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A Comprehensive Review of the Development of Anode Materials for Lithium-Ion Batteries

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Abstract: *With the sharp increase in global demand for renewable energy and electric vehicles, lithium-ion batteries, as a key technology for energy storage, have become a hot topic of research for performance improvement and cost reduction. As an important component of lithium-ion batteries, anode materials directly affect the energy density, cycle stability, and safety performance of the battery. This paper reviews the research progress of anode materials for lithium-ion batteries in recent years, focusing on the characteristics, advantages, challenges, and future development directions of several major types of anode materials, including carbon-based materials, silicon-based materials, alloy materials, transition metal oxides, and lithium titanate. Through comparative analysis, the aim is to provide theoretical references and practical guidance for the innovative design of anode materials for lithium-ion batteries.*

Keywords: *Lithium-ion batteries; Anode materials; Carbon-based materials; Silicon-based materials; Alloy materials; Transition metal oxides; Lithium titanate*

1. Introduction

Since the commercialization of lithium-ion batteries in the early 1990s, they have quickly become the mainstream power source in fields such as portable electronic devices, electric vehicles, and energy storage systems, due to their high energy density, long cycle life, and no memory effect. As an important part of lithium-ion batteries, the performance of anode materials has a decisive impact on the overall performance of the battery. Therefore, developing high-performance, low-cost, and environmentally friendly anode materials is one of the core tasks in the development of lithium-ion battery technology. The ideal anode material for lithium-ion batteries should meet the following conditions[1]: high specific capacity to improve the energy density of the battery; good electronic conductivity and ionic diffusivity to ensure fast charging and discharging capabilities; a stable structure to maintain a long cycle life; a low lithium insertion potential to ensure a higher output voltage; abundant resources, low cost, and environmental friendliness [2]. According to the different chemical compositions and lithium storage mechanisms [3], anode materials for lithium-ion batteries can be divided into several major categories: carbon-based materials, silicon-based materials, alloy materials, transition metal oxides, and lithium titanate.

2. Carbon-based anode materials

2.1. Graphite

As the most widely used anode material for commercial lithium-ion batteries, graphite has a layered structure with small volume changes during lithium ion insertion/extraction, and good cycle stability. However, its theoretical specific capacity is relatively low (about 372 mAh/g), which limits the further improvement of the battery's energy density.

Graphite is currently the most widely used commercial negative electrode material for lithium-ion batteries, with a layered structure. During the insertion/extraction of lithium ions, the volume change is small, the cycling stability is good, the cost is low, the lifespan is long, and the weight is light. However, there are also some drawbacks,Mainly includes: Low charging capacity: During high current charging, the charging capacity of graphite materials is relatively low, which limits the fast charging ability of the battery. Surface prone to lithium deposition: Under high rate charge and discharge conditions, lithium dendrites are prone to deposit on the surface of graphite negative electrodes, which not only affects the performance and lifespan of the battery, but may also pose a safety hazard. Layered structure limitation: The layered structure of graphite determines that lithium ions must be embedded from the end face of the material and gradually diffuse into the interior of the particles, resulting in a long diffusion path and low diffusion rate of lithium ions, which limits the fast charging performance. Limited capacity: The theoretical specific capacity of graphite is 372 mAh/g. With the increasing demand for higher energy density batteries, the capacity of graphite can no longer meet the needs of some application scenarios. Cycle performance issues: Graphite may experience layer delamination during long-term cyclic use, leading to a decrease in the cycling performance of the battery. Safety issues: When the graphite negative electrode is charged at high voltage, it may cause overcharging reactions, leading to battery overheating and even thermal runaway and safety accidents.To address these issues, researchers are exploring strategies such as structural design, chemical modification, and surface coating to enhance the performance of graphite negative electrode materials, such as increasing the interlayer spacing of graphite, increasing the surface porosity of graphite, introducing doping elements, and preparing core-shell structures to improve their fast charging performance and cycling stability.

2.2. Other carbon materials

Including soft carbon, hard carbon, and nanocarbon, etc., both soft and hard carbon are composed of randomly distributed curved graphite sheets, but the former can be graphitized at high temperatures, while the latter cannot be graphitized even at temperatures >3000°C. These materials have a higher specific capacity (up to 500-1000 mAh/g), but issues such as low initial Coulomb efficiency and poor cycle stability need to be addressed. Preparing composite materials is an effective way to improve the performance of carbon-based materials. Wang Siyi and others from Hubei University prepared Co9S8/C composites by the molten salt method, and after 100 charge and discharge cycles at a current of 100mA/g, the discharge specific capacity can reach 898.6mAh/g, which can be a potential choice for anode materials of lithium-ion batteries [4]. Yue Hongwei and others from Xuchang University used a one-step in-situ hydrothermal method to prepare carbon-coated ZnSnO3 composite materials, and after 200 cycles at a current density of 200mA/g, the reversible capacity of the ZnSnO3/C composite electrode can reach 1274.9mA/g, and even after 500 cycles at a high current of 5000 mA/g, it still provides a discharge specific capacity of 663.2 mAh/g [5].

Carbon materials represent the most practical negative electrode materials for lithium-ion batteries due to their diverse microstructures and properties, low cost, and wide availability. However, the lower theoretical capacity (graphite) and poor disordered carbon limit their further application in lithium-ion batteries, which has prompted the research community to continuously develop other high-performance negative electrode materials.

3. Silicon-based anode materials

Silicon has a high theoretical specific capacity (about 4200 mAh/g), which is more than ten times that of graphite and is considered to be a very promising next-generation anode material for lithium-ion batteries. However, the volume expansion rate of silicon during lithium insertion is as high as 300%, leading to material pulverization and detachment, which seriously affects the cycle performance. To solve the problem of silicon volume expansion, researchers have developed silicon/carbon composites, silicon/metal composites, and silicon nanostructures, etc., by restricting the size of silicon particles, introducing a buffer layer, or using a porous structure, etc., effectively improving the cycle stability of silicon-based anodes. Li Zhengwei and others from Guilin University of Electronic Technology prepared Si@FNC composite material (silica gel derived carbon/NH4F@nanometer silicon composite) by a one-pot water bath method using agar and NH4F to achieve carbon coating and doping modification of nanometer silicon, and at a current density of 500mA/g, the first discharge specific capacity of the Si@FNC composite material was 2001.0 mAh/g, and after 200 cycles of charge and discharge, it remained at 836.7mAh/g, showing excellent electrochemical performance [6].

Researchers are conducting various studies, including developing new binders, designing silicon-based composite materials, optimizing electrolyte formulations, etc., to improve the electrochemical performance and cycling stability of silicon-based negative electrode materials. For example, by coating carbon or metal oxide layers on the surface of silicon particles, volume expansion can be buffered and structural stability can be improved; The use of self-healing adhesives can improve the mechanical stability of electrodes; Adding specific electrolyte additives can help form a stable SEI layer and reduce electrolyte consumption. With the progress of these studies, the application prospects of silicon-based negative electrode materials will become even broader.

4. Alloy anode materials

4.1. Tin-based alloys

Tin-based alloys have a high theoretical specific capacity and good conductivity, but they also face the problem of volume expansion. By alloy design, nanocrystallization, and compounding, their cycle stability can be improved. The research group of Shandong University of Technology synthesized a series of tin-based nanomaterials such as nano-SnO2, SnO2/C composite materials, and NiO-SnO2 composite metal oxides by a simple hydrothermal method [7]. The SnO2/C composite material electrode had a first discharge specific capacity of 1197.5mAh/g, a first Coulomb efficiency of 55.11%, and after 50 cycles, the capacity was maintained at 190 mAh/g, while the nano-SnO2 material electrode had a first discharge specific capacity of 940.6mAh/g, and the NiO-SnO2 composite material had a higher reversible specific capacity and better cycle performance.

Researchers are exploring strategies such as structural design, surface modification, alloying, and introducing buffer layers to improve the performance of alloy based negative electrode materials. For example, by preparing alloy nanostructures, designing core-shell structures, or using porous materials, the impact of volume expansion can be reduced and structural stability can be improved; The conductivity and cycling stability of alloy negative electrodes can be improved by surface coating or doping. With the deepening of research, the performance of alloy based negative electrode materials is expected to be further improved.

4.2. Other alloy materials

Alloy materials such as aluminum-based and germanium-based also show certain application potential, but they also need to solve the problems of large volume changes and poor cycle performance.

5. Transition metal oxide anode materials

Transition metal oxides store lithium through conversion reactions and have a high theoretical specific capacity. However, the large irreversible capacity loss in the first cycle, voltage hysteresis, and poor cycle stability limit their commercial application. Guizhou Light Industry Vocational and Technical College reviewed the research progress of nickel ferrite, which is easy to obtain raw materials, simple to prepare, and has a high specific capacity, but often accompanies the electrode polarization caused by large volume expansion during the charging and discharging process, which can cause the material to fall off and lead to a rapid decline in battery capacity [8]. To improve the performance of the material, there are mainly three methods: one is to design nano-structured nickel ferrite electrode materials, the second is to form composite materials with carbon materials that can act as a buffering substrate, and the third is to compound with other metal oxides. The main modification strategies for transition metal oxides are through methods such as nanocrystallization, doping, and surface coating.

Researchers are exploring various strategies to improve the performance of transition metal oxide negative electrode materials, such as nanomaterialization, morphology control, composite with carbon materials, and introduction of other metal oxides. For example, nanomaterialization can improve the reactivity and structural stability of materials; Composite with carbon materials can improve conductivity and buffer volume expansion; By introducing other metal oxides, composite materials with better electrochemical performance can be formed. These research advances provide the possibility for the commercial application of transition metal oxide negative electrode materials.

6. Transition metal disulfide compounds

The research on transition metal dichalcogenides (TMDs) as negative electrode materials for lithium-ion batteries has received widespread attention in recent years. These materials are considered important candidate materials for improving the performance of lithium-ion batteries due to their unique physical and chemical properties, such as high theoretical capacity, good conductivity, and relatively low cost[9]. TMDs are a type of layered material composed of transition metal atoms arranged in a hexagonal structure, with VIA group atoms (such as sulfur S or selenium Se) sandwiched between two layers of transition metal atoms. This layered structure enables TMDs to easily achieve reversible storage of lithium during electrochemical intercalation, thereby enhancing their potential as negative electrode materials for lithium-ion batteries.Researchers have prepared TMDs with different morphologies and structures through different synthesis methods, such as hydrothermal method, sol-gel method, chemical vapor deposition method, etc. These synthesis methods can precisely control the size, morphology, and crystal structure of materials, thereby optimizing their electrochemical performance. Numerous studies have shown that TMDs materials exhibit high reversible specific capacity and good cycling stability in lithium-ion batteries. For example, the reversible specific capacity of TMDs materials such as MoS2 and WS2 in lithium-ion batteries is much higher than that of traditional graphite negative electrode materials. Although research on TMDs as negative electrode materials for lithium-ion batteries has made some progress, there are still some shortcomings and challenges: conductivity issues: many TMDs themselves have poor conductivity, which limits their charge transfer efficiency and affects the overall performance of the battery. Volume expansion: During the charging and discharging process, TMDs may undergo significant volume changes, which may lead to structural damage to electrode materials, thereby affecting the cycling stability and lifespan of the battery. The first irreversible capacity is relatively large: TMDs may have a portion of lithium ions irreversibly consumed during the first charge, which is used to form a solid electrolyte interface (SEI) layer, resulting in lower initial Coulombic efficiency. Slow ion diffusion: The diffusion coefficient of lithium ions in TMDs may be low, which limits the charging and discharging rate and rate performance of the battery. Structural stability issue: During cycling, the structure of TMDs may degrade, affecting their long-term stability and electrochemical performance. Synthesis challenge: The synthesis of high-quality TMDs may require complex processes and high costs, which limits their large-scale production and application. Interface stability: The compatibility between TMDs and electrolytes may be poor, leading to interface stability issues that affect the safety and cycling performance of the battery. To overcome these challenges, researchers are exploring various strategies, such as improving the performance of TMDs through nanostructure design, surface modification, and composite with other materials. For example, combining TMDs with carbon materials (such as graphene, carbon nanotubes, etc.) to improve the conductivity and structural stability of the material[10]. In addition, the development of new TMDs materials and synthesis methods is also a current research hotspot. It is also possible to compensate for the shortcomings of TMDs in terms of cycling stability and rate performance by doping other elements or forming composite materials. With the deepening of research, it is expected to further enhance the performance and application potential of TMDs as negative electrode materials for lithium-ion batteries.

7. Lithium Titanate Anode Materials

Lithium titanate (LTO) is characterized by its "zero strain" feature, with minimal volume change during charge and discharge processes, extremely long cycle life, and high safety. Additionally, LTO boasts excellent rate performance and low-temperature performance. Despite its many advantages, LTO's theoretical specific capacity is relatively low (about 175 mAh/g), which limits its application in high-energy-density batteries. Performance can be enhanced through morphological and size control of particles and surface modification. LIN et al. demonstrated that nanostructured LTO materials can significantly increase the quantity of lithium ions inserted and dissolved in a single phase, thereby improving the migration rate and conductivity of lithium ions during charge and discharge. REN et al. prepared a nanocomposite Li4Ti5O12/C using a solid-state method, which maintained a specific capacity of 95.7% after 200 cycles at a 10C rate [11]. Xu Dongsheng and others from Peking University synthesized ultra-thin Li4Ti5O12 nanosheet-based microspheres through a three-step hydrothermal method, with an average thickness of about 6.6nm (±0.25). The hierarchical Li4Ti5O12 microspheres exhibited high specific capacity (156mAh/g at 20C, 150 mAh/g at 50C) and maintained a capacity of 126 mAh/g after 3000 cycles at 20C. CHUM et al. successfully prepared micrometer-sized hollow spherical structured Li4Ti5O12 using carbon spheres as a template. Research found that the initial discharge specific capacity of this material at 0.57 C was as high as 175 mAh/g, with a second discharge capacity of 159mAh/g, and the second discharge capacity at 5.7C was 76% of that at 0.57C. This indicates that the presence of numerous pores increased the contact between Li4Ti5O12 and the electrolyte, resulting in excellent rate performance. Micro-nano hybrid structures can effectively improve the rate performance of lithium titanate, but as the specific surface area increases and the packing density of the Li4Ti5O12 electrode material decreases, it will lead to an increase in irreversible capacity and a reduction in volumetric energy density. LTO itself has poor conductivity, which can be improved through surface modification. Common methods currently include ion doping, carbon material coating, metal material composite, and surface phase modification.

8. Conclusion

The development of anode materials for lithium-ion batteries has evolved from single graphite materials to diversified, high-performance materials. Carbon-based materials, silicon-based materials, alloy materials, transition metal oxides, and lithium titanate each have their characteristics but also their limitations. In the future, through material design, structural optimization, and compounding, it is expected that the performance of anode materials will be comprehensively enhanced, promoting the development of lithium-ion battery technology towards higher energy density, longer cycle life, and higher safety.

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