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ISSN 2959-6157

Types and research progress of cathode materials for sodium ion batteries

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Abstract:

With the increasingly severe global energy problem, green and new energy enterprises are vigorously developing. Lithium-ion batteries in the field of energy storage have to look for other materials due to their resource shortage and market risk of price fluctuations. Therefore, sodium-ion batteries bring a new perspective to mankind to solve the global sustainable development problem, and hope to achieve unprecedented progress in the field of electrochemical energy storage in the future. In this paper, the working mechanism of sodium-ion batteries was studied and the concept of rocking chair batteries was introduced. Also, the cathode materials of sodium-ion batteries are systematically studied through different literatures, and three different materials are studied: polyanionic compounds, Prussian blue compounds and transition metal oxides. Specifically, the olivine structure and NASICON structure of poly-anion compounds, as well as the layered and tunnel types of transition metal oxides, are discussed. And provide the advantages and disadvantages of different cathode materials, as well as their development trends and prospects. This paper shows the structural stability, energy density and electron transport rate of mainstream materials, which is helpful to accelerate the commercialization of sodium-ion battery industry.

Keywords: Energy and environment; sodium-ion batteries; cathode materials; electrical energy storage.

1. Introduction

With the development of human society, the demand for energy is increasing. At present, the main source of energy in the world is still fossil energy, but energy problems such as high consumption of fossil energy, insufficient reserves and long regeneration cycles are gradually emerging [1]. In addition, the use of fossil energy had a significant effect on the environment because of the exhaust and greenhouse gas. In that case, there is an increasingly desire for new energy storage technologies and renewable clean technologies. People start to use sustainable energy sources such as wind, tidal energy, hydro energy

ISSN 2959-6157

and solar energy. On the contrary, these energies have common shortcomings: climate restrictions, geological limits and the cost problems. Additionally, they could just alleviate the detrimental effects that are caused by fossil energy [2]. So, it is crucial for people to look for the energy storage technology which is efficient, environmentally friendly and economical. With the rapid development and application of new energy technology all over the world and the adjustment of energy structure, people progressively start focusing on electric energy storage system and seeing it as a key step in the development of sustainable energy technologies. Among them, lithium-ion batteries are a relatively successful and mature energy storage technology [3]. They are used in the various walks of life, such as electric vehicles, as well as portable electronics. But the problems of this technology are also obvious: That is, lithium resources are scarce and unevenly distributed, so the mining cost is large but the recoverable reserves are low. However, there is a situation where the demand for lithium resources is expanding, and the price of raw materials for lithium-ion batteries (such as cobalt and lithium) has risen. These are the influencing factors that limit the inability of lithium-ion batteries to be applied to large-scale energy storage [4].

Therefore, in order to find battery energy storage technology that can replace lithium as a raw material, people are gradually paying attention to the element in the same group as lithium—sodium. Compared with lithium, sodium is abundant on the earth, ranking fourth. Also, it is widely distributed. So that it is all but impossible to care about the resource shortage. In terms of their potential respect, lithium and sodium have basically same chemical properties. To be specific, they have approximated the same ion radius and ion conductivity. So, sodium-ion batteries also show people the advantages of high ionic conductivity and superior high and low temperature performance. If sodium-ion batteries can be used on a large scale and solve the impasse caused by the current energy crisis, human will have a clear vision for sustainable development in the future.

Nonetheless, sodium-ion batteries, which sound so perfect, are only in the early stages of development [5]. Compared with the application of lithium-ion batteries, sodium-ion batteries are still immature. Since the radius of a sodium ion is greater than a lithium ion's, the internal migration rate of sodium-ion battery materials is low. Also, the structural stability of the electrode material decreases. More importantly, the main problem with batteries is manifested in the battery electrodes. Now we begin the introduction of sodium-ion battery electrodes: The electrode material of the battery is an indispensable decisive factor in determining whether the battery has high efficiency. In sodium-ion batteries, cathode materials are important components that determine the energy storage efficiency, safety and stability of the battery. The principles for efficient cathode material selection are: a suitable structure for electron detachment and a high ionic conductivity. In general, polyanion compounds, transition metal oxides, and Prussian blue compounds are the preferred cathode materials for sodium-ion batteries.

However, here are the problems: These cathode materials have roughly the same shortcomings, namely low structural stability, low ionic conductivity and low energy density. All in all, in order to improve the shortcomings of cathode materials, researchers have begun to explore cathode materials, including improving the structural design, stabilizing the electrode electrolyte and other measures.

2. The working mechanism of sodium-ion batteries

A sodium-ion battery (SIB), is a type of rechargeable battery that stores energy by moving sodium ions between the positive and negative sides, using chemical reactions to charge and discharge.

What allow people to focus on SIB are resource scarcity and urgent industrial needs. In terms of resource scarcity, lithium mainly distributes in Australia and Lithium Triangle (Bolivia, Chile, Argentina), it is evident that there is an issue of uneven distribution. People have to import lithium in order to apply it into their technology. On the contrary, sodium is widely distributed all over the world, like crust, ocean and Salt Lake. Hence, people won't worry about the amount of sodium and we can absolutely regard it as a key to alleviating the problem of human over-reliance on lithium resource. In addition, for industrial needs, people nowadays are paying more and more attention to the use of large-scale energy storage, such as grid peak shaving and the integration of renewable energy. Therefore, low-cost and efficient safe batteries are the focus of people's attention. Lithium and Sodium are in the same group, so they have similar features. However, they have different ionic properties which embody in their cathode and anion materials. Therefore, while maintaining the same operating efficiency as lithium-ion batteries, if people use the original lithium-ion battery production technology and only replace the positive and negative electrode materials, both production costs and difficulty can be significantly reduced. Since 2010, the price of lithium has risen, people have regained the research on sodium, and the role of sodium has gradually changed from an experimental need to an industrial need.

The core operation mechanism of sodium-ion batteries is the reversible migration of sodium ions between the positive and negative electrodes, and at the same time, with the movement of electrons in the external circuit, the storage and release of electrical energy and the conversion between electrical energy and chemical energy are realized. For the charging process that converts electrical energy into chemical energy, sodium ions are detached from the lattice of the cathode material and pass through the interface through the electrolyte, while the cathode loses electrons, which is equivalent to an oxidation reaction. Then, after the sodium ions are embedded in the lattice of anode material, electrons from the external circuit flow into the anode at the same time, which is equivalent to a reduction reaction. For the discharging process, sodium ions will flow in an opposite direction compared with the charging process, which chemical energy will convert into electrical energy [6]. Therefore, SIB can also be defined as rocking chair batteries.

3. The classification, advantages and disadvantages of cathode materials for sodium-ion batteries

There are still many challenges in the commercial application of sodium-ion batteries. Therefore, cathode materials play a non-negligible role in determining the safety and energy density of the battery. The principles of selecting excellent cathode materials are high capacity, suitable and stable structure and high ionic conductivity [7]. Nowadays, the mainstream cathode materials mainly include polyanionic compounds, Prussian blue compounds and transition metal compounds.

3.1 Polyanionic compounds

Polyanionic compound is multinuclear anion cluster formed by covalent bonds between transition metals and oxygen atoms. Its core feature is the construction of a highly symmetrical polyhedral structure through metal-oxygen bonds, forming anionic units with well-defined composition and crystal structure.

Its chemical formula is NaxMy(XaOb)zZw, where M represents transition metal atoms, X is phosphorus, tungsten, etc., and Z is F and OH, etc. The anionic group represented by (XaOb) can accelerate the conduction of sodium ions in the structural framework and stabilize the redox pairs of transition metals. Sodium ions are stored in a three-dimensional framework structure formed by M and X, which achieves high structural stability of polyanionic compounds. At present, the mainstream synthesis methods of such compounds mainly include solvothermal method and solution method. Among them, the solution method is prepared by acid-base neutralization and metathesis reaction at room temperature or low temperature, which is easy to operate and suitable for large-scale synthesis [8].

3.1.1 The olivine structure of polyanionic compounds

In sodium-ion batteries, olivine structure is an important class of cathode material structures. Its crystal composition is similar to that of natural olivine minerals, and it has a stable framework structure and tunable electrochemical properties.

The olivine structure is an orthorhombic crystal system, and its basic structure is formed by the octangular connection of MO6 octahedron (M is transition metal) and PO4 tetrahedron. Therefore, the insertion and detachment of sodium ions in the one-dimensional channel during the charging and discharging process will not damage the framework structure of the material. When charging, sodium ions are detached from the crystal lattice, and ferrous ions are oxidized to iron ions to ensure the stability of cycling. At present, the main method for synthesizing olivine structure is the high-temperature solid-phase method, which is simple but the product particles are coarse and the ion diffusion path is long. Therefore, in order to optimize its performance, people usually use the method of carbon coating, that is, the carbon layer with a thickness of about 2-5nm is wrapped on the raw material to form a continuous conductive channel. Under the carbon coating system, the battery capacity retention rate can still exceed 90% after 1000 cycles at 1C rate. For example, L.P.Zhao et al. prepared an ultra-thin carbon layer coated nanoscale sodium iron phosphate m-NFP@C, which still has a reversible specific capacity of 101.4 mAh/g after 100 cycles at 1.5~4.5 V at 20 mA/g [9].

3.1.2 The NASICON structure of polyanionic compounds

In sodium-ion batteries, the NASICON structure is a class of polyanionic materials with three-dimensional ion transfer channels, which has attracted much attention for high ionic conductivity, chemical stability and structural tunability. NASICON belongs to the orthorhombic crystal system, and its core framework is composed of MO6 octahedron and PO4 tetrahedra connected by sharing oxygen atoms to form a three-dimentional penetrating sodium ion transport channel. Sodium ions migrate through twisted triangular prism sites in three-dimensional channels, giving them excellent ionic conductivity. Compared to the one-dimensional channel of the olivine structure, the three-dimensional channel of NASICON allows the free migration of sodium ions in multiple directions, resulting in better rate performance. At present, there are solution methods for preparing cathode materials with this struc-

ISSN 2959-6157

ture, such as Na3V2(PO4)3, which has a charge-discharge platform of about 3.4V and a theoretical capacity of 117mAh/g. The capacity retention rate of porous Na3V2(-PO4)/C materials prepared by the novel solution-based method is still 50% after 30,000 cycles [10].

Polyanionic compounds have the following advantages when used as cathode materials: long cycle life, high stability, high working voltage and wide application range. Its disadvantages are: poor conductivity, high synthesis process requirements, limited energy density, etc. From the perspective of disadvantages, the insufficient electronic conductivity limits the performance of sodium-ion batteries under high-rate charge-discharge conditions, and the low sodium-ion diffusivity will also affect its rate performance and cycle stability. Therefore, there is still a long way to go in the development of such cathode materials [11].

3.2 Prussian blue compounds

In sodium-ion batteries, Prussian blue compounds have become potential cathode materials due to their unique open frame structure, high theoretical capacity up to 170-190mAh/g and low cost.

The chemical formula of the Prussian blue compound can be expressed as AxM1[M2(CN)6]yV(1-y)·nH2O, where A represents alkali metal ions, M1 and M2 represent transition metals, and V represents cyanide vacancy defects, which are used to coordinate the vacancies occupied by water. The ideal structure is a cubic crystal system, and ferrous and iron ions are bridged by CN-to form a three-dimensional structure, so that sodium ions can move quickly in the tunnel. In addition, in the natural Prussian blue, ferrous ion vacancies and hydrated ions are often present, so the compound has obtained a storage site that can be used as sodium ions [12]. The above conditions make it have good electrochemical performance and structural stability. At present, the mainstream synthesis method of Prussian blue compounds is the precipitation method, in which the solution containing ferrocyanide and the solution containing ferric ions are mixed in a certain proportion, usually in an aqueous solution. This method does not require complex equipment and harsh conditions, and is low cost and has a high product purity.

When used as cathode materials for sodium-ion batteries, Prussian blue compounds have been awarded attention because of their high theoretical ratio capacity, good rate performance and stable structure. However, its shortcomings are still the key difficulties that people need to overcome in the development of cathode materials in the future. Some crystalline water may be introduced during the preparation process, resulting in hindered ion transmission and reduced performance stability. In addition, some Prussian blue compounds may have certain volume changes in the process of sodium ion embedding and de-embedding, and the battery cycle life may be affected in the long run.

3.3 Transition metal oxides

Transition metal oxides are compounds formed by the combination of transition metal elements and oxygen elements through chemical bonding, in which transition metal electrons bring polyvalent redox activity to them, which is the basis of transition metal oxides as battery electrode materials, and the electron orbitals on the surface are easy to absorb reactants and promote chemical bond breakage and formation.

3.3.1 Layered transition metal oxides

The chemical formula of layered transition metal oxides is NaMO2, where M stands for transition metal elements like Mn, Fe. In terms of crystal structure, the transition metal and oxygen atoms form an octahedral coordinated rigid layer, and there is also a sodium layer between the MO2 layer, and the sodium ions can be reversibly deintercalated during charging and discharging. Based on the stacking method of oxygen atoms and sodium sites, there are roughly three core phase classifications: O3 phase, P2 phase, P3 phase, and O2 pjase. In the letters, O stands for sodium octahedron and P stands for sodium triangular prism. The number represents the minimum number of stacking layers required for the oxygen layer to repeat the cycle [13].

O3 and P2 materials play a major role today, with the O3 phase having a high sodium content and significant energy density, but also having the obvious disadvantage of poor stability and not guaranteeing the sustainability of energy density. The P2 phase, on the other hand, has better cycling stability, but has a lower capacity. At present, the commercial preparation technologies mainly include solid-phase method and liquid-phase method, and the layered oxides usually prepared have high quality, but the preparation process is complex and has high cost, which is still a difficulty that people need to overcome [14].

3.3.2 Tunneled transition metal compounds

Tunneled transition metal compounds are a key system with stable structure and long cycle life among the cathode materials for sodium-ion batteries. Because of its unique three-dimensional tunnel skeleton, it provides a rigid migration channel for sodium ions, which is suitable for energy storage scenarios with strict requirements for cycle stability. Its representative material, $Na_{0.44}MnO_2$, has a theoretical specific capacity of about 140mAh/g, and it can have a long life with such a high energy density.

However, there are still some challenges to overcome with tunneling materials compared to layered transition metal oxides. The sodium ion sites in the melancholy tunnel are limited, the specific capacity is usually low, and the rate performance of the tunnel-type material is relatively poor due to the problem that the one-dimensional diffusion channel is easy to block.

When used as cathode materials, transition metal oxides have become the mainstream technology route due to their high capacity, adjustable voltage and resource abundance, but at the same time, there are also shortcomings that cannot be ignored, such as the poor structural stability of layered materials and the energy density limitation and rate shortcomings of tunneling materials. Future breakthroughs will rely on multi-scale structural design to promote sodium-ion batteries as a key player in the field of energy storage.

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4. Outlook

The cathode material of the battery fundamentally determines the performance of the battery. Even though there are a variety of materials that can be used as cathode raw materials for batteries, it is still difficult to prepare batteries with stable structure, high safety, high energy density and cycle life. For example, in the manufacturing process of materials, there are different methods used to prepare them, most of which require water and are in the form of crystals. If the content of crystal water cannot be controlled, the internal structure of the battery will be damaged, and its structural stability will be affected. In addition, there will be problems of electrolyte interface compatibility and low-temperature failure, specifically, the unstable solvation structure of fluorinated fluids at low temperatures, which may lead to a sudden drop in capacity.

In order to promote the next development of cathode materials for sodium-ion batteries, mankind can first take basic research as the starting point, take the structure and performance relationship of materials as the research focus, and explore the root causes of capacity attenuation and structural change from microscopic research. Second, human beings can increase the scope of R&D, which is embodied in increasing R&D funds and manpower, and combining the research results of all parties to accelerate the success of scientific research.

5. Conclusion

In this paper, the systematic study of cathode materials for sodium-ion batteries shows that sodium-ion batteries have gradually become an emerging industry in the field of energy storage due to their abundant resources, low cost, and high safety. Not only do sodium-ion batteries have a similar operating principle to lithium-ion batteries, but they also ensure efficient energy. However, a series of problems are still found in the cathode material. For example, the low energy density of polyanionic compounds, the stability of Prussian blue compounds, and the adaptation temperature of transition metal oxides.Therefore, in response to the following problems, human beings should focus on the relationship between battery structure and performance, and ensure the high efficiency of energy density while ensuring the stability of the structure. In addition, it focuses on the development of enterprises, considers the optimization of battery technology from multiple scales, and takes human resources to increase R&D costs as a way to promote the commercialization process of sodium-ion batteries.

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