effectiveness of vein graphite was evaluated. The optimal concentration for alkali roasting, it was determined, was 20% volume concentration of NaOH. By using this technique, the primary vein graphite's carbon content, cycle stability, and capacity retention rate may all be significantly increased [10].

3.3. Doping Vario-property

Due to graphite's drawbacks, such as its low specific capacity and subpar cycling performance, hard carbon, activated carbon, carbon nanotubes, graphene, porous carbon, carbon fiber, and other carbon materials are widely used to substitute the graphite negative electrode. There are still more effective methods, one of which is doping heteroatoms into the structure of carbon-based materials, despite the fact that these techniques can somewhat improve the electrochemical performance of LIBs. N is more electronegative than C, making it more suitable for regulating the electrical structure of carbon-based materials. By modifying the electronic structure and electron distribution of carbon materials, n-doping enhances the electrochemical performance of LIBs and the dynamic performance of LIBs. Because no defects are formed when carbon atoms are substituted by nitrogen atoms during the N-doping process and high electron mobility is maintained, graphite-nitrogen preserves the mobility of graphene [11]. The several spots where nitrogen atoms have been doped with carbon compounds are shown in Figure 4.

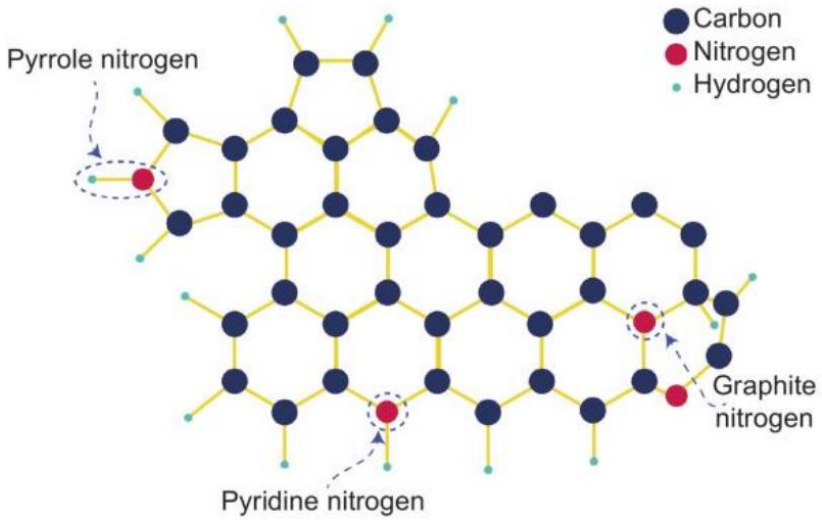

Figure 4. Various nitrogen atom doping locations in carbon-based compounds [11]

3.4. Compound Modification

Use graphene-based composite material instead of graphite to significantly boost its theoretical capacity (twice that of graphite), according to studies. Graphene-based composite material is an excellent negative electrode material. To improve the electrochemical performance of lithium-ion batteries, graphene must be combined with other active materials, as the direct use of graphene composite material as a negative electrode material for lithium-ion batteries was found to be less than ideal and insufficient to meet the demands of modern use. The ion space effect and low stability are to blame for this. The most prevalent silicon-graphene composite materials are TiO_2-graphene composite anodes, $Li_4Ti_5O_{12}$-graphene nanocomposite anodes, ZnO-graphene nanocomposite anodes, MoS_2-graphene nanocomposite anodes, Fe_3O_4-graphene nanocomposite anodes, and MoO_2-graphene nanocomposite anodes. In the charge and discharge process, graphene composite materials enhance electrical conductivity. They also have a superior function for storing lithium, with a higher specific capacity and greater cycle stability [5].

4. Conclusion

The enhancement of graphite anode materials for LIBs is a crucial factor in improving their electrochemical performance. This paper summarizes four methods used to modify graphite anode materials, namely surface modification (including coating and oxidation/reduction treatment), acid-base purification, doping modification, and composite modification, and discusses the detailed processes of these four modification methods and their corresponding improvements. Currently, the

modification of graphite anode materials has proven effective in enhancing the electrochemical performance of LIBs. It has led to improved structural stability, cycle stability, rate performance, and specific capacity of graphite anode materials. Consequently, this advancement enables wider commercial applications of lithium-ion batteries.

However, despite significant progress in the research of LIBs, they still cannot meet the requirements of commercial applications and there are many other issues that need to be overcome. On the one hand, high costs hinder further commercial applications. Therefore, there is still great room for improvement in the low cost and application of carbon-based materials. There is little research on carbon doping in modification methods, which also indicates that the knowledge and principles in this field have not been fully understood and applied, and further research and discovery are needed. In addition, research should focus more on rapid kinetics rather than improving the specific capacity of anode materials. With the deepening of research, significant progress is expected in the research of graphite anode materials for LIBs.

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