Development and Prospect of Electrode Materials for Sodium Ion Batteries

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Abstract. Sodium-ion batteries, with the advantages of low cost and abundant resources, have become an effective complement to lithium-ion batteries in application scenarios such as large-scale energy storage systems and short-distance electric vehicles. Nevertheless, sodium-ion batteries generally lag behind lithium-ion batteries in energy density. The aim of this paper is to provide an overview of current research results on anode and cathode materials and to provide insights into the challenges faced by various materials, such as the deficiencies of hard carbon materials for the anode in terms of sodium storage capacity and stability at the solid electrolyte interface (SEI), and the poor air stability and susceptibility to phase transitions of layered oxides for the cathode. Further, the report proposes several innovative solutions with the goal of developing better sodium ion electrode materials. These strategies include, but are not limited to: improving the microstructure of hard carbon through nano-engineering techniques to enhance its sodium storage capacity; and employing surface coating or doping methods to improve the air stability of cathode materials. Through these research endeavors, this paper expect to provide a solid scientific foundation and new perspectives for the advancement and application expansion of sodium-ion battery technology.

1 Introduction

As the exploitation of fossil fuels intensifies, global energy challenges escalate, prompting a worldwide shift towards renewable energy sources. A critical hurdle for renewable energy is efficient energy storage, with chemical batteries, particularly lithium-ion batteries (LIBs), standing as the predominant solution due to their developed technology and high specific energy. The demand for LIBs is surging; however, China, a major consumer, faces a scarcity of lithium reserves, primarily located in hard-to-exploit lithium saline lakes, leading to over 80% dependency on lithium imports [1]. Additionally, the safety concerns associated with LIBs underscore the necessity for alternative solutions. Consequently, the quest for sustainable, safe, and cost-effective energy storage has steered global attention towards sodium-ion batteries as a promising replacement for LIBs.

Sodium-ion resources globally surpass lithium-ion reserves by approximately 1000-fold, with China's sodium-ion reserves holding a significant advantage, four to five orders of magnitude greater than its lithium-ion counterparts. This abundance makes sodium-ion-based batteries a viable solution to mitigate the scarcity of lithium resources. Sharing the same group in the periodic table, sodium and lithium exhibit similar ion intercalation mechanisms, enabling potential component interchangeability between the two battery types. Sodium-ion batteries (NIBs) not only offer enhanced safety compared to lithium-ion batteries (LIBs) but also perform better across a wide range of temperatures, positioning NIBs as an ideal substitute for LIBs [2].

While sodium-ion batteries (NIBs) offer distinct advantages over lithium-ion batteries (LIBs), challenges persist. The larger radius of sodium ions results in slower extraction and migration speeds, contributing to NIBs' generally lower energy density compared to LIBs. Consequently, enhancing the performance of cathode and anode materials is crucial for NIB advancement. Current research identifies hard carbon as the optimal anode material for NIBs, yet it faces issues like reduced sodium storage capacity and SEI stability [3]. Phosphorus-based anodes have emerged to address low sodium storage, but they suffer from significant volume changes. For cathode materials, transition metal oxides, and Prussian blue analogs are primarily explored, each presenting unique benefits and limitations [4].

2 Anode electrode material

2.1 Sodium phosphate ion battery anode electrode

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Phosphorus exists in four isomeric forms: red, white, black, and purple, each with distinct characteristics and structures. However, purple phosphorus can easily transform into white phosphorus upon heating, and due to white phosphorus's extreme chemical instability, both white and purple phosphorus are typically avoided as electrode materials for safety reasons [5]. Consequently, this discussion will focus on red and black phosphorus as potential electrode materials.

2.1.1 Red phosphorus

First, in terms of theoretical capacity, the red phosphorus electrode has a very high theoretical capacity, and the theoretical capacity of 2596 mAh·g^{-1} is 12 times that of the currently widely used hard carbon anode materials [6]. Second, in terms of global resource reserves, red phosphorus reserves are rich, so the price is relatively low, and it can be used on a large scale. Finally, the redox potential of red phosphorus is relatively safe and can effectively reduce the safety hazards caused by the formation of sodium dendrites [7].

Red phosphorus as an anode material in sodium-ion batteries (NIBs) faces significant challenges due to its poor conductivity and substantial volume changes during charge-discharge cycles. These issues often result in lower Coulombic efficiency and faster capacity degradation, hindering the advancement of red phosphorus in NIB applications [8].

2.1.2 Black phosphorus

Black phosphorus, a prominent two-dimensional material, has garnered international attention for its battery applications due to its theoretical specific capacity of 2596 mAh·g^{-1}, matching that of red phosphorus. Distinguished by superior electrical conductivity and a layered orthorhombic crystal structure, black phosphorus offers excellent interlayer spacing and charge transport properties, making it a promising high-capacity anode material for NIBs [9, 10]. However, similar to other phosphorus allotropes, black phosphorus faces challenges with volume expansion during use, impacting cycling stability and performance.

2.1.3 Metal phosphorus

The high theoretical capacity of elemental phosphorus coupled with its low cost makes it a good alternative for NIB anode materials. However, the low electrical conductivity and high-volume expansion mentioned in the preamble lead to high theoretical value capacities and low actual capacities. Even though composite carbon or changing its structural dimensions can alleviate the above defects, more and more studies have found that the combination of other conductive metal elements and phosphorus can also improve the electrochemical performance and stability of the electrodes effectively. This is because during the process of sodium removal, a portion of the metal phosphide is transformed into pure metal, in turn, it can effectively avoid the powdering of the material caused by volume expansion, to improve the electrochemical performance of the purpose [11,12]. The following is an example of tin phosphide.

Tin phosphide (Sn_4P_3) exhibits a dual sodium storage mechanism of conversion and alloying, yielding a theoretical capacity of 1132 mAh·g^{-1}. Kim's research group in 2014 demonstrated that the Sn_4P_3 anode electrode maintains a reversible capacity of 718 mAh-g^{-1} after 100 discharge cycles [13]. During sodium insertion, Sn_4P_3 initially transforms into amorphous Na_xP, followed by the formation of NaSn particles through the reaction of Sn and Na. This process results in a uniform dispersion of $Na_{15}Sn_4$ particles within amorphous Na_xP, effectively mitigating particle aggregation during charge and discharge cycles. Subsequent sodium extraction regenerates Sn_4P_3, showcasing the material's excellent cyclic stability and reversibility. The study highlights the practical efficacy of integrating conductive metals with phosphorus. However, both phosphorus and tin experience significant volume expansion during sodium storage, necessitating further research and optimization.

2.2 Carbon-based sodium-ion battery anode electrode

2.2.1 Graphite materials

In LIB, the way lithium ions are stored in graphite is to form an intercalation（LiC_6）compound with graphite through an intercalation reaction, it has a theoretical capacity ratio of up to 372 mAh·g^{-1}. A large number of existing LIBs use graphite electrodes as anode electrodes; therefore, graphite electrodes have the advantages of mature manufacturing technology and a complete industrial chain, graphite resources are abundant and there are resource advantages. Although Na and Li are congeners. However, when using the same method to store Na^+, the theoretical capacity has dropped significantly compared to lithium ions. The reason is that the formation energies of compounds are different when alkali metal and graphite form first-order intercalation (Figure 1). The formation energies of Li^+ and K^+ are both much lower than Na^+. Therefore, it is difficult to intercalate graphite and sodium. Although Na^+ can be solvated by using an ether-based electrolyte to increase capacity, the effect is still not ideal [14].

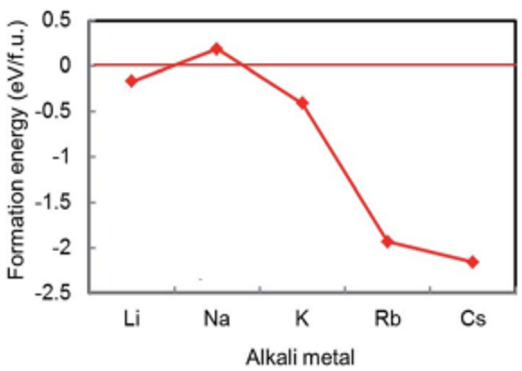

Fig. 1. The formation energies of compounds when different alkali metals form first-order intercalation with graphite [15].

2.2.2 Soft carbon material

Soft carbon materials generally refer to carbon that can be graphitized above 2800 °C. Among them, the surface of the graphite crystallites and the gaps between the crystallites play a role in adsorbing Na^+. In early research, the micro-spherical carbon particles prepared by Alcantara and others were able to achieve a reversible capacity of 285 $mAh \cdot g^{-1}$ [16]. In subsequent studies, the soft carbon material prepared by Luo and others using $C_{24}H_8O_6$ was able to achieve a reversible capacity of 114 $mAh \cdot g^{-1}$ at a current density of 1000 $mA \cdot g^{-1}$, and the rate and cycle performance are very excellent [17]. However, the layer expansion problem caused by Na^+ intercalation in soft carbon materials is still a key point that needs to be solved.

2.2.3 Hard carbon material

Hard carbon materials generally refer to carbon that cannot be graphitized above 2800 °C. Because its crystallite ordering is more disordered than that of soft carbon materials, it has more internal voids and can accommodate more Na^+. The hard carbon material HCC prepared by Liu and others can achieve a reversible capacity of 230 $mAh \cdot g^{-1}$ at a 1 C rate. And after 100 cycles, the capacity is still 97% of the original [18].

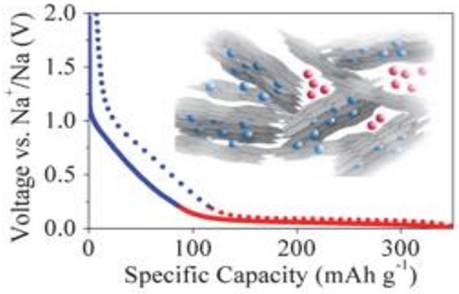

Fig. 2. Capacity-Voltage Diagram of Hard Carbon Materials [19].

The sodium storage capability of hard carbon is highly regarded, yet its underlying mechanism remains a topic of debate. Initially, it was believed to operate via an "intercalation-adsorption" mechanism, suggesting that Na^+ ions undergo intercalation in the sloped regions and adsorption in the plateau regions of the capacity-voltage diagram. Recent studies, including those by Xu et al., have challenged this view by conducting experiments such as sulfur doping in hard carbon and reducing defects at high temperatures. These studies propose an "adsorption-micropore filling" mechanism, indicating that Na^+ ions adhere to the adsorption mechanism in the sloped areas and to the micropore-filling mechanism in the plateau areas, without exhibiting intercalation behavior (Figure 2). Despite these advancements, a comprehensive model for the sodium storage mechanism in hard carbon requires further exploration and refinement.

2.2.4 Carbon nanofiber

Carbon nanofibers have the advantages of high stability, high plasticity, and high embedding sites. Liu et al. obtained a carbon nanofiber electrode material with a reversible capacity of up to 432 $mAh \cdot g^{-1}$ at 100 $mA \cdot g^{-1}$ by embedding graphene on carbon nanofibers. And the cycle stability and rate performance are very excellent [20]. However, considering the higher manufacturing cost of carbon nanofibers compared to hard carbon, its commercial application is still difficult.

3 Positive materials

3.1 Transition metal oxides

Transition metal oxides, as the most promising cathode materials for NIB, are one of the cathode materials because of their energy density, high theoretical discharge specific capacity, and ease of preparation, and they are also the most widely researched topics in the current NIB research. Currently, layered-type oxides and tunnel-type oxides are the two main types. Layered oxides (Na_XO_2, X = a mixture of one or more transition metals of Co, Ni, Fe, Cr) are the most frequently explored.

Layered oxides are mainly classified into octahedral O-type and prismatic P-type, in which Na^+ is able to insert into octahedral (O) or triangular prism (P) vacancy sites. Delmas et al. decided the nomenclature of these layered oxides according to the Na^+ coordination environment as well as the number of repetitive oxygen planes required to characterize the crystalline cells [21]. The octahedral type (O-type) can be categorized as O2 and O3 stacking mode respectively. Prismatic (P-type) structures can be categorized into P2 and P3 types. Among them, O3 and P2 are predominant (Figure 3).

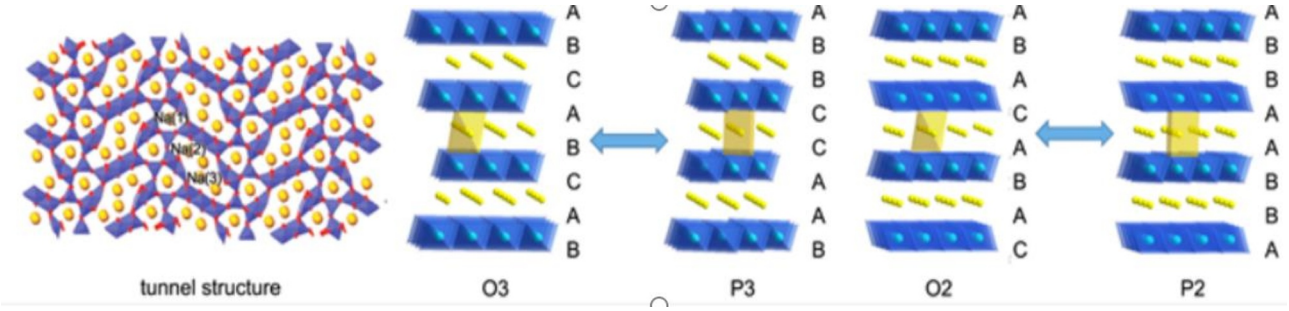

Fig. 3. Structure diagram of O2, O3, P2 and P3 [22]

During the development and application of layered oxide cathodes, there are a number of challenges:

(1) Layered oxide cathodes exhibit a high degree of sensitivity to moisture in the environment, and minor exposures may adversely affect their performance. Representative approaches to address this issue are the design of stable crystal structures or the fabrication of protective layers, through which air stability can be improved.

(2) Layered oxide cathodes often undergo complex phase transitions due to electrochemical processes, including Na^+/vacancy alignment and shifts in interlayer levels. These transitions lead to significant structural and volumetric changes, adversely affecting the battery's capacity and rate performance [23]. In addition, in terms of Na^+/vacancy arrangement, Yuansheng, Shi et al. altered the ordering of sodium ions and vacancies within the layered P2-phase transition metal oxide layer by structural perturbation, and the results confirmed a strong positive correlation between the Na^+/vacancy ordering and the rapid migration of Na^+ in the P2-type layered cathode. It is shown that the ordered occupation in the sodium layer can accelerate the transport of sodium ions, and the above understanding provides strong theoretical guidance for the design of high-rate NIB electrode materials [24].

3.2 Prussian blue compounds

Prussian blue compounds consist of a large multi-channel face-centered cubic structure formed by the coordination bonds between transition metal ions and cyanide groups. The coordination gap of this structure has sufficient space for the insertion and extraction of alkali metal ions such as Li^+, Na^+, K^+, etc. without destroying its spatial structure, it can effectively solve cycle stability problems caused by excessive ion radius.

Prussian blue electrodes based on iron-based materials have been developed to a certain extent due to their low price and stable structure. Goodenough et al. synthesized $Na_{1.92}FeFe(CN)_6$ by hydrothermal method. This material has a reversible specific capacity of 155 $mAh \cdot g^{-1}$ and good cycle stability of 80% of the original capacity after 750 cycles. It can be combined with hard carbon to form a sodium-ion full battery with good electrochemical performance [25]. Although the resource price of copper-based, nickel-based, and cobalt-based materials is higher than that of iron-based materials. However, Prussian blue electrodes synthesized from these materials have higher cycle stability than iron-based materials. For example, the $Na_2CoFe(CN)_6$ material was studied by Yang Hanxi's research group. It still has 80% of its original capacity after 800 operations at 5 C [26].

Although Prussian blue compounds can effectively overcome the cycle stability problem caused by ionic radius. However, due to the very strict requirements on water content control during synthesis, its mass production cost will increase significantly. Its preparation requires the use of cyanide ions, so it also has a certain impact on the environment.

4 Challenges and prospects

NIB has abundant production resources, is safe and reliable, and is cheaper than LIB. However, because its specific energy is still low, there are still some challenges in the electrode materials of NIB：

To address the challenges of phosphorus-based anode materials, such as volume expansion and inadequate electrical conductivity particularly with red phosphorus current strategies include structural adjustments and composite material modifications. Structural adjustments, like introducing a porous structure or nanosizing red phosphorus, mitigate volume expansion during discharge. Composite modifications combine carbon with red phosphorus, leveraging carbon's conductivity to improve that of red phosphorus. Similarly, for black phosphorus anodes, employing carbon composites and adjusting structure enhances stability and performance. Metal phosphides benefit from the electrochemical synergy between conductive metals and phosphorus, though volume expansion remains a concern, necessitating further structural optimization [27].

In sodium-ion batteries, carbon-based materials exhibit limitations. Soft carbon, while conductive, may hinder Na^+ deintercalation due to its intercalation mechanism. Hard carbon's conductivity and sodium storage mechanism are areas of debate. However, doping hard carbon with soft carbon enhances conductivity and introduces more adsorption sites, improving sodium storage. Carbon nanofibers, with their excellent conductivity and storage capacity, show promise. Transforming them into hollow structures or combining them with adsorbent materials could further boost sodium storage, though reducing production costs remains a challenge.

To enhance the stability and performance of transition metal oxide cathodes, which are susceptible to air instability, phase transitions, and adverse reactions with electrolytes, strategies such as cation doping and surface coating are employed. Cation doping, recognized for its effectiveness, facilitates anionic redox reactions and significantly boosts electrochemical performance. Additionally, optimizing the microstructure, particularly the arrangement of Na^+/vacancies, can further improve battery efficiency.

While Prussian blue materials offer advantages like unaffected spatial structure upon alkali metal ion insertion/extraction, notable Na^+ reversibility, and low-cost raw materials, their practical application is hindered by thermal instability and production challenges. Incorporating metals like Ni or applying thermally stable coatings could enhance thermal stability. Moreover, achieving low-defect, low-bound water materials through methods like slow crystallization and hydrothermal synthesis, or coating with conductive materials, can yield Prussian blue electrodes with improved reversible capacity. Several typical typed electrodes are summarized in Table 1 below:

Table 1. Electrode properties of different types of electrodes.

Type	Materials	Reversible Capacity (mAh/g)	Cyclability	Ref.
Carbon-Based	Graphite	≈ 0	-	[14]
	Soft carbon	285	-	[16]
	Hard carbon	222	600 cycles at 0.06 A/g	[18]
	Graphene highly scattered in porous carbon nanofibers	432	91% capacity retention after 1000 cycles	[20]
Phosphorus-Based	P/C nano composites	400	Stable cyclic performance at the level of 350–400 mAh/g	[27]
	Tin Phosphide	718	negligible capacity fading over 100 cycles	[13]
	Phosphorus	2596	-	[6]
Layered oxide	P2-$Na_{2/3}Cu_{1/12}Ni_{1/4}Mn_{2/3}O_2$	130	1 C, 30 cycles	[23]
	O3-$NaNi_{2/3}Sb_{1/3}O_2$	120	0.05 C, 50 cycles	[23]
Prussian Blue Compounds	$Na_{1.92}FeFe(CN)_6$	155	80% capacity retention after 750 cycles	[14]

5 Conclusion

Sodium-ion batteries have garnered significant interest recently due to their resource abundance and cost-effectiveness. However, they face challenges such as lower energy density and unstable cycling compared to lithium-ion batteries, necessitating further research on NIB electrode materials.

Phosphorus-based anode materials, despite their high specific capacities, struggle with volume expansion issues. Carbon-based materials, while common, present their own set of challenges: graphite is unsuitable for NIBs, soft carbon suffers from sodium entrapment and poor cycle stability, and the sodium storage mechanism in hard carbon remains under debate, with potential for capacity improvement. Additionally, the production cost of nanocarbon fiber materials is relatively high. Future development directions include capacity enhancement through doping and stability improvement through coating techniques.

Transition metal oxides, used as NIB cathode materials, encounter issues like reactivity with electrolytes and poor electrode stability. These challenges can be addressed through doping, coating, and protective layers, though specific materials and methods require further exploration. Prussian blue materials, unaffected by sodium ion volume changes, also demand additional research due to their thermal instability and production difficulties. As LIB prices rise, the relevance of NIBs is expected to increase. With ongoing advancements in NIB electrode research, NIBs are poised for broader application and development.

Authors contribution

All the authors contributed equally and their names were listed in alphabetical order

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