Research On the Discharge Mechanism of Lithium-Ion Battery Negative Electrode

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Abstract. The advancement of high-efficiency lithium-ion cells constitutes a critical driver in facilitating the transition toward sustainable energy systems, and the research on cathode materials is of great significance as the core components affecting battery capacity, magnification performance and cycle life. Although a variety of cathode material systems have been developed, including carbon-based materials, alloy materials, metal oxide and new multi-functional materials, they generally have problems such as difficult to consider the capacity and stability, insufficient conductivity, fierce volume expansion or complex interface reaction, which severely restrict the actual application performance. Based on the analysis on the mechanism of lithium storage of cathode materials, the structure evolution characteristics and ion migration behavior of different material systems in the charge and discharge process are systematically analyzed, and the differences of their electrochemical performance are compared. The key factors affecting the lithium storage performance are further discussed, aiming to provide theoretical support and technical ideas for the design and optimization of high-performance cathode materials.

Keywords: Lithium-ion battery, Material of negative electrode, Lithium storage mechanism, Structure evolution, Cyclic stability.

1. Introduction

With the increasing global demand for sustainable energy and growing attention to environmental issues, rechargeable batteries, especially lithium-ion batteries, have become a key technology driving the transformation of the energy structure. Lithium-ion cells are extensively employed in electrified transportation, power storage solutions, and mobile electronic equipment. due to their high energy density, long cycle life, and excellent stability [1, 2]. In the composition of lithium-ion batteries, anode materials play a decisive role in lithium storage performance and battery cycle life, so in-depth research on them is of great significance [3].

Although multiple categories of anode materials exist for lithium-ion cells—such as carbon-based compounds, alloy-based substances, and transition metal oxides, and new compounds [4], current research and application still face some key issues. For example, although carbon-based materials (e.g., graphite) exhibit great cyclic stability but suffer from limited capacity. Alloy materials such as Si and Sn possess high capacity, but there are serious volume expansion issues. Metal oxide materials such as Fe_3O_4 have high capacity, but their conductivity and cycling stability are poor [5, 6]. In addition, there are significant differences in the mechanisms involved in the charging and discharging processes of these materials. For example, graphite mainly stores lithium through intercalation mechanisms, while alloy materials undergo phase transitions and significant volume changes. Conversion materials involve complex redox reactions. These distinct mechanisms critically impact electrode structural stability and overall battery performance [7, 8].

Therefore, a deep understanding of the electrochemical reaction mechanisms of different anode materials during charge and discharge processes, including ion migration pathways, phase transition behavior, and interfacial reactions, is key to improving battery performance and developing new anode materials. This article focuses on the differences in lithium storage mechanisms and structural evolution processes of mainstream anode materials, aiming to provide theoretical basis and practical reference for the material design of high-performance lithium-ion batteries.

2. Basic properties and classification of optimized Li-ion cell anode materials

2.1. Key performance indicators of high-performance negative electrode materials

Under the premise of maintaining the key components of lithium ion battery, the characteristics of negative electrode material fundamentally affect the energy density, power output, cycle life and safety performance of the whole battery. To achieve the goal of high energy density, the cathode material first needs to have a higher specific capacity to ensure that more lithium ions can be stored per unit mass or volume. In addition, the demand for fast charging in modern electronic devices and electric vehicles has also driven the development of high rate performance, requiring materials to maintain stable charging and discharging capabilities at high current densities. At the same time, to extend the service life, the negative electrode material must exhibit good cycling stability, that is, it can maintain a high capacity retention rate even after hundreds or even thousands of charge and discharge cycles. The first Coulombic efficiency, as an important indicator for evaluating the initial irreversible loss of materials, has also become a parameter that must be paid attention to in material development. A high first Coulombic efficiency means that less lithium is irreversibly consumed in side reactions or SEI film formation, which can improve the overall energy utilization efficiency. Finally, safety is always an uncompromising factor in battery system design. Anode materials must have stable thermal behavior under extreme conditions such as high temperature, high rate, or overcharging to avoid thermal runaway reactions. In the actual development process, these performance parameters often constrain each other. For example, increasing the specific capacity may cause a decrease in structural stability. Therefore, in material design, how to achieve an optimized balance between energy, dynamics, and structure is a key scientific issue for achieving high-performance negative electrode materials [9].

2.2. Classification of anode Materials

At present, there are various classifications of negative electrode materials for lithium-ion batteries, mainly divided into carbon-based negative electrodes, alloy-type negative electrodes, metal oxide materials, new multifunctional materials, etc. Each type of material has significant differences in lithium storage mechanism, electrochemical performance, and engineering adaptability. Carbonaceous materials constitute a primary class of the earliest and still widely used negative electrode systems, among which graphite has become the standard choice for commercial batteries due to its excellent structural stability, mature preparation technology, and good lithium insertion reversibility. Graphite has a layered structure that facilitates reversible insertion and extraction of lithium ions between layers, exhibiting excellent cycling stability and high Coulombic efficiency. However, its theoretical capacity (372 mAh/g) has gradually become a bottleneck, making it difficult to meet the pursuit of high energy density [10]. Hard carbon and soft carbon, as amorphous carbon materials, can provide higher capacity than graphite, especially exhibiting better electrochemical performance at low temperatures, becoming possible alternative options in sodium ion or all solid-state batteries in the future.

Alloy materials, especially metal or semi metal alloys represented by silicon, tin, and antimony, have attracted much attention due to their extremely high theoretical capacity. Taking silicon as an example, it forms multi lithiated compounds with lithium (such as Li_4) Si provides a theoretical capacity of up to 4200 mAh/g, which is more than 10 times that of graphite. However, this type of material undergoes significant volume expansion (over 300%) during lithiation, causing material crushing, electrode structure damage, and instability of SEI film, severely limiting its long-term cyclic applications [11]. Therefore, current research focuses mainly on structural regulation, composite design, and nanotechnology to alleviate stress concentration issues. Metal oxide materials such as Fe_3O_4 and SnO_2 typically store lithium through conversion reactions, forming metal nanoparticles and Li_2O during charge and discharge processes. These materials have high specific capacity, but due to their involvement in complete structural reconstruction, they often suffer from irreversible capacity loss, poor rate response, and cycle life [12]. Some of these problems have been partially alleviated through nanostructured, carbon coated, and doped modifications, but their commercial application still faces certain challenges. In recent years, emerging new materials such as metal sulfides, nitrides, and MXenes have demonstrated multiple lithium storage mechanisms, including intercalation, surface adsorption, conversion reactions, and pseudocapacitive behavior. These materials typically exhibit excellent electronic conductivity, tunable structures, and good interfacial chemical properties, particularly demonstrating potential in high rate and flexible devices [13]. Although these materials are still in the experimental research stage, the diversity of their performance combinations provides abundant possibilities for the development of next-generation battery materials.

3. Charging and discharging mechanism for high-performance negative electrode materials

3.1. Charging and discharging mechanism of carbon-based materials

Carbon-based materials presently represent the most technologically mature and commercially prevalent class of anode materials for lithium-ion batteries, with graphite constituting the dominant crystalline form, hard carbon, and soft carbon. Among them, the lithium storage mechanism of graphite is based on the insertion and extraction reactions of lithium ions in the layered crystal structure. During charging, lithium ions are dissolved from the electrolyte, migrated to the graphite anode through the solid electrolyte interface (SEI) facial mask, and embedded in its hexagonal layered lattice, finally forming a stable compound of LiC_6. During discharge, the embedded lithium ions are released back into the electrolyte in a reverse process, achieving electrochemical energy storage and release [14]. This embedding reaction belongs to the quasi solid-state diffusion process, with good overall structural stability and small volume change (<10%), which enables graphite to exhibit excellent cycle life and Coulomb efficiency. However, graphite's theoretical specific capacity of 372 mAh/g remains fundamentally limited, constituting a critical energy density bottleneck for next-generation lithium-ion batteries. Therefore, amorphous carbon materials such as hard carbon and soft carbon have been proposed as alternative or supplementary solutions. Hard carbon has an amorphous structure with micropores and disordered layered regions inside. It can store lithium ions through multiple mechanisms such as insertion, adsorption, and pore filling, with a capacity of over 450 mAh/g. However, the initial coulombic efficiency is generally low, and the SEI film is prone to uncontrolled growth in the microporous structure [15]. Soft carbon is between graphite and hard carbon, possessing a certain layered structure and amorphous characteristics, as well as a certain capacity and cycling stability. In addition, research on new carbon materials such as graphene and porous carbon in recent years has also shown that capacity and rate performance can be effectively improved through nanostructure regulation and conductive network optimization [16]. Overall, carbon-based materials still have commercial advantages due to their stability and process maturity, but their limited capacity has become an important background for promoting the development of higher performance materials.

3.2. Charging and discharging mechanism for alloy materials

The energy storage mechanism between alloy materials and lithium depends on alloying and dealloying reactions. During the charging process, lithium ions react chemically with metals (such as Si, Sn, Sb, etc.) to form metal lithiation compounds, such as silicon and lithium forming a series of Li_xSi alloys. During the discharge process, lithium ions are released from the alloy and restored to their initial state [17]. The lithiation process of alloy materials represented by silicon involves multiple phase transition stages, transforming from amorphous Si to different intermediate products such as $Li_{12}Si_2$, Li_7Si_3, $Li_{13}Si_4$, and finally to a highly lithiated state close to $Li_{4.4}Si$. The volume expansion associated with this reaction process can exceed 300%, which is much higher than that of graphite materials, resulting in particle breakage, loose electrode structure, and unstable SEI film, which has become a major obstacle to its commercialization [18]. To overcome this problem, researchers have proposed various structural control strategies, such as using nanostructure design, hollow/core-shell structure construction, carbon coating, elastic matrix composites, and other methods to alleviate stress concentration and improve mechanical stability. Meanwhile, by constructing buffer phase interfaces or porous conductive networks, electronic conductivity and ion diffusion pathways can also be improved to some extent, enhancing rate performance and cycle life [6, 19]. In recent years, silicon/carbon composite anodes have become one of the mainstream research directions, balancing high capacity and structural controllability. Although alloy materials have extremely high theoretical capacity and broad prospects in the next generation of high-energy density batteries, further solutions are still needed to address core issues such as mechanical stability and interfacial chemical stability.

3.3. Charging and discharging mechanism of metal oxide materials

The storage of lithium in metal oxide materials is mainly achieved through a conversion reaction mechanism, where metal oxides undergo reversible oxidation-reduction reactions during charging and discharging, generating metal nanoparticles and Li_2O. Taking Fe_3O_4 as an example, during charging, it reacts with lithium to generate Fe nanoparticles and Li_2O, and during discharging, a reverse reduction reaction occurs. This reaction involves a large change in the number of electrons, and the theoretical capacity is often high, with some metal oxides reaching 700-1000 mAh/g [20]. However, due to the complete restructuring of the lattice structure and drastic changes in volume accompanying the transformation reaction, the material experiences stress concentration, particle breakage, electrode structure pulverization, and SEI film instability during multiple cycles, significantly affecting the cycle life and rate performance. In addition, metal oxides themselves have low electrical conductivity, which is not conducive to rapid electron transfer at high rates. Therefore, researchers generally adopt a nano strategy to reduce particle size, improve surface area and reactivity, and enhance overall conductivity through methods such as carbon coating and graphene composites [20]. Some metal oxides, such as TiO_2, exhibit good cycling stability due to their embedded lithium storage mechanism and small volume changes, making them one of the few representatives close to commercialization. However, overall, the conversion reaction type negative electrode is still mainly concentrated in the laboratory stage, and its complex phase transition path and interface reaction behavior still need further research and optimization.

3.4. Charging and discharging mechanism of new anode materials

New negative electrode materials include metal sulfides, nitrides MXene, Lithium compounds and other compounds have diverse structural characteristics and composite energy storage mechanisms. Taking MXene material as an example, it has a two-dimensional layered structure and rich surface functional groups, which can achieve rapid lithium ion intercalation. At the same time, it has high electronic conductivity and is suitable for high rate charging and discharging. Some MXene materials can also store lithium ions through surface reactions or pseudocapacitive behavior, making them a hybrid energy storage system that combines capacitive and battery behavior [21, 22].

Metal sulfides and nitrides such as MoS_2 and TiN also exhibit excellent lithium storage performance. Their lithium storage mechanism usually includes intercalation, conversion, and surface adsorption processes, with high theoretical capacity and flexible structural control potential. However, the challenges of such materials mainly lie in volume expansion, dissolution of active components, and significant side reactions. Therefore, it is necessary to further improve their cycling stability and safety performance through structural engineering and interface regulation [13, 21]. In addition, some two-dimensional materials and amorphous structural materials exhibit new reaction behaviors at the nanoscale, providing a broader theoretical space for understanding lithium storage mechanisms. Overall, the diversity of new materials in charge and discharge mechanisms provides more possibilities for the development of negative electrode materials, but also puts forward higher design requirements for interface control, material stability, and composite integration.

4. Critical determinants influencing the charge-discharge dynamics of anode materials.

The charging and discharging mechanisms of negative electrode materials vary significantly in different material systems, and the electrochemical behavior exhibited by these mechanisms in actual operation is influenced by multiple key factors in synergy. Firstly, the structural stability of materials plays a fundamental role in the charging and discharging process. For carbon-based materials, the integrity of the layered structure directly determines the reversible intercalation ability of lithium ions. For alloy materials such as silicon, the drastic volume changes generated during the alloying process often lead to structural pulverization, which affects capacity retention and cycle life [15]. Secondly, the electronic conductivity and diffusion rate of lithium ions are closely related to the rate performance of the material. Highly conductive materials can more effectively support high current charging and discharging processes. In recent years, two-dimensional materials such as MXene have demonstrated excellent rate performance due to their high electronic conductivity and rich ion channel structure [22]. In addition, The solid-electrolyte interphase (SEI) layer formed through electrolyte reduction at the anode/electrolyte interface critically governs the long-term electrochemical stability of battery systems by modulating: (i) Ionic transport kinetics, (ii) Interfacial side reactions, (iii) Mechanical stress evolution during cycling A stable and dense SEI film helps prevent continuous side reactions and lithium depletion, thereby delaying battery performance degradation, while an unstable SEI structure is prone to rupture and reconstruction, resulting in irreversible capacity loss [23].

The microstructure characteristics of materials also have an impact on the ion transport behavior during charge and discharge processes. For example, the finer the particle dimensions, the more reduced the lithium-ion diffusion pathway becomes, resulting in no less favorable kinetic properties. Porous structure can enhance the contact area of electrolyte and help improve reaction rate [24]. In addition, doping, and nanostructure modulation also play an important role in improving the, preparation techniques such as surface coating, heterogeneous integrity of electrode structures and controlling interface reactions. Especially in silicon-based negative electrode materials, nanocomposite design significantly improves volume stability and interface compatibility, which is an important research direction in current materials engineering [25].

Therefore, although different material types determine their unique lithium storage mechanisms, the specific manifestations of these mechanisms in practical applications, such as capacity retention, rate response, and cycling stability, are the result of the combined effects of multiple factors such as structure, conductivity, interface behavior, and preparation strategies. A deep understanding of how these factors regulate the dynamic evolution of charge and discharge mechanisms is a key path to advancing research on high-performance negative electrode materials.

5. Current challenges and solutions

5.1. Challenge

The progression of superior-capability Li-ion electrochemical cells negative electrode materials still faces many challenges. Firstly, alloy materials (such as silicon and tin based materials) undergo volume expansion of up to hundreds of percentage points during the charging and discharging process, leading to particle crushing and electrode structure failure, greatly weakening the cycle life [17]. Secondly, although metal oxide materials such as Fe_3O_4 and SnO_2 have high theoretical capacities, their inherent electronic conductivity is poor, and there is a significant voltage hysteresis problem during charge and discharge processes, which limits their practical applications [20]. For new anode materials such as MXene, although they have shown great potential in capacity and rate performance, further breakthroughs are still needed in long-term stability and interface engineering control [22]. In addition, the generation and durability of the solid electrolyte interphase protective layer (SEI film) exert a significant influence on the functionality of anode materials, particularly in substances exhibiting substantial volumetric expansion or pronounced surface reactivity, SEI film is easy to break and regenerate, leading to irreversible loss of lithium source and accelerating battery capacity degradation [23].

5.2. Solution

In response to the above challenges, researchers have proposed various innovative solutions. For alloy materials, nanostructure design (such as hollow nanoparticles, porous structures, etc.) can effectively alleviate the mechanical stress concentration caused by volume expansion, thereby improving cycling stability [17]. In terms of metal oxide materials, carbon coating, composite nanostructures, and doping strategies can improve electronic conductivity and reduce voltage hysteresis, thereby improving rate performance and cycle life [20]. For new materials such as MXene, optimizing the interlayer structure, introducing stable surface functional groups, and interface engineering design can significantly improve their cycling stability and rate performance [22]. In terms of SEI film, the use of functional electrolyte additives or the construction of artificial interface layers can effectively control the formation and stability of SEI film, reduce lithium source loss, and improve long-term cycling performance [23].

6. Summary and Prospect

The purpose of this paper is to explore the mechanism of lithium storage and structure evolution of high-performance lithium ion battery cathode materials, so as to provide theoretical basis for the design of new cathode materials. The charging and discharging mechanism of four kinds of main cathode materials is systematically analyzed, including: carbon-based materials realize reversible lithium storage mainly through embedding/disembedding mechanism, which has excellent stability but limited capacity; Alloy materials (such as silicon) store lithium through alloying reaction, with high capacity but facing serious volume expansion problems; The metal oxide material stores energy by the transformation mechanism, the capacity is considerable, but the cycle stability and conductivity are poor; New materials (e.g. MXene, metal sulfide) have multiple lithium storage mechanisms, which combine capacity and magnification performance advantages, but are still in the experimental phase. Through comparison and analysis, it can be found that there is a common trade-off among capacity, cycle life and magnification performance of different materials, and the differences in charge and discharge mechanisms face common challenges such as structural stability, conductivity and SEI film stability in practical applications. Therefore, future research should focus on interface regulation, structural design and collaborative optimization of composite engineering to achieve the unity of high capacity and stability.

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