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Progress in Cathode Materials for Sodium-Ion Batteries and Industrialization Research

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Abstract:
With the development of society, humans have begun to pursue and explore more environmentally friendly and cost-effective lifestyles. And sodium-ion batteries, as an emerging industry, are constantly disrupting the traditional battery sector. Since sodium is more abundant than lithium and its cost is also much lower, and it has a high safety factor; it is also an indispensable development direction in the future. This article summarizes the advantages and disadvantages of the anion compounds, Prussian blue-like substances, and layered oxides of the current mainstream sodium-ion battery positive electrode materials, and finds that the cyanide wastewater in the synthesis of Prussian blue needs to be strictly treated, while vanadium-based materials face the problem of mining pollution. In contrast, sodium iron phosphate ($NaFePO_4$) has the advantages of low cost and low toxicity, and may become the mainstream choice for energy storage stations in the future. This article can promote the development of the research on sodium-ion battery positive electrodes and provides a research basis and direction for the design and improvement of subsequent sodium-ion battery positive electrode materials and manufacturing processes.

Keywords: Sodium-ion battery, Positive electrode material, Material performance.

1. Introduction

Driven by the global carbon neutrality strategy, the installed capacity of renewable energy has witnessed an explosive growth. According to the International Energy Agency (IEA), the global share of renewable energy power generation has exceeded 30% in 2023, which poses unprecedented demands for large-scale energy storage systems. Lithium-ion batteries, as the mainstream technology in the energy storage market currently, are facing increasingly severe resource constraints; the crustal abundance of lithium is only 0.006%, and 75% of the world's lithium resources are concentrated in the "Lithium Triangle" region in South America. The price of lithium carbonate sky-rocketed from 200,000 yuan/ton in 2022 to 600,000

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yuan/ton in 2023, with extremely volatile prices, seriously threatening the supply chain security of the energy storage industry [1]. At the same time, key metals such as cobalt and nickel also face geopolitical risks, further amplifying the continuous development risks of lithium battery technology. For example, the cobalt element also shows an extremely concentrated global resource distribution feature. The production share of the Democratic Republic of the Congo alone exceeds 70% (USGS 2023 data), and the country's mineral development has long been plagued by child labor issues and human rights controversies. In 2022, the government of the Democratic Republic of the Congo unilaterally raised the mining tax rate, and political changes directly led to a fluctuation in international cobalt prices exceeding 40%. More challenging is that China's sodium refining technology accounts for more than 80% of the global market and is the largest sodium refining country; 90% of its processing raw materials rely on imports from Congo, and this "resource-processing" cross-border separation model further amplifies the supply chain vulnerability. The resource supply of nickel is also equally pessimistic. Although the global nickel reserves are relatively abundant, high-grade sulfide nickel ore suitable for battery-grade nickel sulfate production is mainly concentrated in Russia (accounting for 18% of the global reserves) and Canada (accounting for 14%), etc. In 2022, after the outbreak of the Russia-Ukraine conflict, the nickel price on the London Metal Exchange (LME) soared by 250% within 24 hours, setting a historical record of 100,000 yuan/ton, directly causing many battery enterprises worldwide to face raw material supply risks. Notably, although Indonesia has become the world's largest nickel producer with a global share of 37%, its policy requires local processing of raw materials, so Chinese enterprises need to invest a huge amount of funds to build "nickel mine-refining-precursor" integrated industrial parks, increasing the cost of the industrial chain [2].

Against this backdrop, sodium-ion batteries have ushered in development opportunities due to their unique resource advantages. Sodium's crustal abundance is as high as 2.3% (383 times that of lithium), and it can be extracted in various ways, such as seawater, salt lakes, and even industrial by-products, and its raw material cost is less than one-tenth of lithium [3]. More importantly, sodium battery technology completely does not require the use of scarce metals such as cobalt and nickel, fundamentally solving the problem of resource bottlenecks and other restrictions imposed by other countries. From a performance perspective, although the energy density of current sodium-ion batteries (120-160 Wh/kg) is slightly lower than that of commercial lithium batteries, they still maintain an excellent low-temperature performance of over 80% capacity at -40°C and higher thermal stability (the starting temperature of thermal runaway is 20°C higher than that of lithium batteries), making them particularly suitable for specific scenarios such as cold-region energy storage and grid frequency regulation.

Meanwhile, the industry's layout of sodium-ion batteries has entered a substantive stage. In 2023, CATL released its first sodium-ion battery product, with an energy density of 160 Wh/kg, a constant-temperature cycle life exceeding 3,000 times, and it can be used in electric two-wheelers and energy storage stations. The 1GWh sodium-ion energy storage system built by Zhongke Haishan has been grid-connected in Jiangsu, with an actual system efficiency of 92%. According to Bloomberg New Energy Finance's prediction, by 2030, the penetration rate of sodium-ion batteries in the energy storage market will exceed 15%, and the corresponding market size will exceed 20 billion US dollars. In low-speed electric vehicles, 5G base station backup power supply and other fields, sodium-ion technology has been accelerating the replacement of traditional lead-acid batteries due to its cost advantages [4]. These series of developments indicate that sodium-ion batteries have gradually moved from the laboratory to industrialization, and are highly likely to become the "second tier" energy storage technology supporting global energy transition.

This article provides further analysis and explanations on the advantages and limitations that sodium-ion batteries will bring under the global "carbon neutrality" goal. Such analysis will be conducted in terms of resource constraints and abundance, cost advantages and risks, performance characteristics and bottlenecks, industrial development and future prospects, etc. This article will conduct a comprehensive exploration of sodium-ion batteries.

2. Sodium-ion Battery Structure and Energy Storage Mechanism

2.1 Basic Structure

A sodium-ion battery (Sodium-ion Battery, SIB) is a new type of secondary battery with a "rocking-chair" working mechanism. The working principle of sodium ions is similar to that of lithium-ion batteries, but lithium-ion batteries suffer from resource shortages and uneven distribution, which can easily lead to safety incidents such as fires and explosions. Compared to lithium-ion batteries, sodium-ion batteries have advantages such as abundant sodium element storage, low cost, wide working range, and excellent cycle performance, making them highly notable in the development of battery technology. Currently, the market intends to replace lithium ions (Li^+) with sodium ions (Na^+) with abundant reserves as the charge carrier. The working principle of sodium ions is as follows: Na^+ can freely insert and withdraw from the positive and negative electrode materials; during charging, sodium ions (Na^+) pass through the electrolyte and insert into the negative electrode material; during discharge, the process is reversed, with sodium ions (Na^+) leaving the negative electrode and returning to the positive electrode, forming a reversible cycle [5]. This process is accompanied by the directional flow of electrons in the external circuit, thereby achieving the storage and release of electrical energy. Compared to lithium ions, Na^+ has a larger ionic radius (1.02 A vs 0.76 A) and weaker Lewis acidity, which makes sodium-ion batteries exhibit unique characteristics in material selection, interface behavior, and electrochemical performance. Additionally, due to the fact that sodium ions can operate stably at -70 ℃ and 100 ℃, they have better stability and are safer.

3. Sodium Ion Cathode Materials

3.1 Anionic Compounds

Anionic compounds are the best choice for batteries with high cycle life. Representative materials include $Na_3V_2(PO_4)_3$ (phosphate vanadium sodium, NVP) and $Na_3V_2(PO_4)_2F_3$ (fluorophosphate vanadium sodium). They consist of a stable three-dimensional framework structure composed of $[VO_6]$ octahedra and $[PO_4]$ tetrahedra, providing a stable Na^+ transport channel, which enables them to have a stable crystal structure and excellent thermal safety. Even at high temperatures (>300 degrees), they can still maintain structural integrity [6]. Moreover, their working voltage is moderate, with the voltage platform of $Na_3V_2(PO_4)_3$ being approximately 3.4 V (vs. Na^+/Na), and that of $Na_3V_2(PO_4)_2F_3$ reaching ~3.9 V. They have high energy density and do not contain expensive or toxic elements such as cobalt. The disadvantages of anionic compounds are that due to their low electron conductivity and voltage (intrinsic conductivity is low $<10^{-9}$ S/cm), they need to rely on dilution and nanoscale dispersion methods like graphene to improve rate performance. This limits the increase in energy density, which becomes the core bottleneck for industrial application. At the same time, due to their relatively low theoretical capacity ($Na_3V_2(PO_4)_3$ only ~117 mAh/g) and some lower voltage platforms (such as the second platform of $Na_3V_2(PO_4)_3$ being only ~1.6 V), cost is also a problem faced by the material. The resources of vanadium are limited, and the price fluctuates greatly. There is no good substitute material for it. In the future, how to balance the material cost and performance optimization will be the key to whether this technology can be scaled up and applied in the energy storage field.

3.2 Prussian Blue Compounds

Prussian blue-like compounds feature an open cubic framework structure and low raw material costs, allowing Na+ to enter and exit rapidly; they have high theoretical capacity, and some materials (for example, $Na_2Mn[Mn(CN)_6]$) can have a theoretical capacity of approximately 170 mAh/g, approaching that of layered oxides; due to their open structure, the diffusion coefficient of Na^+ can reach 10^{-10} cm²/s, making them suitable for high-power applications. Their specific performance is very advantageous, showing great potential in the low-speed electric vehicle field [7]. However, the inevitable lattice vacancies and crystalline water problems during the preparation process directly lead to capacity degradation and reduced rate performance. Research at Argonne National Laboratory in the United States has shown that by controlling the synthesis pH value and heat treatment process, the water content can be reduced to below 4%, significantly improving cycle stability. The vacancies in the crystalline crystals often have defects, and during the synthesis process, lattice water (H_2O) and $[Fe(CN)_6]$ vacancies are easily introduced, resulting in cycle degradation (such as a capacity loss of >30% after 500 cycles) [8]. This case reveals that if we want to achieve its widespread application in energy storage stations, we must solve the structural defect problems at the synthesis process source.

3.3 Heavy Metal Oxides

The representative materials of heavy metal oxides are classified into O3 type ($NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$(NFM)) and P2 type ($Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$). Their advantages include high energy density, with a theoretical capacity of up to 160 - 200 mAh/g, and a working voltage of 3.0 - 3.8 V (vs. Na^+/Na); their structural tunability is also very good, as the voltage and capacity can be optimized by adjusting the proportion of metals such as Ni, Fe, Mn, Cu, etc. in the metal image; their industrialization foundation is also very advantageous, with a synthesis process very similar to that of lithium-ion layered oxides, making it easy to be compatible with production. However, they are very sensitive to moisture, and the generation of Na_2CO_3 and NaOH surface impurity layers can lead to a decrease in efficiency; they are prone to phase transformation and structural degradation, especially under high pressure, where a phase transformation from O3 to O2 is likely to occur at less than 4.0 V, causing particle cracking and capacity attenuation. Excessive metal dissolution, with Fe, Mn, etc. elements dissolving in the electrolyte, can accelerate bat-

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tery failure. These disadvantages make it very difficult for them to be commercialized. The team from Tokyo University of Japan extended the stability of the material in the air to over 30 days by doping with Ti^{4+} [9], confirming the effectiveness of the cation doping strategy. However, it is worth noting that such modifications often come at the expense of some capacity. In the future, more precise surface-body coordinated regulation technologies need to be developed to balance performance and stability.

3.4 Selection of Technology Route: Material Characteristics and Scenario Matching Logic

The differentiated characteristics of the three types of cathode materials determine the differentiation of their application scenarios: Anionic compounds are suitable for stationary energy storage with strict safety requirements; Prussian blue-like materials are more suitable for low-speed transportation with cost sensitivity; while layered oxides target the high-energy-density battery market. The AB battery system (layered oxide + hard carbon anode) released by CATL in 2023 confirms this logic [10]. Therefore, the development of sodium battery technology should not pursue a “universal material”, but rather require precise material design based on scenario needs.

4. Prospects of Sodium Ion Cathode Materials

4.1 Materials and Technological Breakthroughs

The development of sodium-ion battery cathode materials is shifting from single-performance optimization to multi-dimensional collaborative design. For instance, strategies such as multi-anion doping (e.g., PO_4^{3-}/SO_4^{2-} composites) can simultaneously enhance the voltage platform and ionic conductivity by regulating the lattice electronic structure. For example, the $Na_3V_2(PO_4)_2F_3@SO_4$ material developed by the Chinese Academy of Sciences raised the working voltage to above 4.0 V. Additionally, machine learning-assisted material prediction utilized an AI-based machine learning ML algorithm to accelerate the discovery of new high-entropy oxides. However, the synthesis and analysis processes of such complex materials are not yet mature. In the future, it is necessary to combine high-throughput experiments to verify their industrialization feasibility.

4.2 Process Innovation and Large-scale Manufacturing

The transition from laboratory to commercial-scale development showcases the greatest benefit of future development, which is an inevitable trend. Thick electrode technology (>200 μm) can enhance the battery›s energy density and volume, but the traditional coating process is prone to cause cracks, which hinder ionic transmission. CATL, a subsidiary of CATL New Energy Technology Co., Ltd., adopted a gradient pore design to form a high porosity (40%) on the surface of the electrode sheet to promote electrolyte infiltration, while maintaining a dense structure at the bottom to enhance mechanical strength (Joule 2023). On the other hand, interface engineering (through chemical or physical means to manipulate the interaction between electrode materials and electrolytes, thereby solving battery problems) has become the key to improving cycle life, such as constructing an Al_2O_3/polymer composite layer on the surface of $NaNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ to simultaneously inhibit transition metal dissolution and electrolyte decomposition (ACS Nano 2024). These technological advancements indicate that the manufacturing system of sodium batteries is shifting from “lithium battery imitation” to dedicated process development.

4.3 Cost and Sustainability

The storage capacity of resources on Earth and the life cycle cost of energy itself determine the applicable boundaries of sodium batteries. According to the 2023 data from Benchmark Mineral Intelligence, the cost of layered oxide cathode materials is only one-third that of lithium-ion NCM, while the Prussian blue compounds are due to the lower price of iron-based raw materials. However, the cyanide wastewater generated during the synthesis of Prussian blue needs to be strictly treated, and the vanadium-based materials face controversy over mining pollution. This will be a challenge regarding whether environmental feasibility can be achieved in the next step. In contrast, sodium phosphate iron ($NaFePO_4$) has the advantages of low cost and low toxicity, and may become the mainstream choice for energy storage stations in the future. In the recycling field, the cobalt-free feature of sodium batteries simplifies the recycling process. The direct recycling method developed by the Swedish company Northvolt can achieve a positive recycling rate of over 95% for cathode materials. In the future, sodium batteries need to build a “resource-manufacturing-recycling” closed loop in scenarios such as low-speed electric vehicles and large-scale energy storage to truly replace lithium batteries.

4.4 History and Future of Sodium Ion Batteries

The cathode materials for sodium-ion batteries have undergone a transformation from the research on NaOH in

1980, to the early imitation of lithium-ion batteries, and then to the development of an independent system. Their development has been rapid and continues to be optimistic. The current technological breakthrough lies in how to solve the core contradictions, such as the Prussian blue-like materials increasing the cycle life from 500 times to 2000 times through defect passivation technology, thereby extending their lifespan; layered oxides alleviating phase transition problems through the design of ionic disorder, and a series of other issues. In the coming years, with the improvement of the exclusive supply chain for sodium batteries (such as the mass production of hard carbon anodes), the cost of cathode materials is expected to drop below $10/kg, driving sodium batteries to be used in electric vehicles with a range of less than 500 kilometers and 10 kWh. How to make it circulate in the market and showcase its greatest advantages. This judgment reveals the ultimate logic of the sodium battery industry - the emergence of sodium batteries is not to replace the old development technology, but to restructure the application scenarios, opening up more life scenarios and ways.

5. Conclusion

In the context of the continuous advancement of global energy transition and the "carbon neutrality" strategy, sodium-ion batteries possess advantages such as abundant resources, low cost, and high safety, making them one of the most promising emerging technologies in the energy storage field. They can gradually be applied to or industrialized in some low-speed transportation vehicles. Through analysis and research on the battery's performance in fixed energy storage and its positive electrode materials, such as anionic compounds, Prussian blue-like substances, and layered oxides, each with its own advantages and challenges, people can continuously explore and showcase their greatest advantages. In conclusion, sodium batteries demonstrate excellent comprehensive competitiveness in terms of performance, safety, and resource acquisition, and are expected to complement lithium batteries, promoting the diversified development of energy storage systems. This research not only systematically reviews the core structure, energy storage mechanism, and key material characteristics of sodium-ion batteries, but also fills the gap in the current analysis of the adaptability of different positive electrode materials in application scenarios, providing theoretical support for material selection and technical routes in related industries. This study is conducive to promoting sodium batteries from the laboratory to industrialization, helping to establish a safer and more sustainable global energy storage technology system, and also providing research basis and directions for the design of sodium battery positive electrode materials and the improvement of manufacturing processes.

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