Advances in Sodium-Ion Battery Technology: Enhancing Energy Density for Future Applications

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Abstract. Achieving high energy density in sodium-ion batteries (SIBs) is crucial for advancing their potential as a substitute for lithium-ion batteries, particularly in large-scale energy storage systems. However, the development of SIBs faces several challenges, including limitations in cathode and anode materials, issues with dendrite formation, low ionic conductivity, and significant electrolyte volume expansion. These barriers directly impact the energy density and overall performance of SIBs. Current research has concentrated on producing cutting-edge anode materials like hard carbon and optimizing cathode materials like layered oxides and polyanionic compounds in order to get over these restrictions. Additionally, advancements in electrolyte formulations are crucial to ensure greater stability and ionic mobility. Emerging technologies, including the use of nanostructured materials and novel cell architectures, have also been explored as potential solutions to enhance energy density. This paper synthesizes these advancements and evaluates the pathways to improving cycle stability, minimizing volumetric changes, and enhancing safety features. With continued research, SIBs could become a key component in future sustainable energy storage solutions, offering cost-effective and high-performance alternatives to existing technologies.

Keywords: Sodium-ion battery; anode material; cathode material; electrolyte.

1. Introduction

With the rapid advancement of technology, electric vehicles (EVs) have emerged as a revolutionary force in the automotive industry. These vehicles offer numerous advantages, including the use of renewable energy resources, lower emissions, and higher energy efficiency. Among the key components driving the success of EVs are energy storage systems, with batteries playing a crucial role in determining vehicle range, charging times, and overall efficiency. However, one of the most persistent challenges in this field is improving the energy density of batteries, a factor that directly impacts how much energy can be stored in a given volume or mass.

In recent years, lithium-ion batteries (LIBs) have dominated the market due to their relatively high energy density, long cycle life, and reliable performance. Despite these strengths, the limitations of LIBs, such as resource scarcity, high cost, and potential safety issues, have prompted scientists to explore alternative energy storage technologies. One promising alternative is the sodium-ion battery (SIB), which shares a similar structure with LIBs, comprising anodes, cathodes, separators, electrolytes, and current collectors.

SIB offers several notable advantages over lithium-ion counterparts, including enhanced safety, faster charging speeds, and significantly lower manufacturing costs. With sodium being an abundant and cost-effective resource, SIBs are considered a future trend in large-scale energy storage, especially as electric vehicle adoption continues to grow. However, the challenges associated with SIBs, particularly their lower energy density compared to LIBs, cannot be overlooked. This discrepancy is primarily due to sodium's larger atomic mass and higher standard electrode potential, which directly impact the battery's energy storage capacity.

As the energy density of a battery is intimately linked to the performance of its anode and cathode materials, improving these components is critical for advancing sodium-ion technology. Researchers are continuously working to optimize both the anode and cathode materials in SIBs to bridge the energy density gap with LIBs. The development of advanced materials and innovative designs holds

the key to unlocking the full potential of SIBs, positioning them as a viable alternative for the next generation of electric vehicles and large-scale energy storage systems.

2. Cathode Materials

2.1. Layered Lithium-Rich Cathode Materials

Currently, Li-rich materials are classified into two types: layered Li-rich materials and cationic disordered lithium-salt phase Li-rich materials. However, the specific structure of layered Li-rich materials has been debated, with the two most widely accepted theories being the two-phase layered structure and the single-phase solid solution structure.

The lithium-rich cathode material has a unique charging and discharging mechanism due to the co-participation of anion REDOX reaction; that is, it has a long charging platform at about 4.5 V in the first cycle charge, but at the same time, it has the disadvantage of low initial coulomb efficiency in the first cycle.

Doping is one of the most commonly used strategies to maintain structural stability, improve electrical conductivity and reduce voltage decay. The capacity and voltage stability of Li-rich cathode materials are related to the stability of layered structures. The introduction of electrochemical inert ions in the lattice maintains the integrity of the structure, reduces the catalytic activity on the surface of the material, and reduces the reaction with the electrolyte, especially in the highly charged state, which is effective in inhibiting voltage decay and improving long-period performance. According to charge properties, element doping can be divided into cationic doping, anionic doping and cation-cationic co-doping. According to the doping site, cationic doping can be further divided into TM layer substitution (Mg^{2+}, Zn^{2+}, Al^{3+}, Co^{3+}, La^{3+}, etc.) and Li layer substitution (Na^{+}, K^{+}, etc.) Anion doping can be divided into low-priced anion doping (F^{-}, Cl^{-}, S^{2-}, etc.) and polyanion doping (SO_4^{2-}, PO_4^{3-}, etc.) [1, 2].

2.2. Orthophosphate and Pyrophosphate

The sodium ion is larger than the lithium ion; hence, the material structure has to include a larger sodium site and ion migration channel for the reversible desorption reaction. The polyanion sodium vanadium phosphate $Na_3V_2(PO_4)_3$ is a sodium ion superconductor (NASICON) material. The NASICON structure framework produces a stable sodium site, and the open three-dimensional ion migration channel promotes sodium ion diffusion. NASICON structural material, which features a rapid sodium ion transport channel and a stable three-dimensional frame structure, has been extensively researched in the field of electrode materials and solid electrolytes. Usually, these compounds often have a rhomboidal cell shape that is stable from a thermodynamic perspective. However, some $A_3M_2(PO_4)_3$ (A = Li, Na, M = Cr, Fe, Zr) materials also exist in monoclinic structures and exhibit reversible structural phase transitions at high temperatures. $Na_3V_2(PO_4)_3$ is a representative NASICON structural material, which has been widely considered as a cathode material for SIBs. $Na_3V_2(PO_4)_3$ in the NASICON structure is a covalent skeleton [$V_2P_3O_{12}$] composed of VO_6 octahedron and PO4 tetrahedron, between which a three-dimensional interconnected tunnel structure and two sodium ion distribution gap positions (M1 and M2) are formed. In SIBs, $Na_3V_2(PO_4)_3$ operates at 3.4 V and 1.6 V, respectively, based on V^{3+}/V^{4+} and V^{2+}/V^{3+} REDOX pairs, so $Na_3V_2(PO_4)_3$ can be used as both positive and cathode materials. The corresponding theoretical capacities are 118 and 50 mAh, respectively [3].

Although $Na_3V_2(PO_4)_3$ has structural stability and a high operating voltage, its low conductivity remains the most significant barrier to commercial deployment. Chen's group first reported a one-step solid phase preparation of carbon-coated $Na_3V_2(PO_4)_3$, showing a voltage platform of 3.4 V (vs. Na^{+}/Na) in organic SIBs [4]. The initial cycle charge-discharge capacities were 98.6 $mAh \cdot g^{-1}$ and 93 $mAh \cdot g^{-1}$, respectively. These results suggest that carbon coating can significantly enhance $Na_3V_2(PO_4)_3$'s sodium storage capabilities. To address this problem, researchers have employed a variety of techniques in recent years, mostly focusing on element doping, surface coating modification, and

micro-nano structure management [5, 6]. To optimize the microstructure of $Na_3V_2(PO_4)_3$ and further enhance its electronic conductivity and structural stability, various synthesis strategies were tried. Mai et al. synthesized three-dimensional $Na_3V_2(PO_4)_3$ nanofibers using a self-sacrificing template method based on hydrothermal reaction [7]. Initially, they put forth a reaction time-based outside-in morphology evolution method. In both half and full sodium ion batteries, the artificially produced $Na_3V_2(PO_4)_3$ cathode material demonstrated outstanding cycle stability and rate performance. Recently, Cao et al. prepared a series of $Na_3V_2(PO_4)_3$/C graded microspheres composed of nanosheets by hydrothermal reaction [8]. The $Na_3V_2(PO_4)_3$/C nanocrystals were firmly coated with nitrogen-doped carbon. They investigated the effects of hydrothermal reaction time and precursor concentration on the micro-nanostructure of $Na_3V_2(PO_4)_3$/C and hypothesized a mechanism for structural growth. $Na_3V_2(PO_4)_3$/C porous microspheres are an excellent cathode material for SIBs, releasing 99.3 $mAh \cdot g^{-1}$ at 100 C rate and preserving 79.1% capacity after 10,000 cycles at 20 C rate. The unique micro-nano structure design and nitrogen-doped carbon coating effectively form a double-continuous electron and ion diffusion channel, increase the contact area between the electrode and the electrolyte, and improve structural stability, resulting in excellent electrochemical performance of $Na_3V_2(PO_4)_3$/C porous microspheres.

Element doping is another effective method to optimize the electrochemical performance of $Na_3V_2(PO_4)_3$. Yang et al. doped lighter Mg to the V site in $Na_3V_2(PO_4)_3$, which could effectively improve the performance of the electrode material [9]. Compared with the undoped $Na_3V_2(PO_4)_3$, the MG-doped $Na_3V_{2-x}Mg_x(PO_4)_3$/C composite prepared by simple sol-gel method has significantly higher rate performance and cycle performance. In addition, $Na_4MnV(PO_4)_3$ cathode material shows 97% first cycle coulomb efficiency and up to 1000 cycle life, which is a promising high specific energy cathode material. More recently, they have developed a $Na_3MnZr(PO_4)_3$ SIB cathode material with a higher voltage platform [10]. To further improve the carbon coating effect and its electronic conductivity, Wang et al. introduced nitrogen doping into the carbon coating layer [10]. The electrochemical characteristics of nitrogen-doped carbon-coated $Na_3V_2(PO_4)_3$ cathode materials are obviously improved especially the rate performance. In addition, they explored in detail the effect of nitrogen atom doping at different locations on electrochemical properties, and the results showed that nitrogen doping can introduce some flaws in the carbon-coated layer and promote the transport and storage of Na^+. Polyvalent ion doping at the V position (such as Ni^{2+}, Cr^{3+}, Al^{3+}) and univalent ion doping at the Na position (such as Li^+, K^+) can regulate the electronic structure and ion diffusion channel of $Na_3V_2(PO_4)_3$.

3. Anode Material

3.1. Carbon-Based Anode

Carbon materials are carbon-rich materials formed mainly by the sp^2 hybridization of carbon atoms. Due to the diversity of sp^2 hybridization bonds, carbon materials can have a wide range of micromorphologies and structures. Carbon materials' salt storage performance is highly dependent on their microstructure.

3.1.1. Soft carbon

Soft carbon is a special kind of carbon material. It is an internal carbon microcrystalline. Carbon sheets have short-range order-long-range disordered stacking features, indicating that they are turbostratic structures. This structure has a better carbon layer arrangement than hard carbon, which results in enhanced electrical conductivity. Soft carbon can be transformed into high graphitized carbon after high-temperature heat treatment (above 2000 °C), so soft carbon is also known as graphitized carbon; its main form of existence is petroleum or coal series coke, and it is rich in dense aromatic hydrocarbons (coal pitch, petroleum pitch, or mesophase asphalt, etc.) after carbonization. Tirado et al. studied in detail the sodium storage properties of petroleum coke with different textures and microstructure and found that coke with smaller carbon microcrystalline size had better sodium

storage properties [11]. The study of Ji et al. shows that by using PTCDA as raw material and selecting appropriate preparation conditions, high-rate soft carbon anode with excellent properties can be produced [12]. In addition, the main sodium storage capacity of these soft carbons is concentrated above 0.2 V, thus effectively avoiding the formation of sodium dendrites.

Off-site X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) confirmed that the intermediate distance of soft carbon rose from 0.36 to 0.42 nm during the sodium storage procedure. Ji et al. then investigated the structure changes of soft carbon during sodium storage in detail using in-situ TEM and XRD [13]. The results reveal that the intercalation of sodium ions in the layered structure causes the layers to expand, with some sodium ions trapped at the intercalation site. The study also discovered that soft carbon is more reversible than hard carbon materials in the slope zone where sodium is stored. As a result, soft carbon materials demonstrate excellent cycle performance and rate retention during the salt storage process.

3.1.2. Hard carbon

The carbon microcrystals in hard carbon have less carbon lamellar stacking along the C-axis direction and are generally arranged in random orientation. There are more nanovoids in hard carbon, which can better accommodate active ions for electrochemical energy storage. Hu et al. studied in detail the effect of heat treatment temperature on the sodium storage performance of hard carbon microspheres, and the data showed that the hard carbon microspheres carbonized at 1600 °C had the highest platform capacity (220 $mAh \cdot g^{-1}$) and excellent cycling performance [14]. By matching with P_2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ cathode materials, the full battery shows a 3.5 V operating voltage and excellent cycle performance.

Current research focuses on the mechanism of sodium storage in hard carbon materials. The adsorption of sodium ions at the surface-active site, the filling or adsorption mechanism of sodium storage in the nanopore, and the interlayer embedding mechanism of sodium storage are the three main methods of storing sodium in hard carbon materials. Diverse perspectives exist among researchers regarding the mechanism of sodium storage and the associated area within a given volume-voltage curve. The primary problem is the attribution of sodium storage techniques in slope and platform regions, even though the mechanism of sodium storage in hard carbon materials is still up for debate. For the mechanism of sodium storage in hard carbon, more researchers are still needed to establish a better and more accurate sodium storage model through advanced characterization techniques.

3.2. Phosphorus-Based Materials

Hard carbon is the most commercially promising anode material in the field of SIBs. However, the low operating voltage of hard carbon materials with the intercalation mechanism of sodium storage makes it easy to generate sodium dendrites, resulting in security risks. At the same time, its theoretical capacity is very limited. The materials that store sodium by alloying mechanism have a high theoretical capacity and safe operating voltage and, at the same time, have excellent kinetics of sodium embedding/sodium removal reaction to ensure the energy density and power density of SIBs. At present, in the reported high-capacity alloy anode materials, Phosphorus (P) can form Na_3P with Na^+ through the three-electron transfer alloy mechanism, so it has a very high theoretical capacity of 2596 $mAh \cdot g^{-1}$. At the same time, the abundant reserves make phosphate-based materials become one of the anode materials for SIBs with great practical application prospects.

3.2.1. Red phosphorus

As an anode material for SIBs, red phosphorus has many advantages. Its theoretical capacity is as high as 2596 $mAh \cdot g^{-1}$, which is 12 times that of the most widely used hard carbon anode materials at present. Secondly, the global phosphorus storage is rich, and the price is low, which is conducive to its large-scale practical use. In addition, the REDOX potential (0.4V-Na /Na^+) of the red phosphate-based anode material is relatively safe, so it can avoid the production of sodium dendrites in the charge and discharge process, which may cause safety risks. However, the poor conductivity of red

phosphorus, accompanied by a large volume change during the charge and discharge process, resulting in low coulomb efficiency and rapid capacity decay, seriously hindered the development and application of red phosphorus in SIBs. At present, the volume expansion and electrical conductivity of phosphate-based anode materials can be effectively improved through various strategies such as structure size control, nanocrystallization and composite with conductive buffer materials.

3.2.2. Black phosphorus

In recent years, as one of the two-dimensional materials, the application of black phosphorus (BP) in SIBs has been an attentional topic. Black phosphorus not only has the same high theoretical specific capacity (2596 $mAh \cdot g^{-1}$) as red phosphorus but also has superior electrical conductivity. In addition, the solubility of black phosphorus in the electrolyte is low, and it has a layered orthogonal crystal structure, and the interlayer distance is significantly higher than that of graphite. Black phosphorus is a potential anode material for high-capacity SIBs due to its wide layer spacing and efficient charge transport properties [15]. Despite the above advantages, the large volume expansion of black phosphorus during the charge-discharge cycle still leads to poor cycle stability and rate performance. Combining with carbon materials is an effective tactic to improve these defects. Carbon materials can be prepared into a variety of structures and sizes according to demand, thus alleviating their anisotropic volume expansion.

3.2.3. Metal phosphorus

Phosphorus becomes latent due to its low cost and high theoretical capacity. However, its defects, such as poor electrical conductivity and high volume expansion rate make its actual capacity much lower than the theoretical capacity and limited cycle life. As mentioned above, its inherent defects can be effectively overcome through structural size regulation or composite with other materials, especially carbon materials. More and more studies have shown that the strategy of combining phosphorus with other conductive metal elements to form metal phosphates can also effectively improve the electrochemical performance and stability of phosphate-based electrodes. This is because part of the metal phosphide can be converted into pure metal elements in the process of sodium removal, thereby preventing the powder of the material caused by volume expansion while improving the electrical conductivity of the electrode [16].

4. Electrolyte Innovations and Enhancements

Although researchers have actively developed sodium oxide ion solid electrolytes to achieve high ionic conductivity and electrochemical stability, the material's ionic conductivity at room temperature is still insufficient for human needs, prompting researchers to seek alternatives. Sulfide solid electrolytes are among the most promising alternative electrolytes for a variety of reasons. The electrostatic force between sulfur and sodium ions is 62-70 times smaller than that of oxygen due to the sulfur atom's large radius and low electronegativity. Because of this, sulfide electrolytes typically behave faster than oxide electrolytes.

At the same time, sulfide electrolytes can be synthesized at lower temperatures than oxide solid electrolytes, lowering manufacturing costs. In the actual assembly of the battery, to achieve good interface contact, the oxide solid electrolyte generally needs hot pressing treatment. In contrast, the sulfide solid electrolyte only needs cold pressing treatment, which can make the electrolyte and the electrode material maintain good contact, thereby reducing industrial production costs. [17].

5. Conclusion

SIBs have been regarded as an ideal system for large-scale energy storage systems after LIBs because of their abundant raw material resources and low prices. Therefore, the exploration of sodium storage electrode materials with abundant resources, economic and environmental protection and

excellent electrochemical properties has become a research hotspot. Although phosphate cathode materials have a good application prospect, in theory, defects such as poor electronic conductivity and low capacity limit their wide application.

In the future, efforts should be made in the cathode materials of polyanionic phosphate systems, including the development of new high-specific energy phosphate cathode materials and a study on the electrochemical mechanism of phosphate cathode materials. With the help of a series of in-situ battery characterization technologies, the phase transformation and interface action mechanism during the working process of electrode materials were analyzed, and the internal relationship between the structure, composition and morphology of micro and nanoelectrode materials and their electrochemical properties was explored, providing more accurate and scientific guidance for electrode material optimization and battery system optimization. Development of high-pressure resistant electrolytes adapted to phosphate cathode materials. The effects of electrolyte composition, concentration and additive on electrolyte activity and electrochemical stability window were studied. Development of sodium-ion all-battery. The interaction between the positive phosphate electrode, the electrolyte, and the anode, the electrochemical performance of the whole battery system in high and low-temperature environments, and the compatibility and matching were studied.

For cathode materials, soft and hard carbon materials with low graphitization degrees have been widely concerned and studied because of their high sodium storage activity, acceptable sodium storage capacity and excellent cycling and magnification properties. Because of its unique microstructure and morphology, new carbon materials have high sodium storage capacity and rate performance, so it is the future development direction of high-power carbon-based sodium storage anode materials. Considering that many factors such as cycle life, energy density, power density and manufacturing cost need to be comprehensively investigated and balanced in practical application, at present, only low-cost hard carbon anode is the best choice for practical application of SIBs. In future research, improving SEI stability of hard carbon materials, increasing coulomb efficiency during sodium storage, improving the electrical conductivity of hard carbon, and reducing voltage lag during sodium storage will become urgent problems to be solved in practical applications.

References

[1] Zhu Changbao, Kopold Peter, van Aken Peter A., et al. High power-high energy sodium battery based on threefold interpenetrating network. Advanced Materials, 2016, 28(12): 2409-2416.

[2] Jian Zelang, Zhao Liang, Pan Huilin, et al. Carbon coated Na_3V_2 $(PO_4)_3$ as novel electrode material for sodium ion batteries. Electrochemistry Communications, 2012, 14(1): 86-89.

[3] Fang Yongjin, Zhang Jiexin, Xiao Lifen, et al. Phosphate framework electrode materials for sodium ion batteries. Advanced Science, 2017, 4(5): 1600392.

[4] Chen Shuangqiang, Wu Chao, Shen Laifa, et al. Challenges and perspectives for NASICON-type electrode materials for advanced sodium-ion batteries. Advanced Materials, 2017, 29(48): 1700431.

[5] Yuan Yong, Wei Qingyuan, Yang Shaokang, et al. Towards high-performance phosphate-based polyanion-type materials for sodium-ion batteries. Energy Storage Materials, 2022, 50: 760-782.

[6] Rajagopalan Ranjusha, Zhang Zhengna, Tang Yougen, et al. Understanding crystal structures, ion diffusion mechanisms and sodium storage behaviors of NASICON materials. Energy Storage Materials, 2021, 34: 171-193.

[7] Ren Wenhao, Zheng Zhiping, Xu Chang, et al. Self-sacrificed synthesis of three-dimensional Na_3V_2 $(PO_4)_3$ nanofiber network for high-rate sodium–ion full batteries. Nano Energy, 2016, 25: 145-153.

[8] Li Hui, Yu Xiqian, Bai Ying, et al. Effects of Mg doping on the remarkably enhanced electrochemical performance of $Na_3V_2(PO_4)_3$ cathode materials for sodium ion batteries. Journal of Materials Chemistry A, 2015, 3(18): 9578-9586.

[9] Gao Hongcai, Seymouret Ieuan D., Xin Sen, et al. Na_3MnZr $(PO_4)_3$: a high-voltage cathode for sodium batteries. Journal of the American Chemical Society, 2018, 140(51): 18192-18199.

[10] Klee Rafael, Maciej Wiatrowski, Aragón María J., et al. Improved surface stability of C+M_xO_y@$Na_3v_2(PO_4)_3$ prepared by ultrasonic method as cathode for sodium-ion batteries. ACS Applied Materials & Interfaces, 2017, 9(2): 1471-1478.

[11] Alcántara Ricardo, Pedro Lavela, Ortiz Gregorio F., et al. Electrochemical, textural and microstructural effects of mechanical grinding on graphitized petroleum coke for lithium and sodium batteries. Carbon, 2003, 41(15): 3003-3013.

[12] Luo Wei, Jian Zelang, Xing Zhenyu, et al. Electrochemically expandable soft carbon as anodes for Na-ion batteries. ACS Central Science, 2015, 1 (9): 516-522.

[13] Jian Zelang, Bommier Clement, Luo Langli, et al. Insights on the mechanism of Na-ion storage in soft carbon anode. Chemistry of Materials, 2017, 29(5): 2314-2320.

[14] Li Yunming, Hu Yong-Sheng Hu, Qi Xingguo, et al. Advanced sodium-ion batteries using superior low cost pyrolyzed anthracite anode: Towards practical applications. Energy Storage Materials, 2016, 5: 191-197.

[15] Bai Linyi, Sun Liqun, Wang Yang, et al. Solution-processed black phosphorus/PCBM hybrid heterojunctions for solar cells. Journal of Materials Chemistry A, 2016, 5(18): 8280-8286.

[16] Li Wei-Jie, Chou Shu-Lei, Wang Jia-Zhao, et al. A new, cheap, and productive FeP anode material for sodium-ion batteries. Chemical Communications, 2015, 51(17): 3682-3685.

[17] Chi Xiaowei, Liang Yanliang, Hao Fang, et al., Tailored organic electrode material compatible with sulfide electrolyte for stable all-solid-state sodium batteries. Angewandte Chemie, 2018, 57(10): 2630-2634.