Towards High-Performance Sodium-Ion Batteries: Starting from Electrode Materials

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Abstract. Lithium-ion batteries (LIBs), the most successful secondary battery in the energy storage field, have been deeply and widely used in all aspects of life (such as transportation commuting, electronic products, and clean energy storage), but the development of the most commercially successful battery is in crisis due to the problems of high cost and resource shortage. Sodium has attracted attention in energy storage because of its rich resources and low price. However, sodium ions have a larger ion radius compared with LIBs, which results in worse ionic conductivity. Therefore, this characteristic of sodium ions has become an important factor restricting the development of sodium-storage electrode materials. Whereas the restriction of developing electrode materials in sodium-ion batteries (SIBs), the emphasis of research has focused on enhancing the electrochemical performance of high-performance anode and cathode materials and promoting the commercial application of SIBs. This paper will introduce the current research status and progress in cathode and anode materials of SIBs, and the future development direction of cathode and anode materials for SIBs will be summarized by analyzing the mechanism and defects of related electrode materials.

Keywords: Sodium-ion batteries, Cathode materials, Anode materials, Energy storage.

1. Introduction

The massive use of fossil fuels, represented by coal and oil, has inevitably affected the natural environment. Therefore, cleaner energy, such as solar, wind and tide, has become the successor of fossil fuels. However, the clean, renewable energies mentioned also face the challenge of time and place differences. To this end, energy storage devices have received extensive attention from researchers. In the 1980s, LIBs and SIBs were developed and studied at the same time. Compared with LIBs, the performance of electrode materials of early SIBs is poor, which leads to the stagnation of the development of SIBs. Therefore, LIBs, widely used in electric vehicles and portable 3C devices, have developed into an important "rocking chair battery" in the energy storage market [1]. However, the relatively expensive price and the scarce earth storage capacity of lithium resources make it very urgent to find cheaper and resource-rich alternatives to lithium. Specifically, lithium possessing a lesser resource abundance (0.002 %) and the growing demand for batteries have led to the rise in lithium salt prices. Therefore, new secondary batteries, such as SIBs, aluminum ion batteries, and lithium batteries, have developed rapidly [2]. Compared with LIBs, which are the most widely used, SIBs have the following advantages: (1) the reserves in the crust are large (2.75 %); (2) SIBs show a similar charge and discharge mechanism to LIBs, so some fault mechanisms are common to these two batteries; (3) Sodium will not react with the aluminum collector. Compared with LIBs, the anode of SIBs can use aluminum as the electrode collector instead of copper, which can reduce the raw-materials cost of the batteries. However, the ion radius of Na⁺ (0.106 nm) is larger than Li⁺ (0.076 nm). The larger ion radius means that the migration speed of Na⁺ in electrode materials is slower, which will lead to the worse ionic conductivity of sodium ions. Therefore, the electrode materials of high-performance SIBs need to meet the gap required for sodium-ion insertion to obtain high conductivity, which poses a challenge in finding suitable sodium-embedded anode and cathode materials [3]. This paper will explore the solution and development direction of the current dilemma of SIBs by introducing some SIBs cathode and anode materials that have been researched.
2. Operation Mechanism of SIB

The storage and release of electrical energy is achieved through the reversible transfer of Na\(^+\) between the two different electrodes. The voltage of the cathode electrode rises because of sodium ions being expelled from the lattice of the active cathode material during charging. Sodium ions continue to move toward the anode surface in the electrolyte. The charging of the SIB is realized by a voltage difference between the two electrodes. The deintercalation of Na\(^+\) from the anode electrode and the intercalation in the cathode electrode are happening successively. The movement of electrons provides power to the electrical devices attached to the external circuit. The migration of Na\(^+\) shows in Figure 1 [4]. Take the SIBs with the cathode material of NaMnO\(_2\) and the anode material of hard carbon as an example; the cathode and anode reactions and the total reaction are shown in (1) ~ (3)

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\begin{align*}
\text{NaMnO}_2 & \rightarrow \text{Na}_{(1-x)}\text{MnO}_2 + x\text{Na}^+ + xe^- \quad (1) \\
\text{C} + x\text{Na}^+ + xe^- & \rightarrow \text{Na}_x\text{C} \quad (2) \\
\text{C} + \text{NaMnO}_2 & \rightarrow \text{Na}_{(1-x)}\text{MnO}_2 + \text{Na}_x\text{C} \quad (3)
\end{align*}
\]

3. Cathode materials

The structure and performance of electrode materials, such as specific capacitance, have a great impact on the energy density, safety, and cycle performance of SIBs. The research emphasis of cathode materials is on the rich active sites and smooth Na\(^+\) migration channels. The sodium storage properties of four-layered Na\(_x\)CoO\(_2\) with different structures have reported by Hagenmuller et al. in 1980 [5]. With the in-depth research, the disadvantages of SIBs in energy density result in the attractive battery being difficult to have practical application, which is the significant reason for the research of SIBs almost stagnant compared with LIBs. However, with the increasing demand for energy-storage devices, SIBs with more resource advantages have attracted research attention again [1]. The cathode materials mainly include transition metal oxide materials, polyanion materials, Prussian blue materials, and amorphous materials [3].

3.1. Transition Metal Oxides

According to the structure of materials, transition metal oxides are divided into layered and tunnel-like. Na\(_x\)MO\(_2\) is used to represented transition metal oxides, where M refers to transition metals, and X is the stoichiometric number of Na (0<\(x\)<1). The MO\(_6\) octahedron mainly supports the layered structure, so it can ensure that the movement of Na ions will not change the material structure during the electrochemical cycle. Layered metal oxides possess four structures (O3, P3, O2 and P2) [5, 6].
Na\textsubscript{0.44}MnO\textsubscript{2} is a typical tunnel-type sodium storage material belonging to the orthorhombic system (Figure 2) [7]. Na\textsubscript{0.44}MnO\textsubscript{2} as a cathode material with reversible ion-storage (Na\textsuperscript{+}) performance has been reported by Doeff et al., but this tunnel-type material has poor cycle performance [8].

![Figure 2](image)

Figure 2 The structure of Na\textsubscript{0.44}MnO\textsubscript{2} [7].

Compared with layered oxide, the oxide with a tunnel structure is supported by an Mn-O octahedron. The improvement of cycle stability in the tunnel-structured cathode material can be attributed to the relative stability of the electrode structure. However, the low initial sodium content of Na\textsubscript{0.44}MnO\textsubscript{2} play a negative impact on the reversible capacity of cathode material. Therefore, increasing the sodium content and stability of tunnel structure in cathode materials is the research focus of this kind of electrode materials in the future [9].

3.2. Polyanionic Compounds

Polyanionic compounds can generally be expressed as Li\textsubscript{x}M\textsubscript{y}[(XO\textsubscript{m})\textsuperscript{n}]\textsubscript{z} or Na\textsubscript{x}M\textsubscript{y}[(XO\textsubscript{m})\textsuperscript{n}]\textsubscript{z} (M = a metal ion with variable valence; X = P, S, V, Si and other elements). Structurally, X polyhedron and M polyhedron form a polyhedron frame by coplanar connection, while A ion is distributed in the gap of the network. These compounds have the following characteristics as cathode materials: (1) the framework is very stable, which can obtain higher cycling and safety; (2) Some X polyhedrons may induce the electrochemically active $M^{n+}$ / $M^{(n-1)+}$ and increase the voltage of charge and discharge. However, these compounds have the problems of low electronic conductivity and volume energy density. Polyanionic compounds, such as phosphate, pyrophosphate and sulfate, have outstanding electrochemical properties [10].

3.2.1. Olivine Phosphate Compounds

As an analog of LiFePO\textsubscript{4}, NaFePO\textsubscript{4} was earlier used in the research of SIBs. NaFePO\textsubscript{4} has two crystal forms: maricite and olivine. The structures of three different compounds have shown in Figure 3 [6]. Olivine sodium iron phosphate has good electrochemical properties. The comparison of electrochemical performance between NaFePO\textsubscript{4} and LiFePO\textsubscript{4} in respective battery systems is conducted by Zhu et al., which concluded that the low sodium ion diffusion coefficient and high charge transfer resistance of NaFePO\textsubscript{4} were the reasons for the limited electrochemical performance of NaFePO\textsubscript{4} [11].
3.2.2. Na$_3$V$_2$(PO$_4$)$_3$ NASICON Framework Compounds

NASICON (Na$^+$ superionic conductor) has a three-dimensional (3D) framework structure. Na$^+$ is located in the gap of the framework and has excellent ionic mobility. Na$_3$V$_2$(PO$_4$)$_3$ is the main representative of cathode materials with a sodium fast ion conductor structure. To find a material synthesis method suitable for large-scale applications, Fang et al.

synthesized Na$_3$V$_2$(PO$_4$)$_3$ materials through high-energy ball milling pre-reduction and then used CVD technology to achieve in-situ growth of graded high conductivity carbon modified Na$_3$V$_2$(PO$_4$)$_3$ / C electrode. The synthesized NASICON framework compound can improve the rate capacity and cycle performance of the electrode material. Besides, Na$_3$V$_2$(PO$_4$)$_3$ / C particles are connected by conductive carbon fibers, which greatly improves the material's conductivity. The reversible specific capacity of the cathode material can still reach 38 mAh·g$^{-1}$ at 500 C current density (Figure 4 (a)). The capacity retention rate is 54% after 20000 cycles (rate = 30 C) shown in Figure 4 (b) [12].
3.2.3. Mixed Anionic Compounds

For polyanionic compounds, by using mixed anions, a new structural system can be constructed, and better electrochemical activity can be obtained. Selecting strong electron-withdrawing groups (such as F, etc.) can improve the voltage of the material through induction [13, 14]. The mixed polyanion system was first studied in the electrode materials of LIBs by Goodenough et al., which refers to the compounds composed of two different anions [13]. Komaba et al. improved the conductivity of Na2FePO4F through carbon coating, which greatly improved the electrochemical performance of the material [14].

3.3. Prussian Blue-Like Large Frame Compounds

The common composition of Prussian blue compounds is AₓMᵧ[MB(CN)₆] · zH₂O (A = alkali metal ions, Mₐ and Mₜ = transition metal ions). Abundant structural systems can be obtained by selecting different transition metal ions, such as Ni²⁺, Cu²⁺, Fe²⁺, and Mn²⁺, rich structural systems can be obtained, and different sodium storage properties can be shown. The framework of Prussian blue compounds shows in Figure 5 [15].

![Figure 5](image)

**Figure 5** The framework of Prussian blue analogues [15].

3.4. Organic Compounds

Organic cathode materials possess wide application prospects because of high theoretical specific capacity, environmental friendliness and low price. Cathode materials are required to have a high redox potential. Organic electrode materials do not contain transition metal elements, which are environmentally friendly, low-cost, diverse, and can be reasonably designed according to the structure. The compounds are flexible and have broad prospects. It will be of great significance to construct a suitable structure, improve organic materials’ voltage and cycle stability, and reduce the solubility of materials in the electrolyte [16].

3.5. Amorphous Compounds

Amorphous compounds are solids in which the atoms in the solid are not arranged in a certain spatial order. The reason sodium ions react on the surface of particles is that amorphous compounds have no lattice restrictions, which will avoid the instability of electrode structure. The negative material easily forms an amorphous phase, such as carbon material, phosphorus, titanium dioxide, etc., while the positive material is difficult to form an amorphous phase. FePO₄ easily forms an amorphous phase. Amorphous materials have no lattice restrictions, and it is possible to obtain better electrochemical properties than crystalline materials by constructing appropriate amorphous materials [17].

4. Anode materials

Studying the sodium storage mechanism of SIBs negative electrode materials can help design new high-capacity electrode materials and improve the whole battery’s electrochemical performance.
different ways of sodium storage can be divided into three main sodium storage mechanisms: intercalation reaction mechanism, alloying reaction mechanism and conversion reaction mechanism [18-20].

The anode material, through an intercalation mechanism to store sodium ions, usually has layered structures, because there are more ion storage positions between layers. The intercalation reaction will not significantly change the material's overall structure, so the electrode has good structural stability and cycle performance. Anode materials, however, that store sodium through the intercalation reaction mechanism usually have relatively low capacity because of the limited number of active centers in the electrode materials [18].

The alloying reaction is carried out by forming or fracturing a series of chemical bonds. The electrode material will combine with sodium in the alloying process to form a binary alloy. The alloying product's final phase determines the material's theoretical capacity and the change in the alloying reaction volume. Therefore, anode materials based on alloying mechanism will have higher theoretical capacity due to multi-electron transfer, but the electrode volume will change greatly during each alloying cycle [19].

The conversion mechanism uses transition metal oxidation states to rise the specific capacity of the anode material. Compared with the intercalation reaction, tremendous electron transfers are involved in the conversion reaction. Hence, the theoretical capacity of conversion materials is usually two to three times that of intercalation materials. However, electrode materials' structure will collapse or appear mechanical instability during the conversion process [20].

4.1. Carbon-Based Materials

Although sodium-ion and lithium-ion batteries have similar electrochemical working principles, when graphite-based materials are used as anode electrodes, the capacity of lithium is close to 372 mAh·g⁻¹. The capacity of sodium is only 35 mAh·g⁻¹ (graphite-based materials as the anode). Subsequent studies found that the low capacity of graphite as a sodium ion negative electrode is since the binding energy of sodium and graphite is less than that of lithium and graphite. At the same time, when sodium ions are embedded in graphite, the graphite will be stressed, and the energy stability of sodium graphite interlayer compounds (Na-GICs) formed is poor. Therefore, it is necessary to expand the space of the graphite layer, which can obtain more space and energy to promote the insertion of sodium ions [21].

Hard carbon, non-graphitizable carbon, has received extensive attention. The reason for hard carbon has been widely researched can be divided as follows: (1) edges and defects on the surface of hard carbon; (2) Voids between graphite layers; (3) Micropores formed between randomly oriented graphite. During discharge, sodium ions are first stored in the pore wall and defects on the hard carbon surface through surface adsorption. This process corresponds to the slope area in the charge-discharge curve. When the discharge is below 0.1 V, sodium ions form a platform area through graphite interlayer insertion and micropore filling [22]. Stevens and Dahn report the model named “House of cards” for Na⁺ or Li⁺ intercalation in hard carbon (Figure 6) [23].

Figure 6 Sodium/lithium filled hard carbon [23].
4.2. Titanium-Based Materials

Titanium compounds, TiO$_2$ and Na$_2$Ti$_3$O$_7$, are promising energy storage materials because of their stable structure, non-toxic to the environment and low price. TiO$_2$ Crystal is composed of a common side TiO$_6$ octahedron. The internal open channel can enhance the conductivity of ions and provide the gap position required for sodium-ion storage. Titanium-based materials possessing layered stable structure can insert sodium ions by intercalation mechanism, which means the high safety. However, the limited intercalation capacity and low conductivity reduce its specific capacity and magnification performance. The electrochemical performance of anode materials can be improved by designing nano-porous structure. In addition, anode materials composite with carbon-based material can alleviate the volume change during the Na$^+$ insertion. These modification methods are the future development direction of titanium-based anode materials with high specific capacity and conductivity [24].

4.3. Alloy Materials

Alloy materials can usually show a large theoretical capacity, because a single atom can be combined with one or more sodium atoms. For example, silicon has the complete sodium state of NaSi, and its theoretical capacity is 954 mAh·g$^{-1}$. The theoretical capacity of NaSi (the complete sodium state) is much larger than the theoretical capacity obtained by pure carbon. Because of their excellent specific capacity and environmental friendliness, researchers consider alloy materials as potential substitutes for anode materials of SIBs [10].

Alloy materials based on alloying sodium storage mechanism can exhibit large sodium storage capacity because a single atom can combine with one or more sodium atoms. However, the volume of alloy negative electrode materials will change greatly during the cycle, which reduces the cycle capacity and cycle life, and limits its practical production and application. Using structural regulation, element doping and material composite can significantly reduce the volume expansion, maintain the structure stability, and improve the conductivity and cycle life. Hence, the development of binary metal alloy compounds is also the future key research direction of alloy materials [24].

4.4. Conversion Materials

Transition metal oxides, metal sulfides, metal nitrides and metal phosphides based on the conversion mechanism will combine O, S, N and P with sodium ions in the process of sodium formation and will form elemental metals while forming sodium compounds. In the charge and discharge process, conversion materials are usually accompanied by multi-electron transfer, which shows high sodium storage capacity. However, in practical application, conversion materials will produce excessive volume expansion and form unstable SEI film, reducing the coulomb efficiency in the first week. Researchers will use conversion materials to design nanostructures to overcome the problem of excessive attenuation of the first cycle capacity. The designed nanostructure of anode materials can increase the contact area between the anode and electrolyte, which will help to promote the Na$^+$ transport kinetics. When graphene and heteroatom-doped carbon matrix are compounded with conversion materials, the larger specific surface area possesses more active sites, which can improve the reversible capacity of the anode materials. Better conductivity can improve the overall conductivity of the electrode and be conducive to the enhancement of rate capability. Therefore, improving the electrochemical properties of anode materials can attribute to composite containing conversion materials and carbon-based materials. Conversion materials can also show large theoretical capacity due to multi-electron transfer during the charge and discharge processing. However, similar to alloy materials, volume expansion will also occur in sodium storage, resulting in low coulomb efficiency in the first week. Conversion materials are usually improved the electrochemical properties by using designed nano-structural, carbon-based composite and doping elements [25].
4.5. Organic Materials

The large-scale use of inorganic materials will increase the application cost of SIBs and bring environmental pollution and other problems. In contrast, organic molecular materials can be obtained directly from renewable biomass resources, with simple preparation methods, low cost, easy recycling, and no environmental pollution. In addition, organic materials can also use different synthetic methods to adjust the molecular structure so that it has the advantages of charge-discharge stability, structural diversity and multi-electron reaction. Therefore, organic materials as an anode electrode of batteries have attracted increased attention. Compared with the inorganic anode, the organic anode has a wide range of sources because of no environmental pollution and has the advantages of recycling and regeneration. In addition, organic materials also have the flexible advantages of adjustable molecular structure. By adjusting the synthesis method, the addition and elimination of functional groups can be realized, and the reversible redox reaction of multiple electrons can be realized. These advantages are conducive to the production of high electrochemical performance. Therefore, organic materials deserve special attention in developing sustainable, flexible, low-cost green batteries [26].

5. Conclusion

Cathode materials of SIBs are a crucial part of promoting the performance of SIBs. Layered oxides have high capacity and charge-discharge voltage, but because there are many phase transitions in the charge-discharge process, long-term cycling will lead to the collapse of the structure. Polyanionic compounds have stable electrochemical properties and high thermal safety due to their stable framework structure, but the capacity of polyanionic compounds is generally not high due to large anion groups. Prussian blue materials have a large tunnel structure, and the structure is relatively stable during the circulation process, but the vibrating density of the materials is low, the crystalline water is difficult to remove, and there are hidden dangers to heating safety. There is no lattice restriction in the structure of amorphous materials. The structural stress of ions intercalation in cathode materials is relatively small. As a result, the cathode material has stable electrochemical properties. It is a new direction for developing the future structure and system of sodium storage cathode materials. However, few amorphous sodium-rich cathode systems are currently available, so it is necessary to put forward new ideas in synthesis and structural design. Numerous studies on the cathode materials of SIBs show good electrochemical performance (capacity, cycle performance, etc.). However, few cathode material systems can still be used in actual large-scale integrated circuits, considering resource utilization, environmental friendliness, efficiency and other factors.

Anode materials also have a significant influence on the electrochemical performance of SIBs. Carbon-based materials have the advantages of wide sources and low prices. However, graphite has the problem of a small intercalation gap, making it difficult to provide a large sodium storage capacity. Titanium-based materials with layered structures usually embed sodium ions in the way of intercalation, which has excellent cycle stability. On the other hand, electrode materials with layered structures can also improve conductivity and energy density. However, the limited sodium storage location leads to its low specific capacity and low conductivity. The anode material can improve rate capability through nanostructure design and element doping.

Carbon-based materials have high conductivity, and their composites are expected to be the best solution to improve titanium-based materials' electrochemical properties. Alloy materials can show large sodium storage capacity, but alloy anode electrode materials will have huge volume expansion during the intercalation, reducing the service life. Structural collapse is alleviated by designing nanostructure array electrodes, and the large void space of the material is also conducive to the rapid transmission of ions and electrons. Compared with alloy materials, conversion materials also have a large theoretical capacity, and the problem of electrode structure damage will also occur in the cycle. The electrochemical performance of conversion materials can be improved by adopting structural nano design, carbon-based composite, and element doping. Organic anode materials have attracted increasing attention with the advantages of wide sources, no pollution and recyclability. Under the
circumstance of rapid development in energy-storage devices and limited lithium resources, SIBs will be further studied and applied.

References