

Research Progress on Modification of Cathode Materials for Polyanionic Sodium-Ion Batteries

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Abstract. As one of the main anode materials for sodium-ion batteries, polyanionic anode materials for sodium-ion batteries have the advantages of long cycle life, high safety, low price and suitable for large-scale energy storage, but there are also problems such as low energy density and low conductivity. In order to optimize the energy density, conductivity, service life and other properties of polyanionic sodium ion cathode materials, doping, surface coating and structural design are needed to modify them. Reasonable modification methods have been proved to significantly improve the properties of materials. In this paper, phosphate, sulfate and other types of polyanionic sodium-ion batteries are first introduced, then the latest research results of element doping, surface coating and structural design are reviewed, and the existing research results are evaluated. Finally, the modification methods of the positive electrode materials of polyanionic sodium-ion batteries are prospected, which provides important research ideas for the commercial application of sodium-ion batteries in the future.

Keywords: Polyanion, Sodium-Ion Batteries, Adulterate, Surface Cladding, Structural Design.

1. Introduction

In the new era of rapid development, high-quality energy support is needed, but the large consumption of fossil energy has caused serious carbon emissions. In order to actively achieve the ambitious goal of "carbon peak and carbon neutrality", we should use clean energy,[1] such as wind and solar energy, which are affected by climate conditions and cannot be controlled according to demand. Therefore, energy storage technology is needed to integrate intermittent energy into real-time stable energy.[2,3]

With the continuous development of lithium batteries, lithium resources account for only 0.002% of the earth's content,[4] it cannot support large-scale, sustainable energy storage needs. The sodium resource, which accounts for 2.75% of the earth's content,[5] is more than 1,000 times that of lithium resources and has the advantages of low price and sufficient resources. It can support large-scale, sustainable energy storage needs, so sodium-ion batteries are gradually replacing lithium-ion batteries.

The cathode is an important development direction for sodium-ion batteries. It is divided into layered transition metal oxides, polyanionic compounds, Prussian blue, etc,[6] and polyanionic cathode materials are favored by researchers due to their higher cycle stability,[7] better safety, simpler preparation process, and lower price.

2. Classification of the Cathode of Polyanion Sodium-Ion Batteries

The molecular formula of the cathode material of polyanion sodium-ion battery is generally $NaxMy(XOn)$, where X represents non-metallic elements such as silicon (Si), phosphorus (P), sulfur (S), and M represents transition metal elements such as manganese (Mn), cobalt (Co), and iron (Fe).[7,8] It is a three-dimensional skeletal structure composed of strong covalent bonds, which has excellent thermal stability, high redox potential, and long cycle life.[9] Next, polyanionic cathode materials such as phosphate and sulfate are introduced from the perspective of crystal structure and performance characteristics.

2.1 Phosphates

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (VNP), as a representative of sodium phosphate cathode material, has a NASICON structure, based on $\text{V}^{3+}/\text{V}^{4+}$ redox reaction, and the structure is reconstructed during cycling, the theoretical specific capacity is 117.6 mAh/g, and the working voltage is 3.4 V.[10] The $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ cathode material improves the electronegativity of the group by introducing high electronegativity fluorine, and it has a stable and open three-dimensional skeleton structure, the space group is $\text{P}42/\text{mnm}$. [10] Na site shown in Figure. 1 (a) consists of Na1 and Na2 sites, with Na^+ transport channels along the $[1\ 1\ 0]$ and $[0\ 0\ 1]$ directions, the theoretical specific capacity is 128 mAh/g, the voltage range is 3.3-4.0 V, which belongs to the orthorhombic crystal system. Since the electronegativity of phosphate is lower than that of pyrophosphate, it is also possible to synthesize the cathode material $\text{Na}_4\text{M}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ of mixed phosphate polyanionic sodium-ion batteries, as shown in Figure. 1(b). The P-O-P bond of pyrophosphate forms a layered structure with PO_4 tetrahedron and MO_6 octahedron. [10,11]

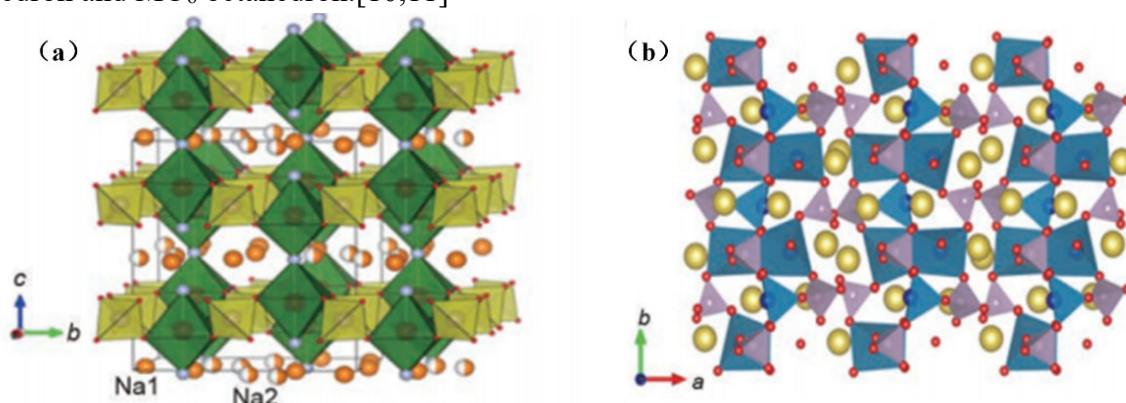


Figure. 1 (a) crystal structure of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$; (b) crystal structure of $\text{Na}_4\text{M}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ [10]

2.2 Sulfates

The properties of sodium sulfate ions are similar to those of sodium phosphate ions, $(\text{SO}_4)_2^-$ makes the voltage plateau of the material higher, Compared with phosphate, and the sodium sulfate ion cathode material has better safety compared with phosphate. [11] The structure of the $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ cathode material is significantly different from that of a typical $\text{Na}_x\text{M}_y(\text{XO}_n)$ material (Figure. 2), where the Na site is composed of Na1, Na2, and Na3 sites, and the Na^+ of the Na2 and Na3 sites moves rapidly in the three-dimensional frame structure migration path. The three-dimensional skeleton structure of Na^+ migration consists of Fe_2O_{10} dimer and FeO_6 octahedral colaterality, then it is bridged with SO_4 tetrahedron, it is a monoclinic crystal system. The structure of $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ material is relatively stable, the working voltage is as high as 3.8 V, the specific capacity reaches 121 mAh/g, [10,12] and the cost is relatively low, so it has the prospect of large-scale development.

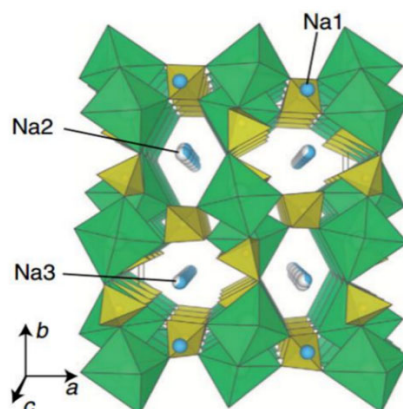


Figure. 2 crystal structure of $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ [10]

2.3 Mixed Polyanions

Different polyanionic units interact to form other polyanionic compounds. $\text{Na}_2\text{Fe}(\text{C}_2\text{O}_4)\text{SO}_4\cdot\text{H}_2\text{O}$ is other type of polyanionic material (Figure. 3), forming a two-dimensional $[\text{FeC}_2\text{O}_4]_\infty$ plate along the ab plane, and then connecting with the $(\text{SO}_4)^{2-}$ group in the c-axis direction to form a three-dimensional skeleton structure with a quadruple symmetric Na2 site and a triple symmetric Na1 site.[10,11] The induction of sulfate and oxalate made $\text{Na}_2\text{Fe}(\text{C}_2\text{O}_4)\text{SO}_4\cdot\text{H}_2\text{O}$ has two voltage platforms, and $\text{Na}_2\text{Fe}(\text{C}_2\text{O}_4)\text{SO}_4\cdot\text{H}_2\text{O}$ uses a single-phase reaction mechanism, The space group is P62m, which belongs to the hexagonal crystal system, and the specific capacity reaches 170 mAh/g, 0.5C rate charge and discharge 500 times, still 85% capacity, the coulomb efficiency is 99%.[10,11]

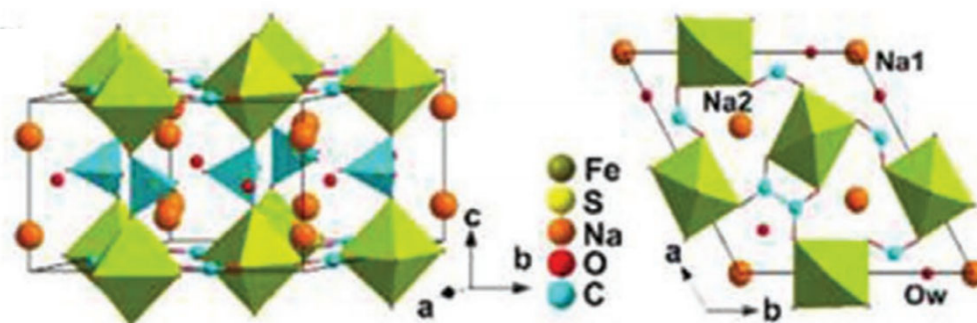


Figure. 3 crystal structure of $\text{Na}_2\text{Fe}(\text{C}_2\text{O}_4)\text{SO}_4\cdot\text{H}_2\text{O}$ [11]

Polyanionic sodium-ion battery cathode materials have excellent thermal stability, high redox potential and cycling stability,[12] and Table 1 mainly lists the research results of several typical phosphate, sulfate and other mixed polyanionic sodium-ion battery cathode materials.

Table 1 Characteristic parameters of different polyanionic sodium ion cathode materials

Material category	chemical formula	Crystal structure	Electrochemical properties
Phosphates	NaVPO_4F [13]	I4/mmm	3.9 [V], 135 [mAh/g]
	$\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ [14]	Pn2 ₁ a	3.2 [V], 129 [mAh/g]
	$\text{NaV}_2(\text{PO}_4)_3$ [15]	R/3c	3.4 [V], 116 [mAh/g]
Sulfates	$\text{Na}_6\text{Fe}_5(\text{SO}_4)_8$ [16]	C2/c	3.6 [V], 110.2 [mAh/g]
	$\text{Na}_2\text{Fe}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$ [17]	P2 ₁ /c	3.25 [V], 70 [mAh/g]
	NaFeSO_4F [18]	C2/c	3.7 [V], 105 [mAh/g]
Other single classes	$\text{Na}_2\text{Fe}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{H}_2\text{O}$ [18]	P2 ₁ /c	3.3 [V], 116 [mAh/g]
Mixed classes	$\text{Na}_2\text{Fe}(\text{C}_2\text{O}_4)(\text{HPO}_4)$ [19]	P2 ₁ /c	3.2 [V], 71 [mAh/g]
	$\text{Na}_2\text{Fe}(\text{C}_2\text{O}_4)(\text{SO}_4)\cdot\text{H}_2\text{O}$ [20]	P62m	3.2 [V], 170 [mAh/g]

3. Modification Method

Researchers have conducted many experiments on the problem of poor volumetric energy density and conductivity of polyanionic materials, and usually use modification methods such as element doping, surface coating and structural design.

3.1 Elemental Doping

Elemental doping is a method of doping ions into a structure to optimize bulk phase conductivity. Ability to optimize the material's properties such as energy density, cycle life, and conductivity, making materials more in line with development requirements.[21] To optimize the performance of $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}(\text{NVOPF})$, Zhang et al.[22] selected the Nb^{5+} doping method and prepared the $\text{Na}_3\text{V}_{1.90}\text{Nb}_{0.10}\text{O}_2(\text{PO}_4)_2\text{F}$ material with a 0.7~1.0 μm hollow spheroid structure by polyol-assisted hydrothermal method. The transport distance of ions is greatly shortened, the discharge specific

capacities at 0.1C and 10C rates can reach 126.4 mAh/g and 98.1 mAh/g respectively, at 10C high magnification, the capacity retention rate after 500 cycles is 95.2%, before doping, it can only reach 66.8% of the capacity, and it can be seen that the doping of Nb^{5+} greatly improves the service life of the material. In order to improve the conductivity, specific capacitance and rate performance of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) materials, Zhao et al.[23] used citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and urea ($\text{CH}_4\text{N}_2\text{O}$), NVPF@C-N materials were successfully prepared by low-temperature hydrothermal reaction, the discharge specific capacities at 1C, 10C and 30C rates are 121 mAh/g, 110 mAh/g and 100 mAh/g, respectively, which improves the conductivity and specific capacitance of the material. The research also found that the NVPF@C-N material still reached 87% capacity after 1000 cycles at a high rate of 10C. The element doping method is used on a large scale for the modification of polyanionic materials, which can better improve the comprehensive properties of the materials.

3.2 Surface Coating

Surface coating is the application of one or more layers of coating on the active substance, which is a method of surface treatment of the base material, which can play the role of modifying, isolating and improving the properties of the material.[24] Generally speaking, during cycling, the cathode material and the electrolyte will undergo side reactions, resulting in irreversible loss of sodium ions and reducing the performance of the material. Surface coating modification methods can reduce this phenomenon. It is found that carbon material coatings are the majority, because carbon material coatings can optimize the conductivity of materials and further improve materials. Zhang Liming[25] prepared carbon-coated NMCP/C, NMCP/C@1% Al_2O_3 and NMCP/C@4% NFPP materials based on $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$ (NMCP), with discharge capacitances of 148.0 mAh/g, 144.4 mAh/g and 131.2 mAh/g at 0.5C rate, NMCP/C@1% Al_2O_3 and NMCP/C@4% the capacity retention rates of NFPP materials were 70.0% and 71.6% after 150 cycles at 2C rates, which were 20.2% and 21.8% higher than those of NMCP/C materials, respectively, and the energy density of NMCP/C materials is 448.3 Wh/kg at 0.1C rates. Zhang et al.[26] a 6 nm thick carbon layer was coated on NMCP by colloidal method, with a specific capacity of 129 mAh/g, the average operating potential is 3.53 V, and the energy density is higher than that of lithium iron phosphate batteries. It provides a good start for the application of polyanionic materials.

3.3 Structural Design Method

The structural design approach refers to optimizing the microstructure of a material. It is mainly designed by controlling the microstructure of the material and the position of the grain boundaries.[26] $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ (NFPP) is a representative of other polyanionic sodium-ion batteries, has an open three-dimensional NASICON structure,[27] small phase change during cycling, good safety and structural stability, but low electronic conductivity. Ahsan et al.[28] successfully prepared NFPP/C composites by solvothermal method, and synthesized NFPP/C microspheres were synthesized by template method, the discharge specific capacities of 0.2C and 100C are 128.5 mAh/g and 79 mAh/g, which greatly improved the performance. Finally, the three-dimensional porous decorative microspheres of NFPP/rGO were prepared by spray drying process, at 0.1C rate, the specific capacity was 128 mAh/g, at 10C rate, it can still reach 62.3% of the capacity after 6000 cycles. Gu et al.[29] successfully prepared smaller NVPOF nanoparticles based on $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$, which effectively shortened the diffusion distance of Na^+ , the specific capacity at 0.1C rate can reach 123.2 mAh/g, and it can still reach 96.2% of the capacity after 200 cycles at 1C rate, and the structure is extremely stable. The results show that the smaller and more uniform the particle size, the more stable the material structure, the shorter the sodium ion transport path, and the better the electrochemical performance.

4. Summary and Outlook

Polyanion sodium-ion battery technology is a new type of clean energy technology, which has good cycle life and stability, but the problem of low specific capacity limits its development. With

the continuous research of scientific researchers, surface coating, elemental doping and structural design have been shown to significantly optimize the cathode material for polyanionic sodium-ion batteries. Elemental doping optimizes the energy density and conductivity of materials, The carbon coating increases the conductivity of the material. In the future, we can combine the characteristics of several modification methods, retain their excellent properties, and at the same time carry out multi-element doping, multi-layer coating, and combine multiple structures to create new modification methods, improve the overall performance of materials to achieve sustainable energy needs at scale.

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