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Modification Strategies for Hard-Carbon-Based Anode Materials in Sodium-Ion Batteries

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Abstract. Sodium-ion batteries offer abundant resources, low cost, and high safety, making them promising for large-scale energy storage. Hard carbon, a key anode material, enables Na+ storage through its disordered structure, enlarged interlayer spacing, and abundant defects and pores. However, these features also cause electrolyte side reactions and sluggish Na+ transport, leading to low initial Coulombic efficiency (ICE), poor rate capability, and limited low-voltage plateau capacity. This paper explores the correlation between hard carbon microstructure and sodium storage, and the mechanisms by which different modifications improve electrochemical performance. Drawing on representative studies published in recent years, this review summarizes the progress in hard-carbon anode modification, with particular emphasis on structural regulation, sodium-storage mechanisms, and electrochemical performance optimization. It also discusses the advantages, limitations, and potential synergies of different modification strategies. The results reveal that the electrochemical performance of hard carbon is influenced by multiple factors like surface structure, carbon layer arrangement, pore characteristics, and the transport process, while a single structural optimization cannot simultaneously meet the requirements of ICE, rate performance, and plateau capacity. The coordinated regulation of multi-scale structures is key to balancing performance. However, current research on hard carbon still faces issues such as insufficient quantitative relationships between structural parameters and sodium storage behavior, unclear matching rules for different scale structures, and a gap between laboratory performance and actual application requirements. Future efforts should integrate structural characterization, theoretical analysis, and engineering evaluation to establish structure-performance relationships and advance hard carbon anodes.

Keywords: Sodium-Ion Batteries, Hard-Carbon Anodes, Modification Strategies, Sodium-Storage Mechanisms, Synergistic Optimization

1. Introduction

Under the background of the rapid development of the "dual carbon" strategy and the new energy storage industry, sodium-ion batteries, with their abundant resource reserves and cost advantages, have become a crucial research direction for the next-generation low-cost energy storage systems. Among various sodium-ion battery anode materials, carbon-based materials are viewed as the most

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commercially promising option due to their wide availability, environmental friendliness, and low cost. However, traditional graphite anodes struggle with Na^+ intercalation owing to thermodynamic incompatibility, while soft carbon tends to graphitize at high temperatures, thus reducing interlayer spacing and limiting Na^+ storage. In contrast, hard carbon retains a unique microcrystalline structure with short-range order and long-range disorder at high temperatures, while also maintaining large interlayer spacing. Since Stevens and Dahn first confirmed hard carbon's sodium storage potential and proposed the classic "intercalation-pore filling" model in 2000, hard carbon has become a key anode material for sodium-ion batteries [1]. Although hard carbon exhibits excellent sodium storage potential, its complex microstructure also poses significant challenges. For example, the abundant surface defects and open pores cause severe electrolyte side reactions during the first cycle, forming a thick solid electrolyte interphase (SEI) film, and leading to low initial coulombic efficiency (ICE). In addition, long ion diffusion paths and slow pore-filling kinetics limit high-rate performance. To bridge the gap between laboratory research and commercial application, researchers have focused on optimizing hard carbon via various strategies. This study adopts a systematic literature review and analysis method to examine the current mainstream modifications of hard carbon-based anode materials in sodium-ion batteries and the synergistic effects of different strategies, with emphasis on morphology and pore structure engineering, heteroatom doping, and interface regulation, while exploring their future development prospects.

2. Sodium-storage mechanisms and structural limitations of hard-carbon anodes

2.1. Structural characteristics and sodium-storage behavior of hard carbon

The sodium storage behavior of hard carbon is closely related to its unique microstructure. Unlike the long-range ordered lattice structure of graphite, during the pyrolysis process of hard carbon, the rearrangement of carbon layers is restricted, thus resulting in a short-range ordered and long-range disordered amorphous carbon structure. Its microstructure is commonly described by the "falling leaves" or "house-of-cards" model, which indicates that highly curved and randomly cross-linked graphene-like microcrystallites are arranged in a disordered manner. Here, the micro-crystalline boundaries and disordered regions formed due to incomplete rearrangement of the carbon layer further resulted in multi-scale structural features, including defect sites, increased interlayer spacing (d002 usually > 0.37 nm), and nano-scale closed pores formed by the interwoven disordered carbon domains. These defect structures, carbon-layer arrangements, and pore structures jointly influence the distribution and storage modes of Na^+ within the carbon framework [2, 3].

2.2. Sodium-storage mechanisms of hard carbon

The complex microstructure of hard carbon gives rise to diverse sodium-storage modes. It is now generally accepted that Na^+ storage in hard carbon mainly involves three fundamental processes: defect adsorption, interlayer insertion, and pore filling, as shown in Figure 1 [4, 5]. Defects and edge sites on the hard-carbon surface and within the carbon framework can interact with Na^+ and provide adsorption sites. Besides, graphite-like microcrystallites formed by turbostratic stacking have larger interlayer spacings than graphite, reducing the steric constraints on Na^+ entering between carbon layers and enabling reversible interlayer insertion.

Early studies typically used relatively independent sodium storage models to describe the above process. The "intercalation-pore-filling" model proposed by Stevens and Dahn in 2000 attributed Na^+ storage to interlayer insertion and pore filling [1]. With advances in in-situ characterization and

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kinetic analysis, it has been discovered that the internal structure of hard carbon exhibits a high degree of heterogeneity, and different sodium storage processes are not independent of each other; instead, they may occur concurrently and act synergistically during sodiation [4, 5]. In situ Raman spectroscopy, in situ XRD, GITT, and XPS revealed a synergistic mechanism involving adsorption, insertion, and pore filling through defects, graphite like microcrystals, and internal pores; closed pore regulation further demonstrated the importance of internal pores in Na^+ storage [5, 6].



Figure 1. Schematic illustration of sodium-storage mechanisms in hard carbon

2.3. Structural limitations of hard carbon and their relationship with performance

Hard carbon capacity, ICE, and rate performance depend on multiple microstructural parameters. Different structural adjustments often involve trade-offs among the performances. For example, surface defects can provide sodium storage sites but also increase interface reactions; pore structure determines low potential storage space and electrolyte contact; carbon layer arrangement controls Na^+ migration and interlayer insertion. Thus, the performance optimization of hard carbon is not the adjustment of a single structural parameter, but a balance among different structural factors.

Surface defects and open pore structures reflect the contradiction between capacity and ICE. Defects and edge regions can increase the number of active sodium storage sites, which is beneficial for capacity improvement [7]. However, excessively high defect concentration and open pore ratio will expand the contact interface between the carbon material and the electrolyte, promote the formation of the SEI membrane and increase irreversible Na^+ consumption, thus reducing the ICE [8]. Thus, the increase in the surface active structure cannot simply be translated into an increase in the effective capacity. The change in pore structure determines the balance between the platform capacity and the side reactions. However, the closed-pore structure is conducive to the formation of low potential capacity, but the increase in pore structure is usually accompanied by a change in the proportion of open pores, and open pores will enhance the electrolyte infiltration and intensify the interface reaction. Thus, the effect of pore structure on performance depends on the competitive relationship between its sodium storage contribution and side reactions [3, 6, 8]. The arrangement state of the carbon layers further affects the coordination between the sodium storage capacity and kinetics. Appropriate increase in the layer spacing and smaller microcrystalline size can reduce the resistance of Na^+ insertion and promote interlayer migration. However, excessive disorder increases defects and hinders ion transport, while excessive order reduces available sodium storage space. Therefore, the balance between capacity and rate performance relies on the matching of interlayer spacing, microcrystallite size, and defect distribution [5, 9].

3. Performance optimization strategies for hard-carbon anodes and their mechanisms

3.1. Interfacial regulation and presodiation strategies

Irreversible Na^+ consumption during the first cycle of hard carbon mainly arises from SEI formation and surface side reactions. Interfacial regulation and presodiation improve ICE by reducing sodium

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loss and replenishing active sodium, respectively.

Interface regulation mainly achieves this by altering the reaction environment on the surface of hard carbon, thus reducing electrolyte decomposition and the formation of irreversible SEI. Surface coating and surface chemical regulation can minimize the direct contact between high-activity defect sites and the electrolyte, inhibit continuous side reactions, and adjust the composition and structure of the SEI membrane, reducing the consumption of active Na^+. Studies have shown that the stability of the interface layer and the ionic transport characteristics affect the ICE and cycling performance of hard carbon. Thus, interface regulation needs to strike a balance between reducing interface side reactions and maintaining Na^+ transport [10-13].

Pre-sodiumation involves introducing additional Na^+ before battery assembly to compensate for the sodium loss caused by the formation of SEI and other irreversible reactions during the first cycle. Based on the method of sodium supplementation, pre-sodiation can be divided into electrochemical, direct contact, and chemical methods. Among these, electrochemical pre-sodiumation can precisely regulate the amount of sodium supplementation, but the process is relatively complex; direct contact pre-sodiumation is simple in operation, but may face issues with sodium distribution uniformity and safety; chemical pre-sodiumation uses reducing sodiumating reagents to rapidly supplement sodium [14]. Prior some studies have pre-treated hard carbon with sodium-containing organic molecules to compensate for irreversible sodium loss and improve interface stability, enhancing ICE [14, 15].

3.2. Optimization of transport structures and regulation of rate capability

The rate performance of hard carbon is mainly limited by the solid-phase diffusion of Na^+ and the electron transfer rate. Therefore, the relevant regulation focuses on reducing the ion migration path and the charge transfer resistance. The adjustment of pore structure can improve the infiltration of the electrolyte within the electrode and shorten the transmission distance of Na^+ from the electrolyte to the sodium storage site. The construction of appropriate mesoporous and macroporous structures facilitates ion transport while retaining micropores for sodium storage. However, excessive increase in open pores may lead to a contradiction between the transmission structure and interface stability. Thus, pore design needs to control pore size and connectivity [16, 17].

In addition to the pore structure, the arrangement state of the carbon layers also determines the migration behavior of Na^+ in the solid phase. Appropriate increase in the layer spacing and smaller graphite-like microcrystal size can reduce the spatial limitation during the Na^+ insertion process, shorten the interlayer diffusion distance, and thus improve the sodium storage kinetics. The in-situ XRD and Raman characterization results show that the interlayer structural parameters are closely related to the Na^+ intercalation behavior [5]. Moreover, the doping of heteroatoms can regulate the electronic structure of the carbon framework and boost the electron transport ability, but its effect depends on the doping type and content. Excessive introduction may damage the integrity of the carbon structure and impair electrode performance [11, 18-20]. Meanwhile, when a single structural adjustment cannot simultaneously improve ion and electron transport, composite structures can serve as a complementary strategy. For instance, introducing ion-conductive sodium titanate into hard carbon can facilitate Na^+ migration and construct a dual ionic-electronic conducting network, thereby reducing electrode polarization and improving rate capability [21].

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3.3. Construction of closed-pore structures and regulation of plateau capacity

The capacity of the low-voltage platform mainly originates from the confinement storage of Na^+ by the internal pores within hard carbon. The key to regulating the pore structure lies in increasing the effective sodium storage space rather than merely increasing the material's porosity. Compared to open pores, closed pores reduce direct electrolyte contact and provide stable nanoscale spaces for Na^+ accumulation and clustering, increasing plateau capacity and reducing irreversible reactions.

The formation of closed pores is closely related to the precursor structure and the rearrangement of carbon layers during the carbonization process. In the high-temperature carbonization process, the contraction of the carbon framework and the local reorganization of carbon layers can gradually close some pores, forming nanoscale closed pores. Based on this process, researchers have changed the structural evolution behavior during the carbonization process through methods like precursor cross-linking, pre-oxidation treatment, and adjustment of thermal treatment conditions, promoting closed pore formation [20, 22-24]. For instance, pre-oxidation treatment can regulate the degree of precursor molecule cross-linking, thus enabling the formation of more suitable pore structures and graphite-like microcrystalline regions during carbonization. Existing studies show that appropriately increasing the content of closed pores and regulating the graphite-like microcrystalline structure can help improve the platform capacity and Na^+ transport behavior [9].

In addition, the transformation of open pores to closed pores during the heat treatment process is also an important way to regulate the platform capacity. As the carbonization temperature increases, the contraction of the carbon layer and the rearrangement of the structure can gradually close some open pores, increasing the proportion of internal confined space, hence increasing the storage space for Na^+ and enhancing the platform capacity [2]. As a result, the key to controlling the closed pore structure lies in controlling the pore diameter, quantity, and degree of closure, so that the formed pore structure can effectively participate in the low potential sodium storage process.

3.4. Multiscale structural synergy and its mechanisms

The electrochemical performance of hard carbon is not determined by a single structural parameter alone, but is jointly shaped by the coupling effect among the surface state, carbon layer arrangement, and pore structure. At different scales, structures participate in interface reactions, Na^+ migration, and sodium storage processes. Thus, the key to performance optimization lies in coordinating the matching relationship among various structural units, so as to achieve effective connection of active sites, transport paths, and sodium storage space.

The matching relationship between the surface and bulk structures determines the reversibility of hard carbon during sodium storage. For example, surface defects can provide sodium storage sites, but overly exposed active areas will increase interface reactions. In contrast, reasonable regulation of the distribution of bulk defects and the degree of surface activity can retain the sodium storage capacity while reducing irreversible sodium consumption [10, 11, 13, 20]. Thus, structural design is not simply reducing defects, but requires controlling the location and mode of action of defects. At the same time, the coordination of transmission pathways and sodium storage spaces determines the utilization efficiency of the internal structure. Continuous ionic transmission channels can promote the migration of Na^+ into the carbon layer and pore structure, while appropriate interlayer structure and closed pore distribution determine the storage position and capacity contribution of Na^+ within the material [17, 18, 22, 24]. When the transmission pathways match the sodium storage spaces, the internal sodium storage structure can be fully used, avoiding capacity loss caused by transmission limitations. Furthermore, for systems with significant sodium loss during the first cycle, structural

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regulation can be combined with pre-sodiumation to reduce capacity loss by optimizing interfacial reactions and replenishing the initial sodium inventory [13, 14]. Therefore, the core of multi-scale synergy is not to superimpose different modification methods, but to establish a mutually matching relationship between different structural scales, enabling hard carbon to achieve a more reasonable balance among capacity, ICE and rate performance.

4. Challenges and prospects for modification strategies of hard-carbon anode materials

4.1. Common bottlenecks of modification strategies and the need for synergistic design

The current hard carbon modification strategies can improve electrochemical performance through interface regulation, structural optimization, and sodium compensation. Their further development is still limited by mechanistic understanding and engineering evaluation systems. Firstly, the current understanding of the modification effects still mostly relies on macroscopic electrochemical results. There is a lack of clear correlation between structural evolution and performance changes induced by different modification processes. For example, heat treatment, doping, or surface modification often alter the defect state, pore structure, and surface chemical environment, making it difficult to accurately distinguish the contribution of a single factor to the sodium storage behavior. Thus, the link between modification processes, structural evolution, and performance changes can be clarified through in situ characterization and theoretical calculations. Existing modification methods lack universal structural criteria, and the same strategy can produce different carbon structures and performance with different precursors and preparation conditions. This variation makes it difficult to link precursor type, preparation conditions, and target performance. Future research should establish quantitative links among these factors to enable predictable structural regulation across material systems. Meanwhile, laboratory results often fail to reflect practical requirements. Many high performance hard carbon materials are tested at low mass loading, high electrolyte usage, or in half cells, whereas practical sodium ion batteries require high ICE, high tap density, long cycle life, and low manufacturing cost at high loading. Modification strategies should therefore be evaluated under full cell conditions using these engineering metrics.

4.2. Hard-carbon design pathways for large-scale applications

The transition of hard carbon from laboratory research to practical use requires suitable sodium storage structures and performance that meet the demands of large scale production and full cells. For precise control of structural parameters, it is necessary to combine in situ characterization, multiscale simulation, and data driven analysis to study carbon layer rearrangement, pore evolution, and interface film formation, clarify their links with capacity, ICE, and rate performance, and guide targeted structural design. For preparation, future research should shift from complex post treatment to precise precursor and carbonization control. Although template methods, activation treatments, and multistep doping can improve pore structure and surface properties, they may increase process complexity and cause batch variations. By adjusting precursor composition, crosslinking degree, and heat treatment conditions, key structural parameters can be controlled to regulate closed pore ratio, interlayer structure, and surface activity, and boots reproducibility in large scale production. In addition, hard carbon should be evaluated under full cell conditions rather than only in half cells. Moreover, Na^+ transport efficiency at high mass loading, the effect of tap density on volumetric energy density, and ICE retention and structural stability during long term cycling should also be considered. At the same time, large-scale application requires hard carbon to have a stable precursor

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source, low production cost and good batch consistency.Future hard carbon design should establish a match among sodium storage structure, electrode performance, and manufacturing feasibility to meet the requirements of practical sodium ion batteries.

5. Conclusion

This review examines the structure performance relationships and optimization strategies of hard carbon anodes for sodium ion batteries. It covers interfacial regulation, transport optimization, and closed pore construction, with a focus on multiscale synergy among interfaces, transport pathways, and sodium storage spaces. Existing studies show that hard carbon performance is not determined by a single structural parameter but by the interplay among surface reactions, ion transport, and internal sodium storage. Future hard carbon design should shift from single structure optimization toward multiscale synergistic regulation. The establishment of quantitative links between structural parameters and sodium storage behavior can improve ICE, capacity, and rate capability. Meanwhile, existing studies still focus mainly on half cell performance and pay insufficient attention to practical metrics like high areal loading, tap density, ICE retention, cycling stability, and batch consistency. Therefore, future studies should combine in situ characterization, theoretical modeling, and scalable processing to bring hard carbon from laboratory optimization to full cell applications.

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