Research Progress on Cathode Materials for sodium-ion batteries

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Abstract. In recent years, the new energy industry has developed rapidly, and sodium-ion batteries (Hereinafter referred to SIB) is becoming the new favorite in the industry due to their lower cost and higher safety. This article mainly discusses the advantages and disadvantages of SIB and the research progress of cathode materials that have the greatest impact on the performance of SIB. SIB with polyanionic compound cathodes have the advantages of good stability, cycle performance and safety, but its specific capacity is low and its conductivity is poor. Layered oxide materials have the advantage of high specific capacity and high compatibility with lithium battery ternary cathode process equipment. It is also the fastest technical route for industrialization at present. However, due to the deintercalation process of sodium ions, the layered metal oxide is prone to structural changes or phase transformations, resulting in the degradation of battery cycle performance. Prussian blue cathode materials are easy to synthesize, Na+ migrates quickly, and the battery capacity is large, but its battery capacity is prone to rapid decline. In general, sodium-ion batteries have good development prospects, but there are still some problems waiting for researchers to solve. This article summarizes the current research progress and problems that need to be solved on cathode materials for sodium-ion batteries, hoping to provide new ideas for researchers.

Keywords: Sodium ion battery, cathode material, transition metal oxide, prussian blue, polyanionic material.

1. Introduction

In recent years, the new energy industry has developed rapidly, and the demand for lithium batteries in the energy storage industry has increased significantly. However, while demand is rapidly expanding, the price of lithium carbonate has soared. The price of lithium carbonate fluctuates significantly from 200,000 yuan/ton to 600,000 yuan/ton. It brings great instability risks to the cost of lithium batteries. Since 2023, the price fluctuation of upstream lithium carbonate has continued to have an impact on the lithium battery industry. Sodium-ion batteries have attracted more and more attention, and many companies have deployed the sodium battery industry. Under the guidance of demand and industry development, sodium battery products have developed rapidly [1].

Compared with lithium batteries, SIB have more cost advantages. Sodium sources are widely available and easy to extract. At the same time, SIB have the advantages of fast charging and relatively high safety performance, which is expected to make up for the shortcomings of lithium-ion batteries in related aspects. Sodium-ion batteries have great potential as energy storage batteries. Cathode material is one of the key components of SIB, which greatly affects the energy density and power density of the battery. The development of cathode materials determines the application of sodium-ion batteries.

This article summarizes the advantages and disadvantages of SIB and points out the problems encountered in current sodium-ion battery research by reviewing the research progress of sodium-ion battery cathode materials. Hope to provide new ideas for researchers.

2. Composition and Working Principle of SIB

2.1. Composition of SIB

There are two main types of sodium-ion batteries: pouch cells and coin cells. Soft-pack batteries are characterized by high loading capacity of positive and negative pole materials and the packaging material is aluminum-plastic film, which is common in products of companies and enterprises.

The commonly used button batteries in laboratories are composed of positive poles (aluminum foil current collector + positive electrode slurry), negative poles (copper foil current collector + negative electrode slurry), positive electrode shell, negative electrode shell, separator, electrolyte, steel sheet, and spring sheet. Aluminum foil is selected as the current collector for the positive electrode to prevent oxidation of the current collector during use. Copper foil is selected as the negative electrode material because it is relatively stable and does not participate in oxidation-reduction reactions. The positive and negative electrode shells act as seals to prevent reactions with the external environment. The function of the separator is to avoid direct contact between the positive and negative poles, so that the inside of the battery only relies on ion movement to conduct electricity. The electrolyte is mainly composed of sodium salt and organic solvent, which is used to assist the transfer of sodium ions. The main function of the steel sheet is to compact the sandwich structure and shorten the swimming distance of ions between the positive and negative poles. The main function of the spring leaf is to disperse the stress at different positions of the battery so that the internal structure of the battery is evenly stressed [2, 3].

2.2. Composition of SIB

The working principle of SIB is similar to that of lithium-ion batteries. Charge transfer is achieved through the extraction and insertion of metal ions, as shown in Fig. 1 [4]. During discharge, sodium ions escape from the negative electrode material and enter the electrolyte. Electrons in a circuit flow from the negative terminal to the positive terminal, releasing energy. During charging, sodium ions escape from the positive pole material and enter the negative pole material through the electrolyte. External circuit electrons flow from the positive material to the negative material. Ideally, the detachment and insertion of ions during charging and discharging should not cause changes in the material structure and should not cause side reactions with the electrolyte. However, in the current technology, due to the large radius of sodium ions, the detachment and insertion will inevitably cause structural changes in the material, resulting in reduced battery cycle performance and poor stability. Therefore, materials improvement and modification research are needed to significantly improve the electrochemical performance of batteries.

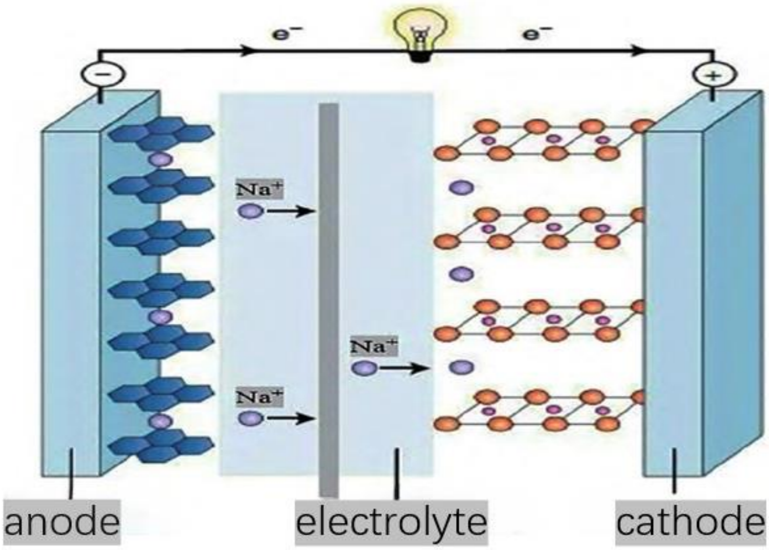

Figure 1. Composition of sodium-ion battery. https://wap.cnki.net/qikan-SDQE202312042.html

3. Advantages and Disadvantages of SIB

3.1. Advantages of Sodium-ion Batteries

First, the cost of SIB is low. Because lithium and aluminum are easy to react to produce lithium aluminum alloy, when it comes to the selection of anode and cathode materials, relatively aluminum foil can be used as the low-priced positive electrode material of lithium batteries, but the negative electrode material but only copper foil, which is more expensive, can be used, while aluminum foil can be used to make both the anode and cathode of SIB, and the relative cost is lower.

The second is that sodium-ion batteries have fast charging speed and high safety. They can adapt to high and low temperatures between -30 and 80 degrees Celsius without much energy attenuation, and they have also demonstrated good performance through a variety of Shock and stress tests. It has good stability, so from a safety perspective, it is better than lithium-ion batteries.

3.2. Disadvantages of SIB

Why can't sodium-ion batteries, which are low-cost, safe, and have stable high and low temperature performance, fail to replace lithium-ion batteries?

On July 29, 2021, CATL released its first-generation sodium-ion battery, which is a precursor to commercialization. According to CATL, sodium-ion batteries are planned to mass-produced in 2023.

However, the release of the first generation of sodium-ion batteries in the CATL era is not the beginning of replacing lithium-ion batteries. According to industry experts, the development of SIB technology at this stage is more of a supplement to lithium-ion batteries than a replacement for lithium-ion batteries. The fundamental reason for substitution is that sodium-ion batteries also have very significant shortcomings.

To describe it simply: the volume of sodium ions is much bigger than that of lithium ions, so it travels slower and is less likely to pass through cell separator. Besides, electrons carried by this sodium ion is actually less than that of lithium. This results in a very concrete disadvantage, low energy density.

The first generation of sodium-ion batteries’ energy density has reached 160 Wh/kg, meanwhile，the energy density of lithium-ion batteries has now easily been over 200 Wh/kg.

In addition, compared with the cycle life, the current life of lithium iron phosphate batteries has reached 6,000 times, while the life of sodium-ion batteries can only reach 2,000 times. Therefore, the life of sodium-ion batteries is still unable to meet the current energy storage needs

4. Types of Cathode Materials and Applications in Sodium-ion Batteries

Whether it is a lithium battery or a sodium battery, electrode materials are the core components that affect and restrict battery performance. Therefore, the development of high-performance, low-cost electrode materials is an important part of promoting the development of the battery industry. Fig. 2 is a graph showing the relationship between specific capacity and voltage of various kinds of sodium-ion battery electrode materials [5]. It can be seen from the figure that the specific capacity of the positive pole material is lower than that of the negative pole material, which has become a bottleneck limiting the large-scale application of high-energy-density sodium-ion batteries. , therefore, the development of high-capacity, high-voltage, and highly reversible sodium storage cathode materials has become key. At present, sodium-ion battery cathode materials are classified into three categories: polyanionic, transition metal oxide and Prussian blue. The three types of materials have different characteristics and strengths due to their different structures [6].

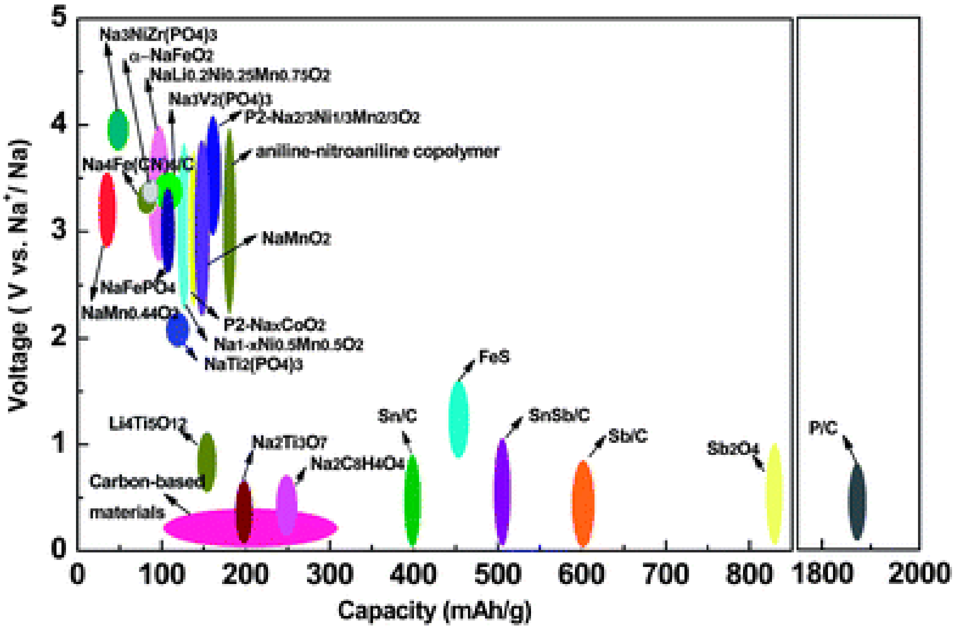

Figure 2. Relationship between electrode material and specific capacity. Room-temperature stationary sodium-ion batteries for large-scale electric energy storage - Energy & Environmental Science (RSC Publishing)

4.1. Polyanionic Compounds

The general formula of polyanionic compounds is $Na_XA_Y[(EO_m)_n^-]_z$, where A is the metal ion in variable valence and E is the element P, S and V. It has the advantages of good stability, cycle performance and safety, but has the problems of low specific capacity and poor electrical conductivity. According to different structures, they can be classified into olivine structure phosphates and NASCICON (Na^+ fast ion conductor) compounds. The preparation method of olivine-structured $NaFePO_4$ as a cathode material for SIB is similar to that of lithium iron phosphate. It has a theoretical capacity of 154m Ah/g and an operating voltage of 2.9V. However, its conductivity is low and there is only one-dimensional Na^+ diffusion channel., affecting the actual performance, currently the conductivity is improved through carbon coating or ion substitution. The NASCICON structural compound is a fast ion conductor with a theoretical specific capacity of about 120m Ah/g, an operating voltage of about 3.3V, a 3D framework structure, a high ion diffusion rate, and good kinetic and cycle stability. However, when pentavalent V is introduced, it is often toxic and harmful to the human body, which will restrict large-scale use to a certain extent. It is of certain research significance to develop and use non-toxic and abundant elements (such as Fe, Mn and Ni) to replace V to prepare NASICON structural compounds. At the same time, polyanionic compounds have larger molar masses and lower theoretical specific capacities, but they can mix different anionic groups or introduce fluoride ions with large electronegativity values to increase the working voltage of the material and thereby increase the energy density [7].

4.2. Transition Metal Oxides

The general formula of transition metal oxide is Na_XMO_2. Among them, M refers to the transition metal element, which can be used vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), drill (Co), nickel (Ni), copper (Cu), etc, with abundant resources of manganese (Mn) and iron (Fe) being the most common. Transition metal oxides can be classified into layered and tunnel structures. When the sodium content is low (x<0.5), the structure of tunnel is the main one. When the sodium content is high, the layered structure is the main structure, with Na^+ located between the layers, forming a layered structure in which MO_2 layers/sodium layers are alternately arranged [8, 9].

Layered oxide cathode materials have obvious advantages and disadvantages. In terms of advantages, it has the advantage of high specific capacity and high compatibility with lithium battery ternary cathode process equipment. It is also the fastest technical route for industrialization at present, so many lithium battery cathode companies have chosen this route. For example, Zhenhua New Materials stated in an investor Q&A in September 2022 that the company chose the layered oxide route and has now achieved ton-level output and sales. However, due to the deintercalation process of sodium ions, the layered metal oxide is prone to structural changes or phase transformations, resulting in the degradation of battery cycle performance. To solve this problem, researchers doped electrochemically active elements such as Mn, Fe, and Ni, relying on the complementary characteristics of different cationic redox pairs to improve the stability of the material. On the other hand, this material is unstable in humid environments: Another major challenge with layered cathode materials is their hygroscopic properties after exposure to air, which causes the material surface to deliquesce and degrade battery performance. This problem directly results in the material being difficult to store and increasing transportation costs. Therefore, many lithium battery cathode companies have chosen this route.

4.3. Prussian Blue Compound

The general formula of Prussian blue analogues is Na_xMP, $[MQ(CN)_6]$, $2H_2O$, MP and MQ represent transition metal elements, mainly iron (Fe), cobalt (Co), nickel (Ni), Manganese (Mn), etc. Because Prussian blue compounds have a unique open framework and three-dimensional large pore structure, they are suitable for the migration and storage of sodium ions [10]. In terms of advantages, iron-based Prussian blue and manganese-based Prussian blue have the advantages of abundant raw materials, low cost, high specific capacity, high-rate performance, and excellent electrochemical stability. In terms of shortcomings, since most current production methods use co-precipitation methods, many crystals water and $Fe\ (CN)_6$ structural defects are often produced. Crystal water easily occupies the sodium storage sites and sodium ion deintercalation channels in the crystal, resulting in the sodium ion content is reduced and the sodium ion migration rate is reduced. $Fe\ (CN)_6$ structural defects and crystal water will cause structural collapse when the material is being charged and discharged, affecting the cycle performance of the material.

Prussian blue cathode material has many advantages. (i) Easy to synthesize; (ii) It has an open framework structure and can quickly migrate Na^+ ions; (iii) The structure is stable; (iv) It has a high theoretical capacity of 170 mAh/g.

The main shortcomings of Prussian blue cathode materials are that coordinated water usually occupies Na^+ storage sites in the Prussian blue framework, resulting in reduced Na^+ storage capacity and slow Na^+ migration ability. In addition, a large number of randomly distributed $[Fe\ (CN)_6]$ defects make the Prussian blue framework structure prone to collapse, leading to rapid battery capacity decline. Finding production methods to avoid or reduce the generation of crystal water has become a top priority in research on Prussian blue cathode materials.

5. Conclusion

Lithium-ion batteries are widely used as power sources due to their high energy density and long cycle life. However, due to the scarcity of lithium resources, the use of lithium-ion battery in energy storage will be limited in the future. The structure and principle of SIB are basically the same as that of lithium-ion batteries. The energy density of SIB is close to that of lithium-ion batteries. Since sodium resources are extremely abundant compared to lithium resources, sodium-ion batteries can become an alternative battery for large-scale applications of lithium-ion batteries. Now, the transition metal oxide system and Prussian blue derivatives as cathode materials have high technological maturity. The energy density of both is above 150 Wh/kg. Batteries with transition metal oxides as cathode materials show considerable discharge specific capacity and Excellent cycle performance.

Prussian blue and analogues (PBAs) are open framework structures formed by metal-cyanide coordination bonds and have enough space to accommodate sodium ions. Therefore, they show good electrochemical performance and are considered to be a promising Sodium-ion battery. However, its industrial application faces some key problems such as irreversible structural phase change and crystal defects, but it is still a very promising cathode material for sodium-ion batteries. Polyanionic compounds are rich in types and forms. This type of material generally has a high operating voltage when used as a cathode material for sodium-ion batteries. At present, if polyanionic materials can solve the problem of poor conductivity through simple and effective process methods and enable them to exert excellent characteristics in terms of stability and rate performance, they are expected to gain faster application and promotion prospects than transition metal oxide materials. Overall, sodium-ion batteries are low-cost and highly safe. However, due to technical problems, it has not yet been applied on a large scale. This article summarizes the research progress of cathode materials that mainly affect the property of sodium-ion batteries, and looks forward to the development prospects of three different technical routes, hoping to provide new ideas for researchers.

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