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Pore Structure and Sodium Storage Performance of Sodium-Ion Battery Anodes

Yuchang Liu

School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing, China
lyc0908@njust.edu.cn

Abstract. Pore structure affects ion transport and interfacial reactions in sodium-ion battery anodes and provides space to accommodate volume changes. This paper focuses on hard carbon, alloy anode and conversion composite materials, discusses the role of pore size, connectivity, pore opening and internal voids in the sodium storage process, and analyzes the advantages and limitations of different pore structures. The article also compares the synthesis strategies such as template method, activation method, carbonization control, dealloying and composite precursor derivatization, and explains how these methods shape the pore structure. Studies have shown that the sodium storage process and failure mechanism of different anode materials are very different, and the functional requirements of the pore structure are also different. The formation of pores is often accompanied by changes in phase composition. The contribution of pore structure cannot be evaluated only by capacity. The evaluation should also consider the sodium storage mechanism and failure process of the material under comparable electrode preparation and test conditions.

Keywords: sodium-ion batteries, anode, pore structure, hard carbon, sodium storage mechanism

1. Introduction

Sodium-ion batteries benefit from abundant sodium resources and the potential for lower costs, but their practical application remains constrained by anode performance. Usiskin et al. emphasized that sodium-based batteries should be evaluated in relation to their intended applications, as low cost and abundant resources do not necessarily translate into high energy density [1]. The review by Gong et al. found that different anode materials have shortcomings in capacity, rate performance and cycle life [2]. Hard carbon can store sodium in the disordered carbon layer and internal voids, but there is still irreversible sodium loss in the first cycle. Alloy materials have high theoretical capacity, and repeated volume changes can easily destroy the structure and electrical contact. In order to improve the performance of the anode, it is necessary to consider both the sodium storage space and ion transport, as well as the interfacial reaction and structural stability in the cycle. The pore structure will affect these processes, but the porosity alone cannot explain the sodium storage performance. The change of pore structure often occurs together with other structural factors, and it is difficult to attribute the performance difference directly to a certain structural feature.

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The key to controlling the pore structure is to first clarify what role different pore types play and under what conditions they are applicable. Li et al. reviewed the relationship between hard carbon microstructure, sodium storage mechanism and initial Coulombic efficiency, emphasizing the importance of structure and interfacial optimization [3]; Gao et al. found that the porous skeleton and alloy composition will affect the cycle stability of nanoporous Bi–Sb [4]. These studies show that the pore structure is characterized from multiple dimensions: pore size and connectivity affect electrolyte infiltration and transport; the pore opening is related to whether ions and solvent molecules can enter; internal voids may be involved in sodium storage, or buffer volume changes. This paper focuses on the effect of pore structure on the sodium storage behavior of hard carbon and alloying anodes, compares various methods for constructing pore structure, and also discusses the limitations of structural characterization and performance evaluation.

2. Pore structure and sodium storage behavior

2.1. Porosity and specific surface area

In the study of pore structures, the first step is to determine whether increasing porosity necessarily improves sodium storage performance. The low-defect, low-porosity hard carbon prepared by Xiao et al. nevertheless delivered a reversible capacity of 361 mAh g^{-1} and an initial Coulombic efficiency of 86.1%, with 93.4% capacity retention after 100 cycles [5]. This result indicates that high porosity is not a necessary condition for hard carbon to achieve high capacity. However, because defect concentration and pore characteristics were modified together, the performance improvement cannot be attributed solely to reduced porosity.

To understand this result, it is necessary to distinguish between porosity and specific surface area. Porosity represents the ratio of pore volume to the total volume of the material, whereas the specific surface area measured by gas adsorption represents the surface area accessible to the probe gas per unit mass of the material. According to a technical report by the International Union of Pure and Applied Chemistry (IUPAC), the adsorptive species, measurement temperature, calculation model, and pore accessibility all influence the specific surface area and pore size distribution determined by gas adsorption [6]. Thus, a lower specific surface area does not directly imply a smaller internal pore volume, nor does higher porosity necessarily indicate more severe interfacial side reactions. In research on Sb anodes, Li et al. found that a hierarchical nanoporous structure could increase the reversible sodium storage capacity of Sb anodes by approximately 27%, yet larger pores offered limited improvement in stability after 200 cycles [7]. These results demonstrate that the role of pore structure is linked to the material's sodium storage mechanism; therefore, one cannot rely solely on comparisons of porosity or specific surface area but must also consider metrics such as initial Coulombic efficiency, cycling stability, and volumetric capacity.

2.2. Pore size and ion accessibility

According to the IUPAC classification based on pore width, pores can be divided into micropores, mesopores and macropores, with widths less than 2 nm, between 2 and 50 nm and greater than 50 nm respectively [6]. In the negative electrode of sodium ion battery, micropores can provide adsorption sites or internal sodium storage space, but an excessive number of accessible micropores may increase interfacial reactions. Mesopores are usually conducive to electrolyte infiltration and ion transport; the macropores can act as transmission channels and provide buffer space for volume change in the alloy material.

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However, the research by Glatthaar et al. shows that there are limitations in classifying only by pore size. They prepared lignin-derived mesoporous carbon by soft template method. In the similar mesoporous range (5–50 nm), they obtained two types of structures: interconnected and relatively isolated channels. It is worth noting that the sample with isolated pores also has a low-potential plateau [8]. This shows that even if the pore size falls within the mesoporous range, the difference in pore connectivity will lead to different sodium storage behaviors.

From the perspective of geometric connectivity, open pores are connected to the outside, and the completely closed pore has no continuous channel to the outside. In some hard carbon studies, however, "closed pores" refer to pores that are inaccessible to gas probes under specific measurement conditions. This usage differs from the geometric definition. For example, pores inaccessible to N_2 may still be detected using CO_2; it cannot be concluded that they are completely isolated from the outside world by the results of N_2 adsorption. This is mainly related to the difference in pore opening size; the pore opening determines whether the gas molecules, electrolyte components and Na^+ ions can enter, and in what state. A large pore body may not contribute to reversible capacity if it lacks an accessible entry pathway. Conversely, pores inaccessible to N_2 may still participate in sodium storage under electrochemical conditions. Using carbon molecular sieves as a model system, Zhang et al. investigated the effect of heat treatment on the solvation structure and interfacial reaction after controlling the pore size [9]. These findings indicate that to evaluate the role of internal pores, it is not only necessary to measure the pore size, but also to analyze the pore opening size and its screening effect on different components.

As shown in Figure 1, when the pore opening is more than 0.5 nm, Na^+ can enter the pore, and the solvation shell is basically intact. In this case, the pores are dominated by solvent-separated ion pairs, and the solvent may decompose significantly. The pore opening size is reduced to 0.35–0.5 nm, and some solvent molecules are blocked outside. Na^+ undergoes partial desolvation, and contact ion pairs become the dominant species. When the pore opening size is less than 0.35 nm, the entry of most solvent molecules is restricted. The interaction between Na^+ and anions is enhanced, and the environment is dominated by ion aggregates. In the solid electrolyte interphase (SEI) film formed at this time, the proportion of inorganic components is higher. This study shows that the pore mouth will affect whether the ions can enter, and will also change the type and coordination state of the solvents and anions in the pores. These changes ultimately affect the formation of SEI and the utilization of internal active sites. It should be noted that the 0.5 nm and 0.35 nm thresholds mentioned here are measured in specific carbon molecular sieves, electrolyte and gas adsorption systems; they cannot be considered as the universal optimal pore opening size for all hard carbon materials.

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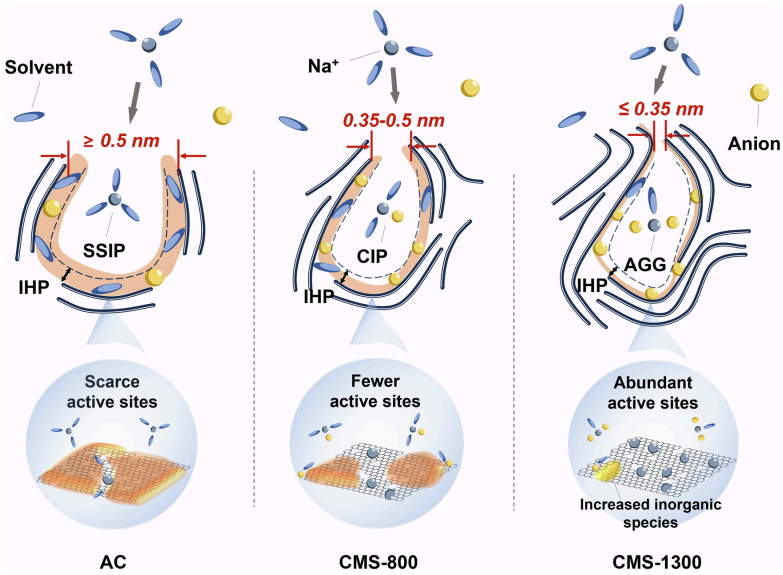


Figure 1. Effects of pore opening size on solvation and SEI formation [9]

Lu et al. further pointed out that the pre-desolvation in hard carbon nanopores is related to the standing time [10]. This shows that factors such as infiltration and pre-test treatment will change the performance of the same material. When optimizing the pore opening size, the electrolyte composition, ion entry rate and side reactions should be considered at the same time. In terms of characterization, a variety of complementary methods should be combined to distinguish the characteristics of the pore opening and the pore body. In addition, the wetting conditions and standing time after the assembly of the cell should also be recorded.

2.3. Roles of pores in sodium storage

The same pore structure may play different roles in different anode materials, depending on the sodium storage mechanism of the material. In hard carbon, the internal pores are mainly considered to be related to the low-potential plateau capacity. Nagmani et al. prepared hard carbon with hierarchical pores and closed pores, and the reversible capacity reached 422 mAh g^{-1} at 0.1 C. About 57% of the reversible capacity came from the low-potential plateau, and the capacity retention rate was 84% after 500 cycles at 1 C [11]. Yuan et al. proposed the concept of accessible closed pores, and found that there is a strong linear relationship between their surface area and plateau capacity, which supports the contribution of accessible internal pores to low-potential sodium storage [12]. However, this correlation alone cannot prove the formation of sodium clusters. The carbon layer structure and the potential range used in the test will also affect the plateau capacity. To evaluate the role of internal pores, it is necessary to confirm whether the pores exist, to determine whether Na^+ can enter, and to find out whether the sodium storage process is reversible.

In alloying anodes, pores are mainly used to accommodate volume changes during repeated alloying/dealloying processes, and continuous skeletons help maintain electron transport channels. The nanoporous Bi_2Sb_6 prepared by Gao et al. was cycled for 10,000 cycles at 1 A g^{-1}, with an average capacity loss of about 0.0072% per cycle [4]. The continuous skeleton helps to maintain the electrical connection, and the pores provide buffer space for volume expansion. Previous studies have attributed long-term stability to porous structure, alloy effect and appropriate Bi/Sb ratio. This stability cannot be attributed solely to the presence of pores [4]. The study of Sb by Li et al. further

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shows that improved ion transport may not bring better cycle stability [7]. This means that the introduction of hierarchical pore structure may not be able to simultaneously improve ion transport and structural durability.

The above studies show that the role of pore structure must be evaluated in combination with specific materials. For hard carbon, the internal pores mainly provide reversible sodium storage space. For alloy materials, the design of pore structure pays more attention to strain buffering and structural integrity. Table 1 compares the main functions, supporting evidence, and possible trade-offs of different pore structures.

Table 1. The functions and trade-offs of pore structures

Structural features	Main functions	Supporting evidence	Key considerations
Open micropores and surfaces	Surface adsorption and electrolyte contact	Li et al. [3]	Sodium loss during SEI formation and initial Coulombic efficiency
Interconnected mesopores	Electrolyte access and shorter pathways	Glatthaar et al. [8]	Pore tortuosity and electrode density
Narrow pore openings and internal pores	Desolvation and low-potential storage	Zhang et al. [9], Nagmani et al. [11], Yuan et al. [12]	Ion accessibility and transport limitations
Pores and continuous frameworks	Strain buffering and electrical contact	Gao et al. [4], Li et al. [7]	Framework evolution and volumetric capacity

3. Pore structure construction and regulation

Different anode materials are different in composition and sodium storage mechanism, and the pore-forming methods are naturally different. Carbon-based materials usually rely on template method, activation technology, or control of carbonization conditions to regulate pore structure. Alloy materials can form porous skeletons by dealloying. For conversion-type materials, composite precursors can be used to form pores and conductive networks simultaneously.

3.1. Templating and activation

The template method is to introduce a specific structure before carbonization to leave space for subsequent pore formation. Glatthaar et al. prepared lignin-derived mesoporous carbons with different pore sizes and connectivity by selecting different block copolymer templates [8], indicating that template selection will affect pore size and morphology. The association between isolated pores and the low-potential plateau is primarily correlative; carbon layer structure and surface chemistry may also play a role. Factors such as template cost, template removal, and material yield limit its large-scale application.

The activation method is to etch the carbon skeleton with gas or chemical reagents, mainly generating open micropores and mesopores. Moderate activation can improve electrolyte wetting and ion transport while increasing the accessible surface area. Li et al. summarized the strategy of improving the initial Coulombic efficiency through microstructure optimization and surface

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modification. When optimizing hard carbon, irreversible capacity loss must be considered [3]. The activation conditions have to strike a balance between improving ion transport and controlling interfacial reactions and irreversible sodium loss in the first cycle.

3.2. Precursor selection and carbonization

In addition to external pore-forming, the internal pores of hard carbon can also be formed during the carbonization of the precursor. The precursor composition affects the growth and arrangement of the carbon layer, and the carbonization temperature further controls the rearrangement of the carbon layer, the shrinkage of the pores, and the evolution of the internal voids. Tang et al. compared waste wood and its components, and found that crystalline cellulose contributes to the formation of long strip carbon layers, which act as pore walls, while lignin and hemicellulose affect the curvature and graphitization order of the carbon layer [13]. The optimized sample has a reversible capacity of 430 mAh g^{-1} at 20 mA g^{-1}, and a plateau capacity of 293 mAh g^{-1} at the second cycle. The capacity remains 85.4% after 400 cycles at 500 mA g^{-1}.

Figure 2 shows that the precursor composition and carbonization temperature are the key factors to regulate the internal pore structure of hard carbon. The precursor composition affects the arrangement of the carbon layer, and the carbonization temperature changes the process of internal pore formation and shrinkage. The carbonization conditions should be selected according to the specific characteristics of the precursor [13]. The temperatures of 1100, 1500 and 1700 °C in the diagram correspond to the specific conditions in the original study and cannot be regarded as the general process parameters applicable to all hard carbon materials. Carbonization also changes defects, surface functional groups and interlayer spacing; therefore, the performance improvement cannot be attributed only to the increase in the number of closed pores.

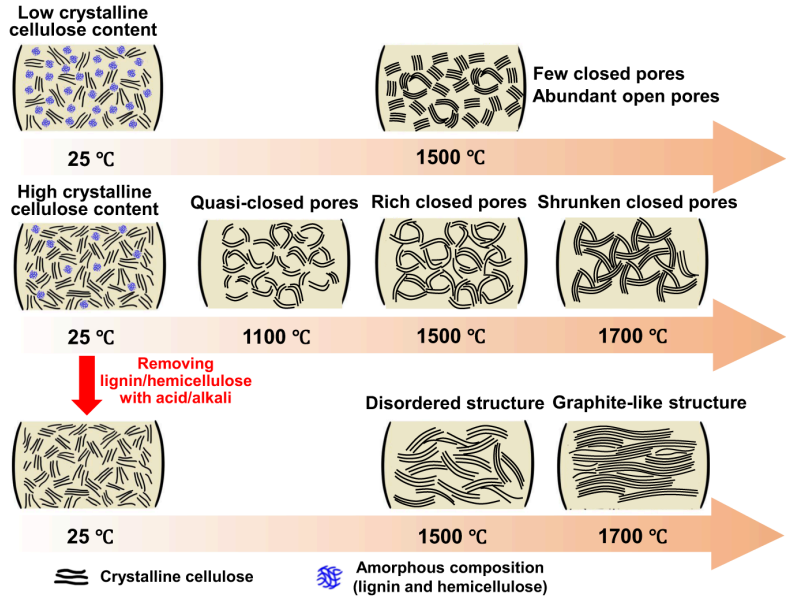


Figure 2. Effects of precursor composition and carbonization temperature on internal pore formation [13]

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3.3. Pore engineering in alloying and conversion-type anodes

For Sb and Bi alloying anodes, dealloying can prepare continuous porous skeletons. Gao et al. prepared nanoporous Bi–Sb by dealloying Mg-based ternary precursors, which provided a path for the construction of continuous porous skeletons for alloying anodes [4]. However, Li et al. compared Sb with different hierarchical pore structures and found that the introduction of larger pores can increase the sodium storage capacity, but may not improve the cycle life [7]. Therefore, the design of the pore structure for alloying materials should simultaneously consider pore size hierarchy and framework continuity, and structural changes following cycling should be used to assess whether improved transport is accompanied by maintained framework stability.

For conversion-type materials, composite precursors can be used to regulate pore structure, active phase distribution, and conductive networks simultaneously. Chen et al. reviewed the applications of metal–organic framework-derived porous carbons and metal compounds as sodium-ion battery anodes [14]. This kind of preparation process usually changes the pore structure, carbon content and phase composition at the same time. In comparison, the active phase composition and carbon content should be kept consistent as much as possible. In addition, the initial Coulombic efficiency, voltage hysteresis and cycle stability are also included in the evaluation.

4. Conclusion

This review shows that the pore structure design of the negative electrode of sodium ion battery must match the sodium storage mechanism of the material. For hard carbon, pores promote low-potential sodium storage, while pore openings and connectivity affect ion entry, desolvation and interfacial reaction. Therefore, it is necessary to find a balance between the internal sodium storage capacity and the irreversible sodium loss in the first cycle. In alloy materials, pores are mainly used to buffer volume changes, and continuous skeletons are essential for maintaining electron transport and cycle stability. For conversion composites, the pore structure needs to be coordinated with the conductive network and the active phase distribution to improve the reversibility of the reaction. The effectiveness of a pore structure depends on whether it addresses the material's main limitations without compromising other aspects of performance.

Current research remains limited in comprehensively characterizing pore structures and distinguishing their specific contributions to performance. Some pores are inaccessible to gas probes under specific testing conditions but may still participate in sodium storage under electrochemical conditions. The change of pore structure is often accompanied by the change of defects, surface chemistry and phase composition. Therefore, the effect of a specific type of pore cannot be judged by the increase of capacity alone. Future studies should combine complementary characterization methods to analyze pore bodies and pore openings separately and clarify pore connectivity. The performance evaluation should not only consider the reversible capacity and the initial Coulombic efficiency, but also consider the rate performance, cycle stability and volumetric capacity, and be verified under comparable electrode and full battery conditions. Only by clarifying how pore structure affects sodium storage, ion transport, and structural stability can material-level optimization be translated into improved battery performance.

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