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Research Progress on the Effects of Single Doping at the Vanadium Site of $Na_3V_2(PO_4)_3$ Cathode Materials on the Performance of Na-Ion Batteries

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Abstract. Na-ion batteries (SIBs) have shown extremely broad application prospects in large-scale energy storage system due to the abundance of sodium resources and their low cost. Vanadium phosphate sodium (NVP), as a typical polyanionic cathode material, possesses a three-dimensional network-like skeleton with open characteristics, superior specific capacity performance, high working voltage and excellent cycling stability. However, the relatively low electronic conductivity of sodium vanadate limits its further development. Thus, it can be seen that enhancing the comprehensive performance of sodium vanadate in electrochemical reactions holds significant practical significance. In response to the aforementioned issues, the researchers explored a series of modification methods, with typical examples including carbon coating treatment, nanomaterial processing, and heterogeneous ion doping. Among these, the ion doping strategy has demonstrated significant advantages in improving the energy storage efficiency of sodium-ion batteries. This article reviews the research progress of the single-vanadium-doped modification strategies for vanadium-containing positive electrode materials of sodium-ion batteries in recent years. It focuses on the energy storage principle of Na-ion batteries, the energy storage advantages of vanadium-containing positive electrode materials, the main preparation methods and their advantages and disadvantages, and provides an outlook on the future development trends.

Keywords: Sodium-ion battery, Sodium vanadium phosphate, Cathode material, Vanadium doping, Electrochemical performance

1. Introduction

As the issue of lithium resource shortage becomes increasingly prominent and the demand for renewable energy surges, price moderate and long-life sodium-ion batteries are gradually emerging as a key development direction in the field of large-scale energy storage. Sodium-ion batteries have inherent advantages for large-scale industrialization due to the abundant reserves of sodium resources, their uniform distribution, and the similar working principle to lithium-ion batteries.

Vanadium phosphate sodium (NVP) possesses three-dimensional open ionic transmission channels, a high discharge plateau and excellent thermal stability. Its unique three-dimensional open

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framework structure provides a fast migration pathway for sodium ions. The theoretical specific capacity is as high as 117.6 mAh/g, and the working voltage is approximately 3.4V(vs. Na^+/Na). It is widely recognized by both academia and industry that this material exhibits excellent rate capability and cycle life, making it a promising candidate as a cathode material for sodium-ion batteries [1, 2]. However, pure vanadium phosphate sodium has poor electronic conductivity, limited energy density, and weak sodium ion migration kinetics. This makes it prone to problems such as capacity degradation and deterioration of rate performance [3, 4]. When considering the various requirements in actual energy storage scenarios, it is currently difficult to fully meet them.

To address this issue, researchers have explored a variety of modification strategies, including carbon coating, nano-morphology control, and ion doping. Vanadium doping has been proven to have a very good modifying effect, it can achieve the fundamental-level regulation of the electronic structure without disturbing the original lattice framework of the material. By introducing additional electrons or holes through the doping of charged ions in the crystal, the charge transfer impedance can be reduced and the sodium ion diffusion channels can be widened. This effectively enhances the intrinsic electron conductivity of the material [2, 4, 5].

In conclusion, the positive electrode material of sodium phosphate vanadium can effectively improve its electrochemical performance after doping modification. Through recent research, by employing various doping systems, the electronic conductivity of this material can be significantly enhanced, the migration rate of sodium ions can be accelerated, and problems such as capacity degradation during long-term cycling can also be effectively alleviated. With the continuous deepening of research on the cathode active material of sodium phosphate and the advancement of science and technology, sodium phosphate-vanadium is anticipated to occupy an important position within the large-scale energy storage sector in the future, facilitating the creation of a cost-effective and durable energy storage system.

2. Results and discussion situation

2.1. Introduction to sodium-ion batteries and their devices

A sodium-ion battery refers to a type of secondary battery that is composed of two compounds capable of reversibly inserting and extracting sodium ions as the cathode and anode. The positive electrode, negative electrode, separator, electrolyte, and current collector—these five components together make up a sodium-ion battery. Both the positive and negative electrode materials can accommodate and release sodium ions. It operates on a principle similar to that of a rocking chair. When the battery is being charged or discharged, Na^+ moves back and forth between the positive and negative electrodes, "rocking" from one side to the other, in a repetitive cycle, thus completing the charging and discharging process of the battery. Taking the combination of hard carbon as the negative electrode material and Na_xMO_2 as the positive electrode material as an example [6], The electrochemical reaction equations for charging and discharging are as follows:

Positive electrode reaction:

$$Na_xMO_2 \leftrightarrow Na_{x-y}MO_2 + yNa^+ + ye^-$$

Negative electrode reaction:

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$$nC + yNa^+ + ye^- \leftrightarrow Na_yC_n$$

Overall battery reaction:

$$Na_xMO_2 + nC \leftrightarrow Na_{x-y}MO_2 + Na_yC_n$$

As shown in Figure 1, the device includes positive electrode material, negative electrode material, separator, electrolyte, current collector, etc.

Positive electrode material: Mostly layered transition metal oxides, poly-anionic compounds, and Prussian blue-like large framework compounds, which are the sites where sodium ions are inserted and extracted during charging and discharging.

Negative electrode material: Mostly hard carbon materials, which are also the sites where sodium ions are inserted and extracted during charging and discharging.

Electrolyte: It is generally an organic solution containing sodium salts, serving as a channel for the transport of sodium ions.

Diaphragm: A membrane with electronic insulation properties, placed between the two electrodes to avoid direct contact and resulting short circuits, while allowing sodium ions to pass through.

Current collector: Carries the cathode and anode materials, and is mostly made of aluminum foil.

As a new type of secondary battery system, sodium-ion batteries have highly similar electrochemical principles and working mechanisms to lithium-ion batteries, and thus are regarded as a potential alternative to lithium-ion batteries. Specifically, this is manifested in:

(1) Sodium resources are evenly distributed globally, while 73% of lithium resources are concentrated in South America. Utilizing sodium resources can help avoid the risk of being constrained by lithium resources.

(2) The raw material cost of Na-ion batteries is 30% lower than that of lithium-ion batteries. Therefore, it demonstrates excellent adaptability in large-scale deployments such as grid energy storage.

(3) Sodium-ion batteries can share production line equipment (such as electrode coating processes) with lithium-ion batteries, and the industrialization conversion cost is low.

Therefore, although sodium-ion batteries currently lag behind lithium batteries in terms of energy density, their comprehensive advantages in terms of resources, cost, and safety make them potentially suitable for differentiated applications in specific energy storage and military scenarios.

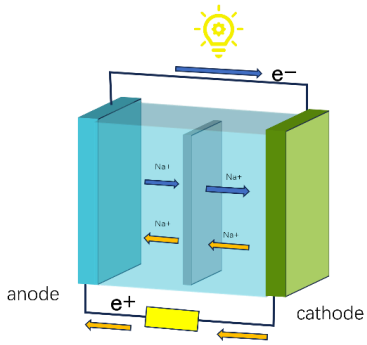


Figure 1. Schematic diagram of the structure of sodium-ion battery working principle

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2.2. Principle of sodium ion battery energy storage

As shown in Figure 2, when the battery discharges, the negative electrode participates in an oxidation reaction. Sodium ions are released from the negative electrode material and transported to the positive electrode side through the electrolyte. Concurrently, electrons flow through the external loop from the negative end to the positive end, which constitutes an electric current. Eventually, sodium ions are embedded in the crystal lattice of the positive electrode material, completing the transfer of energy from chemical to electrical. During charging, under the influence of an external power source, the positive electrode undergoes an oxidation reaction, and sodium ions are released from the positive side material and migrate back to the negative electrode in the opposite direction. The electrons then flow back from the positive electrode through the external circuit to the anode. Finally, the sodium ions re-entrap in the negative electrode material, completing the conversion of electrical energy to chemical energy, and preparing for the next discharge.

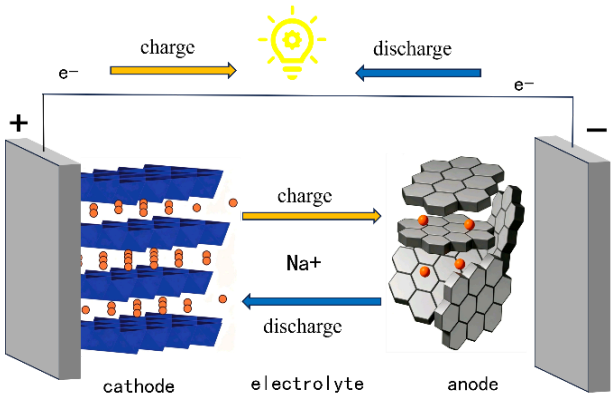


Figure 2. Diagram of the working mechanism of a sodium-ion battery [7]

2.3. Cathode-side materials for na-ion batteries

It is the structural configuration and inherent attributes of the electrode materials that critically influence the electrochemical performance of sodium-ion batteries. Generally speaking, the performance of the positive electrode materials (such as specific capacity, voltage and cycling ability) is considered to be the key factor influencing the energy density, safety and cycle life of sodium-ion batteries. Therefore, the improvement and enhancement of the performance of cathode active materials, as well as the development and exploration of new cathode materials, have always been the research focus in the field of sodium-ion batteries. The most widely studied cathode materials currently include three major types: layered transition metal oxides, poly-anionic compounds, and Prussian blue analogues. The layered transition metal oxides have a two-dimensional layered structure, featuring high specific capacity and high operating voltage. However, it undergoes various irreversible phase changes within different voltage ranges, and its stability in the air is also poor, thereby increasing the cost of energy storage [8]. The Prussian blue analogues possess a three-dimensional open structure with large void sites, low cost, and high theoretical capacity. However, due to their structural defects, they may cause issues such as cycle degradation and poor rate performance [9]. Polyanionic compounds are characterized by a three-dimensional NASICON open framework. This unique architecture endows them with outstanding structural integrity and favorable electrochemical cyclability, collectively positioning them as a highly attractive material family in the field of energy storage.

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Vanadium phosphate sodium, as a typical NASICON-type polyanionic material, possesses the characteristics of structural stability, ionic conductivity, thermal stability, high voltage platform, Long cycle life, high theoretical capacity (117 mAh/g, approximately 400 Wh/kg) and excellent safety make it have broad application prospects. However, its inherent electronic conductivity is relatively weak, which largely restricts the practical electrochemical application of sodium vanadium phosphate cathode materials. Currently, researchers mainly employ strategies such as carbon composites, nanostructured design, and element doping for modification, effectively improving their rate performance and cycle stability, thereby promoting their development towards practical applications [10].

2.4. Preparation method of vanadium phosphate sodium material

At present, the main methods for preparing sodium vanadate phosphate include solid-phase method, sol-gel method, hydrothermal method, electrospinning method, and spray drying method, etc. The purity, particle size and electrochemical performance of the products obtained by different methods show significant differences. The strengths and weaknesses of each approach are outlined in Table 1.

Table 1. Comparison of preparation methods for sodium vanadate phosphate

Serial number	preparation method	Preparation materials	Advantage	Disadvantage	Reference Source
1	High-temperature solid-state synthesis	$Na_3V_2(PO_4)_3$ (Using $NNaVO_3$ as the source of vanadium)	The operation is simple, the equipment requirements are low, and it is suitable for large-scale production.	Uneven composition, wide particle size distribution, prone to generating impure phases	[11]
2	Sol-gel method	$Na_3V_2(PO_4)_3$, $Na_{3.4}V_{1.85}Mn_{0.2}Zn_{0.1}$ - $Mg_{0.1}(PO_4)_3$	Molecular-level uniform mixing, small particle size, high purity, suitable for modification research	High energy consumption, long drying time, and generation of waste liquid	[12, 13]
3	Hydrothermal/Solvent thermal method	$Na_3V_2(PO_4)_3@C-MSs$	Controllable morphology, uniform particle size, good crystallinity, and capable of synthesizing nanostructures	High equipment requirements, long reaction time, low yield, and poor batch consistency.	[14]
4	Spray drying process	$Na_{2.85}V_{1.85}Zr_{0.15}$ - $(PO_4)_3$	It can be used to prepare special micro-nano hollow spherical structures, which is beneficial for increasing the compactness of the material.	The equipment has high requirements and consumes a large amount of energy.	[15]
5	Electrospinning method	$Na_3V_{2-x}Ni_x(PO_4)_3/C$	Forming a fiber network structure, enhancing conductivity, and spatial confinement effect	Low yield, difficult solvent recovery, special equipment, high cost	[14]

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2.5. Sodium phosphate dianion is used for performance research of sodium-ion batteries

Pure-phase sodium vanadate synthesized through the aforementioned route often exhibits limited electronic transport properties and unsatisfactory performance under high-rate conditions. Therefore, researchers often employ the ion doping strategy to enhance the electrochemical performance of it, and the doping primarily targets the Na, V, and P lattice sites. The related studies are presented in Table 2.

Table 2. Comparative analysis of the electrochemical performance of doped sodium vanadate materials

Serial number	Doping ion	Site	Rate (C) / Discharge capacity (mAh/g)	Capacity retention / Cycle number / C-rate	Refs
1	Co	V	101.7,0.1C;69.5,5C	70.41%,500,1C	[16]
2	Cr/Mg	V	100.4,25mAh/g	88%,100,1C	[17]
3	Zr^{4+}	V	107.3,0.2C;108,1C	80.6%,800,10C	[15]
4	Ga	V	152.3,1C	84.52%,600,10C	[18]
5	Fe	V	116.4,1C	80.41%,50,1C	[19]
6	Cr	V	163.2,1C	87.5%,1000,1C	[5]

Introducing ion doping into the sodium vanadate framework enables a fundamental improvement in the native electronic and ionic conductivities of NVP, targeting the material's charge transport behavior at its origin, thereby optimizing the electrochemical response of the sodium vanadate cathode. The doping or substitution at the V site has a significant effect on enhancing the sodium storage performance of sodium vanadium phosphate [2].

3. Conclusion

This article reviews the preparation methods of vanadium sodium phosphate cathode materials, analyzes the advantages and disadvantages of different preparation methods, and compares the doping and modification of different sites of vanadium sodium phosphate. Studies have shown that by appropriately doping the vanadium sites with elements, the crystal structure of sodium vanadium phosphate can be effectively optimized and the electronic conductivity can be enhanced. Improving the rate performance and cycling stability of the materials provides new research ideas for the development and study of high-performance cathode materials for sodium-ion batteries. This type of material possesses a stable framework structure and excellent electrochemical properties, and has great potential for development in the domain of large-scale energy storage technologies.

The structural optimization of vanadium sodium phosphate cathode materials is supported by a theoretical basis established in this research. Furthermore, this work facilitates the further development of high-performance sodium-ion batteries. With the continuous deepening of research on the mechanism of vanadium doping and the advancement of science and technology, modified sodium vanadium phosphate materials are expected to achieve higher specific capacity and better long-cycle performance. Drive the widespread implementation of sodium-ion batteries in large-scale energy storage as well as in real-world low-speed electric vehicle contexts.

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