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# Research Progress on Manganese-Based Poly-Anion Cathode Materials for Sodium-Ion Batteries

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***Abstract.*** Poly-anionic compounds (PACs) have emerged as one of the most promising cathode materials for sodium-ion batteries due to their stability, safety, and suitable working voltage. Manganese-based materials, with manganese as the transition metal element, have high cost-effectiveness and strong high-voltage capacity. They are also safe and environmentally friendly. This paper systematically reviews the research progress of manganese-based poly-anionic materials for sodium-ion batteries through literature research, focusing on the working principle of sodium-ion batteries and the structure and electrochemical performance about six common types of manganese-based poly-anionic materials. The research finds that manganese-based PACs show good application prospects due to their three-dimensional stable framework, high voltage and high energy density potential brought by the double-electron reaction. However, they generally have poor electronic conductivity, some materials have actual specific capacities lower than theoretical values, and low ion diffusion efficiency at low temperatures. Ion doping and structural optimization can effectively improve these deficiencies. In addition, this review discusses the important role of technologies such as artificial intelligence in promoting the sustainable development of sodium-ion batteries in the future.

***Keywords:*** sodium-ion battery, manganese-based poly-anionic cathode material, electrochemical performance, material modification

## 1. Introduction

With the global surge in demand for clean energy, energy storage technology, as a crucial link connecting renewable energy sources and the power grid, has seen its performance and cost become the focus of the industry. The abundance of lithium resources in the Earth's crust is only 20mg/kg, and the ion migration rate decreases at low temperatures, and the capacity degrades severely at low temperatures, making it difficult to meet the large-scale energy storage needs in cold regions. Against this backdrop, sodium-ion batteries (SIB) have emerged as an important candidate technology to replace lithium-ion batteries. This is because sodium resources are abundant (23600mg/kg),low-priced, and the low-temperature performance is excellent (the capacity retention rate can reach over 80% at -20°C).

It is undeniable that SIB has a great potential for improvement in electrochemical performance. Among them, the electrode materials, especially the positive electrode materials, play a crucial role in controlling costs and determining electrochemical kinetics. Currently, the mainstream positive electrode materials for sodium-ion batteries (layered oxides, organic compounds, poly-anionic compounds, Prussian blue and its analogues) all have promising prospects. Among them, poly-anionic compounds have a good development potential. The structural formula of poly-anionic compounds is AxMy[(XOm)n]2, where A is a base (alkaline) metal element, M is a transition metal element (such as Ti, V, Cr, Mn, Fe, Al, etc.), and X is a non-metal element. The PACs positive electrode material has a stable structure, with highly ordered lattice arrangement. The poly-anionic groups are connected into a stable three-dimensional network system through strong covalent bonds, which can effectively resist structural deformation during sodium ion insertion and extraction, thereby prolonging the battery cycle life and ensuring good safety performance. However, PACs also have disadvantages such as poor electronic conductivity, low specific capacity, and poor low-temperature performance. Researchers have solved these problems through modification methods such as ion doping [1].

We selected manganese as the transition metal element and summarized the research progress of sodium-ion manganese-based polyanionic cathode materials. The manganese-based polyanionic materials, with their three-dimensional framework structure, based on the high working voltage of the $Mn^{2+}/Mn^{3+}$ and $Mn^{3+}/Mn^{4+}$ redox couples and the high specific capacity brought by the double-electron reaction, exhibit excellent energy density potential. The two redox couples of the manganese ions can all be achieved below 5V, and the voltage difference in poly-anionic compounds is approximately 0.5V. Therefore, multi-electron reactions of Mn can be realized in cathode materials such as NaMnTi(PO4)3,Na2MnPO4F,NaMnPO4CO3,NaMnSiO4 [2].

Since the morphological structure of poly-anionic cathode materials is an important factor for improving the specific capacity of batteries and thereby affecting their cycle life, this paper focuses on the characteristics and performance of manganese-based poly-anionic cathode materials in sodium-ion batteries, and explores their impact on energy storage performance. This paper will review several common manganese-based poly-anionic materials, including phosphates, fluorophosphates, pyrophosphates, sulfates, silicates, and mixed poly-anions, and put forward suggestions for the development of manganese-based poly-anionic cathode materials in the future, laying the foundation for the research and development of sodium-ion batteries with high energy density and long service life.

## 2. The working principle of sodium-ion batteries

The core components of a sodium-ion battery include the positive and negative electrodes, the separator, the electrolyte, and the current collector. The current collector in a sodium-ion battery can be made of aluminum instead of copper, which reduces the cost of the battery. Sodium-ion batteries have a "swing chair" working principle similar to that of lithium-ion batteries. Energy is stored and released through the reversible shuttle of sodium ions between the positive and negative electrodes. During charging and discharging, $Na^+$ migrates back and forth between the positive and negative electrodes. During charging, $Na^+$ is released from the positive electrode material, passes through the separator, and then embeds in the negative electrode material. At the same time, electrons flow from the positive electrode to the negative electrode, thus storing electrical energy in the form of chemical energy. During discharging, the process is reversed. $Na^+$ is released from the negative electrode and returns to the positive electrode. The current flows back to the positive electrode, and the chemical energy is converted back into electrical energy, providing power to external devices [3].

For example, the battery reaction using NaMnPO4 as the positive electrode material and hard carbon as the negative electrode material is as follows:

Positive electrode reaction: NaMnPO4↔Na(1-x)MnPO4+x $Na^+$+x $e^-$
Negative electrode reaction: x C+x $Na^+$+x $e^-$↔NaxC
Overall reaction: NaMnPO4+x C↔Na(1-x)MnPO4+NaxC

## 3. Manganese-based related poly-anionic cathode materials for sodium-ion batteries structure

### 3.1. Phosphas

The sodium phosphate materials have two different structural poly-morphs: olivine and marinite. The former is thermodynamically unstable and has electrochemical activity, while the latter is thermodynamically stable and has electrochemical inertness. Because in the olivine structure, $Na^+$ is located at Mn1(4a) and $Mn^{2+}$ is located at Mn2(4c), while in the marinite structure, these positions are reversed.

The manganese-based phosphate materials of NASICON-type Na3V2(PO4)3 derivatives are currently a research hotspot. By completely replacing $V^{3+}$ with two $Mn^{3+}$, the formation of NaMn2(PO4)3 can achieve an average voltage of 3.64V, which can increase the battery's specific energy.Another material, Na3MnTi(PO4)3/C(NMTP/C), has excellent cycle stability. The capacity retention rate after 500 cycles at 2°C is as high as 90% [4]. Mengting Deng optimized the Na3MnZr(PO4)3 material by incorporating the vanadium V element to refine the valence structure, increasing the capacity contribution rate by 135.3%, reducing the volume change during the charging and discharging cycles of sodium dissolution, and improving the cycle stability [5].

### 3.2. Fluo-phosphate

Introducing the element with a relatively high electronegativity, F, to enhance the sensing effect of the anion groups and increase the electrochemical potential [6]. Na2MnPO4F has a three-dimensional channel structure, theoretically enabling a double-electron reaction, with a capacity of approximately 250 mAh/g, but its rate performance is poor.

Gu Zhenyi optimized the NVPF to produce the new material NVPF-Na-0.07 (i.e., Na3.14V1.93Na0.07(PO4)2), significantly increasing the ionicity and accelerating the sodium ion migration kinetics. It can provide high-rate capability (77.5 mAh/g at 20 degrees Celsius), and its theoretical capacity of the battery is not affected by cold weather. The capacity retention rate can also exceed 90% at 0.5°C [7]. In typical fluoride phosphate materials NaV2(PO4)2O2F, the sodium ions moving are affected by the large Coulomb repulsion force of the structural anions and the surrounding sodium ions, resulting in poor reaction kinetics and low-rate capability. The Key Laboratory of Lubrication and Sealing Gasket of Northwest University of Technology doped Br bromide ions into typical materials to form Na(3-y)VPO(2-X)BrxF to dilute the charge in the sodium ion transport tunnels. The diffusion rate of $Na^+$ is approximately 5 times that of traditional materials, significantly reducing the Coulomb barriers during the migration process of sodium ions [8].

### 3.3. Pyrophosphate

The structural formula of phosphonate is NaMP207 (M = Fe, V, Mn, Co, etc.). Phosphonate has thermal stability. At 500 - 550℃, the phosphate group will form phophonate group [P207 or(PO4-x)2], and the phosphonate poly-anion is more stable than the phosphate poly-anion [9]. The positive electrode of phosphonate also exhibits a higher redox potential.

The Na2MnP2O7 material has a shared corner crystal structure, which significantly enhances the kinetics. When heated at 600℃, it can irreversibly transform into the trigonal β phase (a layered phase with excellent electronic conductivity). Phosphate-based materials are not numerous. They generally exist in the form of mixed poly-anions and are used in combination with other groups, mainly in iron-based materials, and occupy the main market.

### 3.4. Sulfate

The bonding of sulfate S-O is stronger than that of phosphate P-O. When the d orbitals of transition metals and the O-2p orbitals of the sulfate hybridize, more energy is released. Therefore, the working voltage is high, making it suitable for preparing high-pressure materials. The disadvantage of sulfate materials is that the ion diffusion channels are narrow. The diffusion coefficient of sodium ions in Na2Mn(SO4)2 is only $10^{(-14)}$-$10^{(-13)}$$cm^2/s$, which is much lower than that of phosphate materials, resulting in poor rate performance; at the same time, sulfate materials have a higher water solubility and are prone to dissolution in the electrolyte, leading to a decrease in cycle stability. Therefore, sulfate materials are rarely seen in manganese-based poly-anion materials and require further research.

### 3.5. Silicate

Silicate poly-anion materials have low cost and high element abundance. Na2Mn2Si2O7, due to the rearrangement of Mn coordination and the significant change in sodium ion migration coefficient, can provide a theoretical capacity of 165mAh/g. However, the actual release is only 25% and accompanied by a large volume contraction.

Na2MnSiO4 possesses three-dimensional ionic diffusion channels. The diffusion coefficient of ions in this material is much higher than that of lithium analogues. If other ions such as Al are doped, the ionic diffusion characteristics can be further optimized.

### 3.6. Mixed poly-anion

This material contains two or more poly-anionic groups. Different combinations of these groups can broaden the diversity of the structure and redox potential.

The mixture of phosphate and carbonate, Na3MnPO4CO3, has a special structure. In this structure, the MnO6 octahedron is aggregated by PO4 to form a double-layer structure. The CO3 group and MnO6 share the edge octahedron and point towards the double-layer structure, while $Na^+$ is located at different gap sites and can diffuse in three directions, with a relatively low activation energy barrier. This can significantly increase the specific capacity. Currently, the theoretical capacity is as high as 191 mAh/g. The mixed compound of phosphate and pyrophosphate has an open framework structure and excellent diffusion kinetics, but its working potential is relatively low. Therefore, Fan Haicheng from Wuhan University of Technology and others developed a dual-metal material Na4Fe1.5Mn1.5(PO4)2(P2O7)/C—r GO. It can have two working platforms at 2.92 and 3.95 V. The redox couple corresponding to the iron element, $Fe^{2+}/^{3+}$, has a solid solution reaction, and the couple corresponding to the manganese element, $Mn^{2+}/^{3+}$, has a two-phase reaction, which may have an impact on each other.

## 4. Future prospectives

Currently, manganese-based poly-anionic cathode materials for sodium-ion batteries have become a research hot-spot in the field of large-scale energy storage. There have been significant advancements in the design of material structure and performance optimization. From an industrialization perspective, this type of material still faces three core bottlenecks: the electronic conductivity is generally low (before modification, most materials are less than $10^{(-10)}$ S/cm), and the high-rate performance fails to meet the requirements for rapid charging; secondly, the actual capacity of some materials deviates significantly from the theoretical value (such as Na2MnPO4F\Na2Mn2Si2O7), and the energy density potential has not been fully exploited; finally, the low-temperature performance is insufficient (-20°C capacity retention rate is generally less than 60%), which limits the application of the battery in cold regions.

In the future, more innovative techniques such as material modification can be introduced, for example, precisely controlling the proportion of mixed poly-anionic groups, developing new dopants, etc. We can also combine the development dividends of the current era - artificial intelligence technology. By leveraging machine learning, we can quickly screen out efficient high-quality materials, predict the electrochemical and other properties of the materials, thereby shortening the research and development cycle of new materials. At the same time, using high-throughput computational simulations to study the migration paths and energy barriers of sodium ions under different crystal forms and defect structures can avoid blind experiments.

## 5. Conclusions

This paper conducts a systematic study on manganese-based poly-anionic cathode materials for sodium-ion batteries. The manganese-based poly-anionic compounds (PACs) have demonstrated great potential as positive electrode materials for sodium-ion batteries due to their unique three-dimensional stable framework structure, the high working voltage brought by the $Mn^{2+}/Mn^{3+}$and $Mn^{3+}/Mn^{4+}$redox pairs, and the high specific capacity resulting from the dual-electron reaction. However, these materials generally suffer from poor electronic conductivity, actual specific capacity lower than the theoretical value, and low ion diffusion efficiency at low temperatures. These issues can be effectively improved through modification methods such as ion doping and structural optimization.

This paper comprehensively reviews six major types of materials including phosphate and fluorophosphate, and analyzes their crystal structures, electrochemical properties and modification strategies. This fills the gap in the field of manganese elements as electrode materials for sodium-ion batteries. This research provides a systematic research framework and abundant data support for other researchers, and can further promote the industrial application of manganese-based poly-anionic cathode materials, ultimately promoting the green and sustainable development of the battery industry.

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