

Study on the hard carbon anode from different precursors for sodium ion batteries

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Abstract. Sodium-ion batteries (SIBs) are commonly utilized in power storage applications. It can be used as alternatives to lithium-ion batteries. Nevertheless, the development of SIBs is restricted by anode materials due to the high redox potential and large irreversible capacity. As a common anode material of SIBs, hard carbon exhibits a substantial interlayer spacing and a excellent reversible specific capacity, while the properties and costs are affected by its precursors. This article mainly describes the sodium storage principle of hard carbon and compares the performances as well as modification methods of hard carbon produced from various precursors. The hard carbon basing on coal has the advantages of low cost due to the abundant reserves of coal precursors and low redox potential. Biomass-based hard carbon has natural pores which can assist the sodium ions transport in carbon materials. We further explain the effects of modification strategies such as heteroatom doping, activation treatment and mechanical ball milling on electrochemical properties of hard carbon. Finally, this paper recognizes the existing problems and corresponding solutions of materials made of hard carbon and looks forward to the future research focus on hard carbon materials.

Keywords: Sodium-ion batteries; hard carbon; precursors.

1. Introduction

With the rising global demand for renewable energy and the rapid development of the electric vehicle market, it is particularly important to find an economical, efficient and sustainable energy storage solution. As a portable energy storage technology, lithium-ion batteries have been widely used in recent years. However, owing to the unequal distribution of lithium resources and limited crustal reserves, its long-term sustainability is facing challenges. In contrast, SIBs have garnered significant interest and are considered as a prospective energy storage technology because of the abundant and widely distributed sodium resources. Because of its significant advantages in low cost and stable supply chain, it may replace some lithium-ion batteries in the field of large-scale fixed energy storage applications [1]. However, sodium ion batteries still encounter a lot of challenges, such as low energy density, poor cycle stability and limited charge-discharge rate. In recent years, the electrochemical behavior of SIBs has been significantly enhanced by using new electrode systems and technical means. Among them, the anode material, as a key factor, has an important impact on the cycle performance and energy density of the battery. Hard carbon materials have become the first choice for sodium ion anode materials due to their cost-effective, wide source, large distance between layers and high reversible specific performance. The precursor affects the cost, pretreatment scheme and electrochemical capability. The aim of this study is to summarize recent developments and new schemes in the preparation of hard carbon anodes for SIBs using various precursors. In addition to that, their advantages, disadvantages, the future development direction and trend are analyzed, aiming to provide theoretical basis and practical guidance for the further development of SIBs technology.

2. Hard carbon and sodium storage mechanism

Hard carbon refers to carbon materials that are difficult to convert into graphite after treatment at 2500°C [1]. Different to graphite, hard carbon usually contains more sodium storage sites, which is due to its disordered carbon layer structure. Besides, there are a lot of defects, irregular polycrystalline

structure, and prismatic surface and closed pores in the hard carbon [2]. These characteristics provide the necessary conditions for the widespread use of hard carbon materials in the field of sodium ion batteries

Through the study on glucose pyrolytic carbon by Dahn et al., it was found that hard carbon and graphite have similar discharge/charge curves in sodium ions batteries [3]. The capacity provided by different voltage ranges can be distinguished, and both have slope stage capacity and platform stage capacity. However, the sodium storage principle in hard carbon is different from that of graphite, mainly includes the following four types:

(1) Intercalation-adsorption mechanism: The intercalation behavior of sodium ions is the main reason for the slope curve generated in the high potential region. The platform capacity in the low potential region comes from the adsorption of sodium ions by micropores and defects formed by random stacking of carbon layers [4]. As shown in Figure 1-a below.

(2) Adsorption-intercalation mechanism: The embedding behavior of sodium ions affects the capacity of the ramp region. At low potential, the “adsorption-embedding” is like the two-phase reaction mechanism. As shown in Figure 1-b below.

(3) Adsorption-intercalation-prefilling mechanism: Sodium ions undergo adsorption behavior affecting the high potential slope section. In the low potential platform stage, sodium ions undergo intercalation and filling micropores at the same time [5]. As shown in Figure 1-c below.

(4) Adsorption-prefilling mechanism: It is believed that sodium storage methods in hard carbon does not involve intercalation behavior, but is adsorbed on the surface, at the edges, or at defects of the carbon layer within the high-potential slope stage and filled in nanopores during the low potential platform stage [6]. This is reflected in Figure 1-d.

The sodium storage characteristics in hard carbon is shown in Figure 2. The difference of precursors will change sodium storage sites and pores of hard carbon materials. For example, the organic part of coal contains a large amount of polycyclic aromatic compounds, hydrogen aromatic and heterocyclic clusters, which form a highly graphitized microcrystalline structure when high temperature carbonization, Therefore, it hinders the sodium transport mechanism of sodium ions [7].

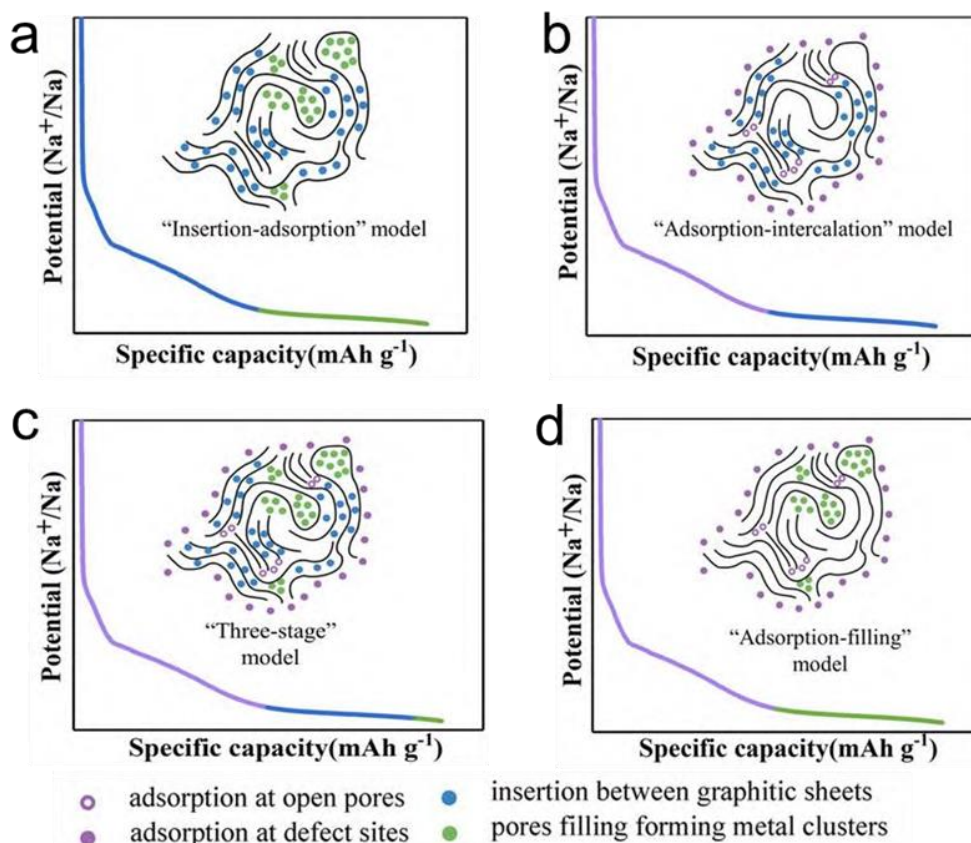


Fig 1. Model for sodium storage mechanism of hard carbon [8].

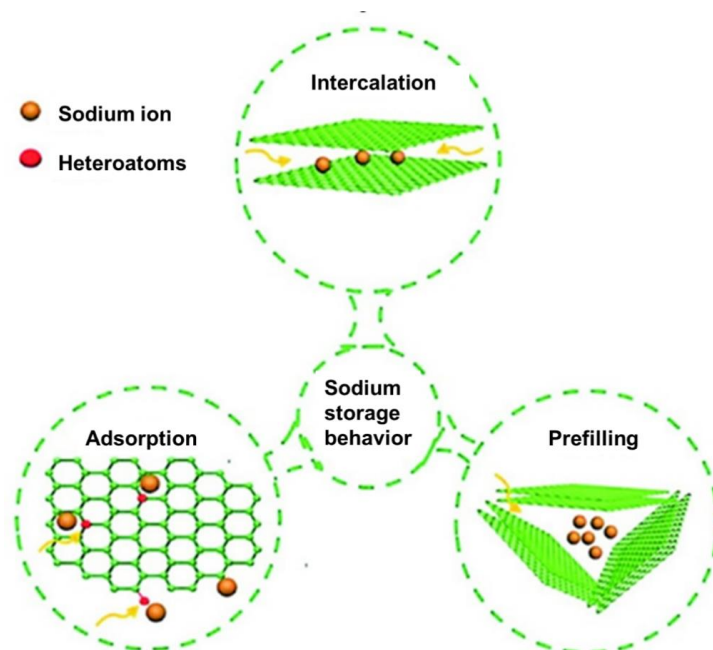


Fig 2. Sodium storage behavior of hard carbon [9].

3. Study on hard carbon precursors

Previously, the common hard carbon materials can be grouped into coal-based and biomass-based according to the precursors [10]. Biomass precursors such as corncob, lignin, peanut shell, mangos teen shell and sop hora wood are abundant and sustainable. Most of biomass- based hard carbon contain natural pores, which are conducive to sodium ion transport and electrolyte diffusion. Biomass-based hard carbon has natural heteroatoms and natural structure that is useful to the storage and transmission of sodium ions and can improve the electrochemical capability. However, it is critical to find suitable pretreatment methods according to different materials and optimize the composition ratio. Coal-based hard carbon is classified according to the amount of volatile substances in the thermal process. Coal serve as precursors for the hard carbon negative electrode material for SIBs, which helps to make it play a greater value. However, the preparation hard carbon materials basing on coal is complex and difficult to industrialize. At present, the mechanism research on the enhancing electrical capability of hard carbon materials is not sufficient, and the selection of pretreatment process is limited [11].

In summary, it is necessary to take corresponding measures to optimize the preparation method. The preparation of coal-based hard carbon removal usually requires acidic reagents which are expensive and environmentally unfriendly. Therefore, it is particularly important to find alternative reagents. In addition to that, other matrix materials can be explored, such as cotton fabrics impregnated with coal solution to prepare flexible self-supporting electrodes [12]. For biomass-based hard carbon, the main pretreatment methods include physical and chemical methods. In recent years, some scholars have tried to combine biological pretreatment to enhance electrical performance as much as possible of hard carbon materials. In addition, both of them can be enhanced the electrochemical performance by heteroatom doping, mechanical ball milling, composite carbon and other methods.

3.1. Coal-based hard carbon

According to the amount of volatile substances in the thermal process, coal is categorized into four types: lignite, subbituminous coal, bituminous coal, and anthracite, which cause diverse electrochemical properties of hard carbon. The lignite contains more functional groups and side chain structures, and its oxygen content is high. The oxygen content of subbituminous coal is moderate.

Bituminous coal has low oxygen content and high reactivity [13]. Anthracite has low volatile content, low oxygen levels and a high carbon composition content. Figure 3 shows the structure of different types of coal. The electrochemical properties of coal-based hard carbon can be improved by some modification methods. The following are several effective modification methods.

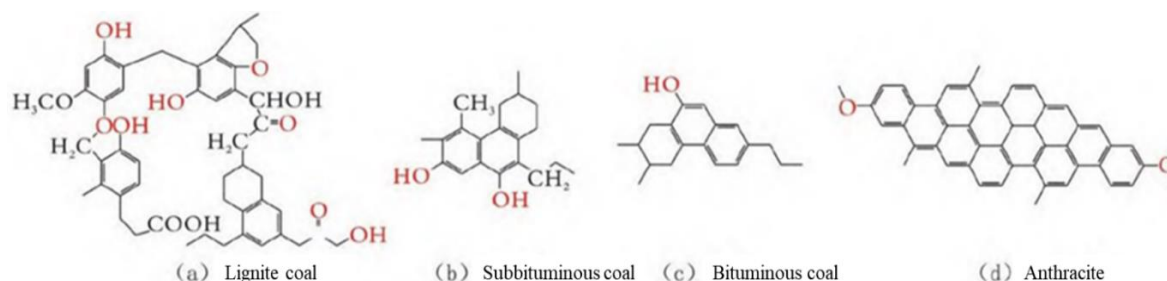


Fig 3. Structure diagram of different kinds of coal [14].

(1) Heteroatom doping

By introducing heteroatoms such as nitrogen, oxygen, potassium, and sulfur, the structural characteristics of hard carbon can be systematically changed, which can significantly affect their sodium storage capacity. Among them, nitrogen doping has been widely studied because it provides more sites. Heteroatom doping can increase the distance between hard carbon material layers, expand the low voltage platform capacity and slope capacity, and reduce the volume expansion of sodium ions, thereby improving the electrochemical performance [7].

(2) Activating treatment

Hard carbon anode materials with special structure can be obtained by chemical activation treatment, such as high temperature carbonization after mixing with nitric acid or potassium permanganate in proportion. The nanopores and surface functional groups created by this process enhance the material's porosity and significantly boost its electrical performance [15]. For example, Sun et al. activated anthracite with KOH at 700°C, subsequently, the material undergoes high-temperature carbonization. This leads to the formation of a closed pore structure. The sample exhibits a reversible specific capacity of 308 mA·h/g, a high energy density of 231.2 Wh/kg. At the same time, the average voltage can reach 3.22V [16]. The activation treatment increases the number of mesopores and the site density of sodium ions, thereby optimizing the electrochemical performance.

(3) Other modification methods

Composite carbon and mechanical ball milling are also effective means for hard carbon. The composite carbon combines the advantages of hard carbon with high cycle stability and soft carbon with high rate performance, which effectively enhances the rate performance of the hard carbon electrode. In addition, the mechanical ball milling uses mechanical energy to initiate chemical reactions and produce multiple effects on carbon materials [17]. Different functional groups are introduced to improve their electrochemical properties.

3.2. Biomass-based hard carbon

Due to the limitation of the composition and structural characteristics of biomass precursors, the biomass-based hard carbon materials prepared by direct carbonization are difficult to meet the electrochemical requirements. Therefore, it is necessary to pretreat biomass precursors using different methods to optimize and improve their composition and structure. Biomass from different sources requires specific pretreatment methods to enhance the electrochemical capability. In the following, the methods of preparing hard carbon from Peanut shell and sophora wood are introduced. Zuo et al. obtained a peanut shell-derived hard carbon precursor by heating the peanut shell powder to 500°C at a rate of 5°C per minute in an argon atmosphere [2]. sophora wood is mainly composed of cellulose, hemicellulose and lignin. Lignin and cellulose play a leading part in the formation of hard carbon materials. After carbonization, sophora japonica can effectively retain its pores and natural structure, which plays a significant role in the storage and transport of sodium ions. Huo et al. heated the

Sephora residue to 500°C at a heating rate of 5°C/min in argon atmosphere and kept it for 2 hours, and then heated it to 1300°C at a rate of 1°C/min to prepare hard carbon samples [18].

(1) Solid phase melting diffusion method

A series of samples of Peanut shell-based hard carbon with different components and proportions were prepared by mixing hard carbon precursor such as glucose, sucrose and starch in proportion by solid phase melting diffusion method. The analysis results show that the addition of sugars helps to form more microporous structures, because sugars fill the original large pore structure of hard carbon that generate more mesopores and micropores, thereby improving cycle stability and rate performance. However, if the proportion of sugars is too high, it may lead to a decrease in specific capacity, because unfilled excess sugars will form derived hard carbon.

(2) Acid-treated

Although the partial carbonization of biomass during sintering has promoted the formation of pores, the insufficient and uniform distribution of these pores may not possible to prepare a hard carbon negative electrode with sufficiently excellent performance. Taking the Sephora wood-based hard carbon materials after sintering as samples, the electrochemical properties of the materials before and after acid treatment were examined. The electrochemical characterization data indicate that the acid-treated hard carbon material has a substantial between layers spacing, which can assist sodium ions to insert and separate in materials, thereby improving the reversible capacity and the first charge-discharge efficiency [18]. However, it should be noted that acid treatment does not significantly boost the cycle durability of hard carbon materials.

(3) Alkali treatment

Alkaline pretreatment refers to using the alkaline reagents to impregnate or mix and grind precursor raw materials before high temperature carbonization. Common alkaline reagents include potassium hydroxide, sodium hydroxide, calcium hydroxide and alkaline salts. It is found that alkaline reagents can not only increase the number of micropores in biomass precursors, increase the specific surface area [19], but also reacts with oxygen-containing functional groups in biomass precursors to form a lot of vacancies during the carbonization process. At the same time, the hydroxide ions of the alkaline reagent quickly occupy these vacancies and introduce many new oxygen-containing groups [20]. Then the alkaline reagent will be converted to metal salts at 400-600°C and further reduced to metal elements at about 800°C. Which leads to the release of many intermediate products in the form of gas. Thus, developed pores are formed to enhance the electrochemical capability. Some researchers also use a variety of alkaline reagents at the same time to achieve better pore-forming effect.

4. Conclusion

In this paper, hard carbon and its sodium storage principle as well as the preparation and modification methods of coal-based hard carbon, peanut-based and sophora wood-based hard carbon are mainly described. Using coal to produce hard carbon helps to reduce environmental impact and coal is rich in resources with a low price, broad prospects. Heteroatom doping of coal-based hard carbon can increase the carbon layer spacing. This expands the low-voltage platform capacity and ramp capacity. Anthracite is activated and carbonized in proportion to nitric acid or potassium permanganate to obtain higher energy density and higher reversible specific capacity. The multiple effects of carbon materials can be achieved by means of composite carbon and mechanical ball milling to improve the electrochemical performance. Using biomass as a precursor to produce hard carbon can give full play to the advantages of its natural pores. This report focuses on hard carbon materials prepared from peanut shells and sophora wood as precursors. Pretreatment of peanut shell-based hard carbon and mixing it with sugar in proportion by solid-phase melting method can significantly enhance the electrochemical capability of carbon materials. Acid pretreatment of sophora wood-based hard carbon can increase the reversible capacity and first cycle efficiency, but it should be noted that this does not significantly enhance the cycling capability. In summary, hard

carbon still has a lot of room for improvement and broad research directions in the field of electrochemistry. Finding suitable materials and adopting the correct method is the key to improve its electrochemical performance. Future research will focus on how to boost the initial coulombic efficiency for hard carbon anode materials, achieve high specific capacity, consider the actual pressure density, low sodium storage potential and optimize cycle performance.

References

- [1] Hou H, Qiu X, Wei W, et al. Carbon anode materials for advanced sodium-ion batteries [J]. *Advanced Energy Materials*, 2017, 7(24): 1602898. Fangfang. Research on power load forecasting based on Improved BP neural network. Harbin Institute of Technology, 2011.
- [2] ZUO Y C, Ji Y, Zhang J T, et al. Study on regulation of pore structure and sodium storage performance from peanut shell-based hard carbon [J/OL]. *Modern Chemical Industry*, 1-13 [2024-07-16].
- [3] Zhou P S. Hard carbon and its composites in sodium ion battery application study [D]. Ningxia University, 2023.
- [4] Stevens D A, Dahn J R. High capacity anode materials for rechargeable sodium-ion batteries [J]. *Journal of The Electrochemical Society*, 2000, 147(4): 127-1273.
- [5] Chen X, Tian J, Li P, et al. An Overall Understanding of Sodium Storage Behaviors in Hard Carbons by an “Adsorption-Intercalation/Filling” Hybrid Mechanism [J]. *Advanced Energy Materials*, 2022, 12(24): 2200886.
- [6] Qiu K, Cao Y L, Ai X P, et al. Analysis of sodium storage reaction mechanism of different types of carbon structures [J]. *SCIENTIA SINICA Chimica* 2017, (5): 573-578.
- [7] Xu Y, Ma L X, Hai C X, et al. Research progress and industrialization challenge of coal-based hard carbon anode materials for sodium ion batteries [J/OL]. *Inorganic Chemicals Industry*, 1-9 [2024-07-16].
- [8] Chen X Y, Liu C Y, Fang Y J, et al. Understanding of the sodium storage mechanism in hard carbon anodes [J]. *Carbon Energy*, 2022, 4(6): 1133-50.
- [9] Zhang L, Wang W A, Lu S, et al. Carbon Anode Materials: A Detailed Comparison between Na-ion and K-ion Batteries [J]. *Advanced Energy Materials*, 2021, 11(11): 2003640.
- [10] SUN N, QIU J, and XU B. *Advanced Energy Materials*, 2022, 12(27): 2200715. Ma Kunlong. Short term distributed load forecasting method based on big data. Changsha: Hunan University, 2014.
- [11] Zhang W H, Han W J, Chen A X, et al. Research Progress on Pretreatment of Anode Materials for Biomass-Based Hard Carbon Sodium-Ion Batteries [J/OL]. *Materials Reports*, 1-21 [2024-07-17].
- [12] Zhang W. STUDY ON MODIFICATION OF COAL-BASED CARBON ANODE MATERIAL FOR SODIUM-ION BATTERY [D]. Beijing University of Chemical Technology, 2023.
- [13] Wu Q P, Man M Y, Song S C, et al. Research progress of coal-based hard carbon in sodium ion battery anode materials [J]. *Chemical Minerals and Processing*, 2023: 1-10.
- [14] Zhang L X, Zhang X, Li C, et al. Research Progress of Application of Coal-Based Carbon Anode Materials in Lithium-Ion Batteries [J]. *Journal of Petrochemical Universities*, 2022, 35(06): 10-8.
- [15] Liu X Q, Li Y H, Zhang S N, et al. Craft Research of Preparing Activated Carbon by Phenolic Resin [J]. *Journal of Shanghai Polytechnic University*, 2016, 33(02): 107-11.
- [16] Wang K F, Sun F, Wang H, et al. Altering Thermal Transformation Pathway to Create Closed Pores in Coal-Derived Hard Carbon and Boosting of Na⁺ Plateau Storage for High-Performance Sodium-Ion Battery and Sodium-Ion Capacitor [J]. *Advanced Functional Materials*, 2022, 32(34).
- [17] JAMES S L, ADAMS C J, BOLM C, et al. Mechanochemistry: opportunities for new and cleaner synthesis [J]. *Chemical Society Reviews*, 2012, 41(1): 413-47.
- [18] Huo J J, Mao W T, Bao K Y. Preparation and sodium storage properties of acacia wood biomass-based hard carbon [J/OL]. *Chinese Battery Industry*, 1-7 [2024-07-17].
- [19] FRANK E, STEUDLE L M, INGILDEEV D, et al. *Angewandte Chemie International Edition*, 2014, 53(21): 5262.
- [20] XI Y, HUANG S, YANG D, et al. *Green chemistry*, 2020, 22(13): 4321.