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Sodium ion (Na^+) batteries – a comprehensive review

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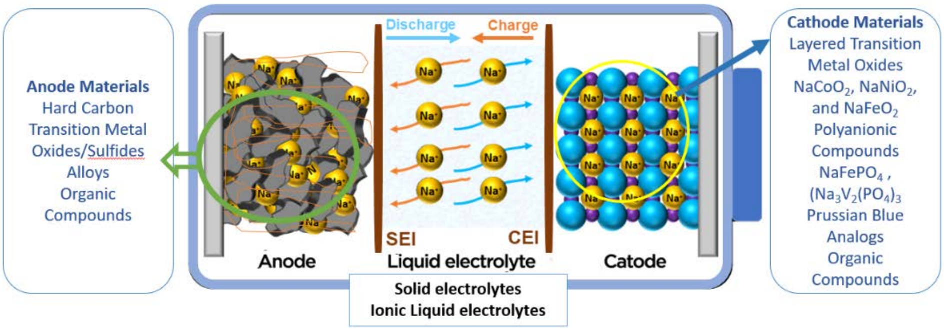
Review

ABSTRACT



Sodium-ion batteries (SIBs) have emerged as a promising alternative to lithium-ion batteries (LIBs) due to the abundant availability and low cost of sodium. Recent advances in SIB technology have focused on enhancing the performance, safety, and cost-effectiveness of these batteries. In line to improve the current output from Sodium ion batteries, a significant progress has been made in the development of high-capacity anode and cathode materials, including hard carbon, sodium titanium phosphate, layered transition metal oxides, and polyanionic compounds. The design and evolution new electrolyte compositions and the design of advanced separators for battery electrolytes have further improved the stability and efficiency of SIBs. The larger size of sodium ion in comparison to lithium ion pose difficulty in movement of ions, however, using density mitigation protocols have assisted in better cycle life of batteries with higher energy densities. Additionally, developments in new solid-state electrolytes with novel cell architectures is helping in improving in performance of SIBs. Despite these advancements, challenges such as lower energy density and shorter cycle life compared to LIBs remain. Nevertheless, ongoing research and development are expected to address these issues, positioning SIBs as a viable option for large-scale energy storage applications, including grid storage and electric vehicles. This review highlights the point-wise progress in SIB technology and discusses the future directions and potential of SIBs in the energy storage landscape.

Keywords: Na ion batteries, solid electrolytes, battery life, energy capacity, polymer cathode.

INTRODUCTION

The increasing demand for efficient, sustainable, and cost-effective energy storage solutions has spurred significant interest in the development of alternative battery technologies. Among these, sodium-ion batteries (SIBs) have emerged as a promising contender, offering several advantages over the widely used lithium-ion batteries (LIBs).[1,2] Sodium, as the sixth most abundant element in the Earth's crust, presents a more sustainable and less expensive resource compared to lithium. This abundance translates into potential cost reductions and enhanced scalability for large-scale applications, including grid storage and electric vehicles.[3,4] As the global demand for efficient and sustainable energy storage solutions continues to rise, particularly for applications such as grid storage and electric vehicles, SIBs offer a potentially more sustainable and economically viable option.[5]

The fundamental principles of SIBs are similar to those of LIBs, involving the movement of sodium ions between the anode and cathode through an electrolyte during charge and discharge cycles. The transition from lithium to sodium presents unique challenges, primarily due to the larger ionic radius and different electrochemical properties of sodium. These differences necessitate the development of new materials and strategies to achieve competitive performance metrics in terms of energy density, cycle life, and safety.[6]

Recent advances in SIB technology have focused on addressing these challenges through innovative approaches in material science, electrolyte composition, and cell design. Researchers have made notable progress in developing high-capacity anode and cathode materials, such as hard carbon, sodium titanium phosphate, layered transition metal oxides,[7] and polyanionic compounds. Advances in anode materials such as hard carbon, sodium titanium phosphate, and various alloys have led to significant improvements in capacity and stability. Similarly, breakthroughs in cathode materials, including layered transition metal oxides and polyanionic compounds, have

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enhanced the energy density and cycle life of SIBs. Enhancements in electrolyte formulations, including solid-state electrolytes, have improved the stability and efficiency of SIBs, while advancements in binders and separators have further optimized their performance.[6]

Recently, research on sodium-ion batteries (SIBs) with a wide temperature range of service performance has significantly advanced, offering deeper insights into their behavior at various temperature ranges. To achieve high capacity and good cyclability, highly reversible cathode materials involving the interstitial introduction of Na^+ are essential. These materials include Prussian Blue analogs (PBAs), polyanionic compounds, organic compounds, transition metal oxides, and NASICON (Na superionic conductor) types.[8]

Additionally, significant progress has been made in the development of anodes for SIBs, utilizing carbonaceous materials, transition metal oxides (or sulfides), intermetallic compounds, and organic compounds. The electrolyte, serving as a crucial medium for internal communication within the battery, is developed and optimized alongside the research on cathode and anode materials. Huang et al. described typical electrolytes and interface models for SIBs, encompassing both liquid and solid states with varied components, properties, and sodium-ion transport mechanisms.

Research focused on SIBs tailored to specific temperature ranges - such as room, high, and low temperatures - has grown alongside the increasing volume of literature on SIBs. The development and enhancement of cost-effective SIBs extend beyond chemistry and materials science, involving fields like crystallography, polymer science, metallurgical engineering, and even disciplines like business economics and thermodynamics. However, due to the complexity of battery systems, the non-equilibrium nature during charge/discharge processes, and the imperfections in non-equilibrium theoretical mechanisms of electrochemistry, reports on key scientific issues related to ion diffusion dynamics and electrode surface non-equilibrium reaction kinetics are limited.

Similar to lithium-ion batteries (LIBs), SIBs operate on a reversible ion shuttling mechanism between two electrodes, facilitated by the electrolyte in a “rocking chair” process. Challenges in ensuring operational safety, managing high reactivity, preventing Na dendritic growth, and mitigating significant volume changes pose obstacles to stable operation. Room temperature (RT) SIBs with metal sodium anodes and flammable organic solvent electrolytes face serious safety issues. However, the introduction of non-flammable, highly-fluorinated structures as bridge solvents has enabled superior miscibility in fluorinated carbonate electrolytes. Dendrite growth, which leads to electrical shorting and cell failure, is mainly due to the cycling instability of the solid electrolyte interface (SEI) on the Na metal anode. Therefore, comprehensive strategies involving electrolyte formulation, artificial SEI engineering, and current collector design have been implemented to stabilize Na metal and permit its long-term operation at RT. However, the performance of SIBs at low temperatures (LT) requires further study and summarization. Given the importance of LT battery operation for applications such as electric vehicles, large-scale energy storage in extreme weather conditions, and space missions, it is urgent to explore sodium behavior at low temperatures.

Despite the progress, SIBs still face challenges such as lower energy density and shorter cycle life compared to LIBs. However, ongoing research and development efforts are steadily addressing these issues, bringing SIBs closer to commercial viability. This discussion provides an overview of the significant strides made in the field of sodium-ion batteries, highlighting the recent technological advancements and ongoing research efforts. By examining the current state of SIB development, this review will elucidate the potential of sodium-ion batteries to become a key player in the future landscape of energy storage solutions.

HISTORY OF SODIUM ION BATTERY

The reversible electrochemical intercalation reaction of layered TiS_2 with lithium in a Li/ TiS_2 cell was first reported by Whittingham in 1976.[9] Both sodium and lithium were found to be capable of intercalating in TiS_2 and other transition-metal dichalcogenides.[10] However, the Li/ TiS_2 cell couldn't be developed into a functional device due to the low open-circuit voltage of the TiS_2 cathode (≈2.2 V versus Li^+/Li) and the instability of the metallic lithium anode.

To address these cathode issues, Goodenough and colleagues proposed a family of layered metal-oxide compounds in the 1980s.[11,12] These compounds had the chemical formula $LiMeO_2$ for lithium and $NaMeO_2$ for sodium (Me = Co, Ni, Cr, Mn, or Fe). Delmas and colleagues' pioneering work in the early 1980s led to the discovery of $NaMeO_2$ compounds.[13,14] Notably, Goodenough's group found that $LiCoO_2$ (LCO) had an open-circuit voltage of 4.0 V, almost double that of TiS_2. In general, the electrochemical properties of lithium-based compounds proved superior to those of sodium-based compounds.

Metallic lithium or sodium remained the preferred anode materials. However, these highly electropositive metals reacted with the electrolyte, causing cell instability. Uncontrolled dendrite growth during plating and stripping cycles led to internal short circuits and battery fires, making metal anodes unsafe. Scrosati proposed using a low-voltage intercalation anode as a safer alternative, marking the birth of the "rocking-chair" battery, where ions shuttle between two intercalation electrodes.[15] Yazami and Touzain discovered that carbonaceous materials could intercalate lithium at a low voltage and high gravimetric capacity,[16] which allowed Yoshino to create the first commercialized lithium-ion battery (LIB) using a soft carbon anode and $LiCoO_2$ cathode in 1991.[17,18] In contrast, sodium intercalation in soft carbons and graphite resulted in significantly lower capacities, hindering the commercial prospects of sodium-ion batteries (SIBs).[19]

Following Sony's commercialization of LIBs,[17,18] SIB research saw a decline between 1990 and 2000,[20] while the market for LIBs grew rapidly. The rising cost and ethical concerns around cobalt extraction spurred the search for cheaper alternatives,[21] leading to the development of new metal-oxide structures like spinel $LiMn_2O_4$ (LMO)[22] and olivine $LiFePO_4$ (LFP).[23] Co-substitution in nickel oxides enhanced structural stability, resulting in mixed metal oxides like $LiNi_{1-x-y}Mn_xCO_yO_2$ (NMC) and $LiNi_{1-x-y}Co_xAl_yO_2$ (NCA).[24,25]

Despite the decline in SIB research, there were advancements in high-temperature sodium batteries,[26] such as the sodium-sulfur (NaS) systems developed by Ford and a Japanese consortium,[27] and the sodium-nickel chloride (ZEBRA) cells.[28] These systems, operating at high temperatures, found applications in stationary grid energy storage, e-mobility, and space missions.[29] However, their high operating temperatures posed challenges like corrosion and low energy efficiency.

Interest in room-temperature SIBs was rejuvenated in 2000 when Stevens and Dahn discovered Na intercalation in hard carbon (HC),[30] which offered a low voltage and high gravimetric capacity close to that of graphite in LIBs. This discovery renewed research interest but did not immediately drive commercialization. Patent filings for SIBs only began to rise significantly around 2012, driven by the supply risk associated with LIB materials. In recent developments, there are many startup companies coming up with new idea of real application-oriented developments in the field of Na-ion batterieis. In 2015, the first "18650" cylindrical SIB cells were developed by the French network for electrochemical energy storage (RS2E), a collaboration between CNRS, CEA, and the Collège de France. Several startups, such as Faradion Limited, Tiamat, and HiNa, have since advanced the commercialization of SIBs. Faradion, founded in 2011, is developing SIB pouch cells using a proprietary layered metal-oxide cathode and commercial HC anode. Tiamat, a spinoff from RS2E founded in 2017, focuses on cylindrical SIB cells with a polyanionic compound cathode and HC anode. HiNa, a spinoff from the Chinese Academy of Sciences, produces SIB pouch cells with a proprietary cathode and anthracite-based HC anode. In 2019, HiNa announced a 100 kWh SIB module installation in Liyang, China, demonstrating the feasibility of large-scale sodium-based energy storage.

Chemistry of Sodium ion battery

The fundamental chemistry of SIBs involves the movement of sodium ions (Na+) between the anode and cathode through an electrolyte during the charge and discharge cycles (Figure 1). Here is listed key chemical components and mechanisms that underpin the operation of SIBs.[31]

Electrodes materials:

Since 2010, there has been significant progress in SIB cathode materials, with a surge in reported materials between 2010 and 2013. The main families of SIB cathode materials include (1) layered metal oxides, (2) polyanion compounds, and (3) Prussian blue analogs (PBA). Researchers aim to create cost-effective SIBs using earth-abundant elements like iron, manganese, and magnesium. HC remains the prominent anode choice due to its cheap and abundant precursors.

Anode Materials

The anode in SIBs is typically made of materials that can reversibly accommodate sodium ions.[32] Common anode materials include:

1. **Hard Carbon**:

Hard carbon is one of the most widely used anode materials due to its high capacity, good cycling stability, and relatively low cost. It stores sodium ions through intercalation and adsorption mechanisms.[33] Hard carbon has emerged as one of the most promising anode materials for sodium-ion batteries (SIBs) due to its unique properties and compatibility with sodium ions. The precursors for hard carbon, such as biomass, polymers, and petroleum by-products, are abundant and inexpensive, making hard carbon a cost-effective choice for SIBs. Using renewable biomass sources for hard carbon production can contribute to the sustainability and environmental friendliness of SIBs. Hard carbon's disordered structure and abundant active sites are well-suited for accommodating the larger sodium ions compared to lithium ions. Hard carbon forms a stable solid electrolyte interface (SEI) layer during the initial cycles, which helps in maintaining the long-term cycling stability of the battery.[34]

The characteristics of hard carbon as an anode material for SIBs are:[35]

Structure: Hard carbon is an amorphous carbon material that lacks the long-range order of crystalline graphite. It consists of disordered carbon layers with micropores and voids that can accommodate sodium ions.

Sodium Storage Mechanism: The sodium storage mechanism in hard carbon involves a combination of intercalation and adsorption processes. Sodium ions first intercalate into the graphitic layers at low voltage and then fill the micropores and voids at higher capacities.

Capacity: Hard carbon can achieve a high gravimetric capacity of approximately 300 mAh/g, which is comparable to the capacity of graphite in lithium-ion batteries (372 mAh/g).

Voltage Profile: The voltage profile of hard carbon during sodium insertion shows a distinct plateau around 0.1 V versus Na/Na^+, indicating stable intercalation. There is also a sloping region associated with sodium adsorption in the pores and defects.[33]

Challenges of Hard Carbon Anodes

Initial Coulombic Efficiency: Hard carbon anodes often exhibit low initial coulombic efficiency (ICE), meaning that the first charge cycle consumes a significant amount of sodium ions to form the SEI layer, reducing the available capacity.

Voltage Hysteresis: The voltage hysteresis between charge and discharge cycles can lead to energy inefficiencies and reduced overall battery performance.

Optimization of Microstructure: Achieving the optimal balance between porosity, surface area, and graphitic domains is crucial for maximizing the capacity and rate performance of hard carbon anodes.[31]

Researchers are exploring various synthesis methods to control the microstructure and enhance the sodium storage capabilities of hard carbon. Techniques include pyrolysis of biomass, templating methods, and chemical vapor deposition. Surface modification and functionalization strategies, such as coating with conductive polymers or doping with heteroatoms (e.g., nitrogen, phosphorus), are being investigated to improve the electrochemical performance and reduce voltage hysteresis.[36]

Developing hard carbon-based composite materials by combining hard carbon with other materials, such as metal oxides or sulfides, can enhance the overall performance by providing additional active sites and improving electronic conductivity.[37]

Electrolyte Optimization: Tailoring the electrolyte composition, including the use of additives, can help in forming a more stable SEI layer, thereby improving the ICE and long-term cycling stability of hard carbon anodes.

Hard carbon anodes hold significant potential for the development of efficient and cost-effective sodium-ion batteries. Ongoing research and advancements in material synthesis, surface modification, and composite development are crucial for addressing the existing challenges and optimizing the performance of hard carbon anodes. With continued innovation, hard carbon-based SIBs could play a pivotal role in the future of sustainable and scalable energy storage solutions.[32]

2. Transition Metal Oxides/Sulfides:

Metal oxides and sulfides are gaining attention as promising anode materials for sodium-ion batteries (SIBs) due to their high theoretical capacities and diverse sodium storage mechanisms. Materials such as sodium titanate ($NaTiO_2$), tin sulfide (SnS_2), and iron sulfide (FeS_2) have shown promise due to their high theoretical capacities. These materials store sodium ions through conversion reactions.

Characteristics of Metal Oxides/Sulfides

Structure and Composition: Metal oxides and sulfides have varied structures, including layered, spinel, and amorphous phases. Common materials include tin oxide (SnO_2), titanium dioxide (TiO_2), iron oxide (FeO_2), molybdenum disulfide (MoS_2), and tin sulfide (SnS_2). Many metal oxides and sulfides are derived from abundant and inexpensive precursors, making them cost-effective for large-scale production. The variety of metal oxides and sulfides available allows for tailoring material properties to meet specific performance requirements.

Sodium Storage Mechanisms: The sodium storage in these materials occurs through multiple mechanisms:

- Intercalation: Sodium ions insert into the crystal lattice without significant structural changes.
- Conversion: Sodium ions react with the metal oxide/sulfide, converting it into metal and sodium oxide/sulfide, providing high capacity.
- Alloying: Some metal oxides/sulfides, like SnO_2 and SnS_2, can form alloys with sodium, further enhancing capacity.

High Theoretical Capacity: Metal oxides and sulfides offer high theoretical capacities. For instance, SnO_2 has a theoretical capacity of about 782 mAh/g, significantly higher than conventional carbon-based anodes. These materials provide significantly higher capacities compared to traditional carbon-based anodes, which is beneficial for high-energy applications.

Challenges of Metal Oxides/Sulfides

Volume Expansion: Significant volume changes during cycling, particularly for conversion and alloying materials, can lead to mechanical degradation and loss of capacity.

Cycling Stability: The repeated formation and breaking of chemical bonds in conversion reactions can cause structural instability and capacity fading over long cycles.

Electronic Conductivity: Many metal oxides and sulfides have inherently low electronic conductivity, which can limit the rate performance and overall efficiency of the battery.

Recent Advances

Nanostructuring: Creating nanostructured metal oxides/sulfides, such as nanoparticles, nanowires, and nanosheets, can enhance electronic conductivity and accommodate volume changes, improving cycling stability.

Composite Materials: Developing composites by combining metal oxides/sulfides with conductive materials (e.g., carbon nanotubes, graphene) can improve electronic conductivity and mechanical integrity.[37]

Surface Modification: Coating metal oxides/sulfides with conductive or protective layers can enhance their stability and performance by mitigating side reactions and controlling SEI formation.

Doping: Introducing dopants into metal oxides/sulfides can enhance their electronic conductivity, structural stability, and sodium ion diffusion kinetics.

Binder and Electrolyte Optimization: Optimizing binders and electrolytes to form stable SEI layers and improve electrode adhesion can further enhance the performance of metal oxides/sulfides anodes.

Notable Materials

Tin Oxide (SnO_2): SnO_2 is one of the most studied metal oxide anodes due to its high theoretical capacity. Research focuses on mitigating its volume expansion through nanostructuring and composite formation.

Molybdenum Disulfide (MoS_2): MoS_2, a layered transition metal dichalcogenide, offers excellent sodium storage capability through intercalation and conversion reactions. It is often combined with carbon-based materials to improve its conductivity and stability.

Titanium Dioxide (TiO_2): TiO_2 is known for its stability and safety, with research exploring its various polymorphs and nanostructured forms to enhance sodium storage performance.

Iron Oxide (Fe_2O_3): Fe_2O_3 is attractive due to its low cost and environmental friendliness. Research aims to improve its cycling stability and mitigate volume changes through nanostructuring and composite strategies.

Metal oxides and sulfides are promising anode materials for sodium-ion batteries due to their high capacity, abundance, and versatility. Despite challenges such as volume expansion and cycling stability, ongoing research and advancements in material design, nanostructuring, composite formation, and surface modification are driving significant improvements. These efforts are crucial for developing high-performance, stable, and cost-effective SIBs for a wide range of applications.[38]

Alloys:

Alloy-based anodes have attracted considerable interest for sodium-ion batteries (SIBs) due to their high theoretical capacities and favorable electrochemical properties. Sodium alloys with metals like tin (Sn) and antimony (Sb) offer high capacities. However, they suffer from significant volume changes during cycling, which can affect their stability.

Characteristics of **Alloy Anodes**

Composition and Structure: Alloy anodes are typically composed of metals that can form alloys with sodium. Common examples include tin (Sn), and antimony (Sb). These metals can alloy with sodium to form compounds like Na_3Sb.

Sodium Storage Mechanism: The sodium storage mechanism in alloy anodes involves the alloying and dealloying processes. During the alloying process, sodium ions react with the metal to form a sodiated alloy, while dealloying reverses this reaction.

High Theoretical Capacity: Alloys offer high theoretical capacities. For instance, tin (Sn) has a theoretical capacity of about 847 mAh/g, antimony (Sb) about 660 mAh/g, and phosphorus (P) about 2596 mAh/g, which are significantly higher than those of carbon-based anodes. This makes them suitable for high-energy applications. Many alloy materials exhibit high initial coulombic efficiency, meaning that a larger proportion of the capacity is utilized in the first cycle, reducing the loss associated with SEI formation. Alloy anodes often have stable and well-defined voltage profiles during cycling, which can improve the overall energy efficiency of the battery.

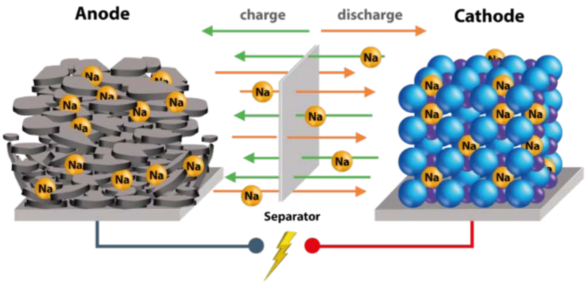

Figure 1. Functioning of Sodium ion battery.

Challenges of Alloy Anodes

Volume Expansion: Significant volume changes occur during the alloying and dealloying processes, leading to mechanical stress, particle pulverization, and loss of electrical contact, which can degrade the anode material over repeated cycles.

Cycling Stability: The mechanical degradation due to volume changes results in poor cycling stability and capacity fading over long-term operation.

Electrochemical Kinetics: Alloy materials may suffer from slow sodium ion diffusion and poor electronic conductivity, which can limit the rate performance and overall efficiency of the battery.

Recent Advances and Research Directions

Nanostructuring: Creating nanostructured alloys, such as nanoparticles, nanowires, and nanotubes, can help accommodate volume changes and enhance the mechanical integrity of the anode material, leading to improved cycling stability.

Composite Materials: Developing composites by combining alloys with conductive materials (e.g., carbon nanotubes, graphene) can improve electronic conductivity and buffer volume changes, enhancing overall performance.

Surface Coatings: Applying protective surface coatings to alloy particles can mitigate direct contact with the electrolyte, reducing side reactions and stabilizing the SEI layer.

Doping and Alloying: Introducing dopants or forming multi-component alloys can enhance the electrochemical properties, structural stability, and sodium ion diffusion kinetics of the anode material.

Binder and Electrolyte Optimization: Using advanced binders and optimizing electrolyte formulations can improve electrode adhesion, enhance SEI stability, and reduce the effects of volume expansion.

Notable Materials and Research Highlights

Tin (Sn): Tin is one of the most studied alloy anode materials due to its high theoretical capacity. Research focuses on developing nanostructured Sn and Sn-based composites to mitigate volume expansion and improve cycling stability.[39]

Antimony (Sb): Antimony offers a good balance between high capacity and moderate volume expansion. Recent studies have explored Sb nanostructures and Sb-carbon composites to enhance performance.

Phosphorus (P): Phosphorus has an exceptionally high theoretical capacity but suffers from extreme volume changes. Research efforts are directed toward creating P-based composites and nanostructures to improve its electrochemical performance.

Multi-component Alloys: Multi-component alloys, such as Sn-Sb and Sn-P, are being investigated to combine the benefits of different metals and improve overall performance.[40]

Alloy anodes hold significant potential for enhancing the performance of sodium-ion batteries due to their high capacity and stable voltage profiles. Addressing the challenges associated with volume expansion and cycling stability through advanced material design, nanostructuring, composite formation, and surface modification is crucial for realizing their full potential. Continued research and innovation in this area are essential for developing high-performance, durable, and cost-effective SIBs for various energy storage applications.[39]

Organic Compounds:

Organic materials have emerged as a promising class of anode materials for sodium-ion batteries (SIBs) due to their structural diversity, tunability, and environmental benefits. Organic anode materials, such as sodium terephthalate, offer the advantage of flexibility and environmental friendliness. Organic compounds are generally lighter than metal-based materials, contributing to the overall reduction in battery weight and improving energy density. They store sodium ions through redox reactions.

Structure and Composition: Organic anode materials are composed of carbon-based compounds, often incorporating functional groups such as carbonyls, quinones, imines, and carboxylates. Common examples include polyimides, quinones, and organic salts. The vast diversity in organic chemistry allows for the design of molecules with tailored electrochemical properties to meet specific performance requirements.

Sodium Storage Mechanism:

- Organic anodes store sodium ions through various mechanisms, including:

  -Redox Reactions: Sodium ions interact with redox-active functional groups.

  - Coordination Chemistry: Sodium ions form coordination complexes with the organic molecules.

  - Cation Intercalation: Sodium ions intercalate into the molecular structure of the organic material.

Flexibility and Tunability: The molecular structure of organic materials can be easily modified to optimize electrochemical properties, such as voltage, capacity, and cycling stability. Organic materials are typically more flexible than inorganic materials, which can help accommodate volume changes during cycling and enhance the mechanical integrity of the electrode.

Limitations:

Electrical Conductivity: Organic materials usually have lower electrical conductivity compared to inorganic materials, which can limit their rate performance and overall efficiency.

Solubility in Electrolytes: Some organic compounds may dissolve in the electrolyte, leading to capacity loss and reduced cycling stability.

Volumetric Energy Density: While organic materials offer good gravimetric energy density, their volumetric energy density can be lower than that of inorganic materials due to their lower density.

Stability: The chemical stability of organic materials under electrochemical conditions can be a concern, particularly in terms of long-term cycling and thermal stability.

Recent Advances and Research Directions

Molecular Design: Designing organic molecules with enhanced redox stability and multi-electron transfer capabilities can improve the capacity and cycling performance of organic anodes.

Polymerization: Polymerizing small organic molecules into larger polymer networks can enhance their stability and reduce solubility issues in the electrolyte.

Composite Formation: Combining organic materials with conductive additives (e.g., carbon nanotubes, graphene) can improve their electrical conductivity and mechanical strength.

Surface Functionalization: Functionalizing the surface of organic materials with specific groups can enhance their interaction with sodium ions and improve electrochemical performance.

Advanced Electrolytes: Developing new electrolytes or additives that are compatible with organic anodes can reduce dissolution issues and enhance overall battery stability.[41]

Polyimides: Polyimides are known for their excellent thermal stability and high capacity. Research focuses on optimizing their molecular structure to improve sodium storage capacity and cycling stability.

Quinones: Quinones and their derivatives are attractive due to their high theoretical capacity and rapid redox kinetics. Modifying their molecular structure can enhance their electrochemical performance.

Organic Salts: Sodium organic salts, such as sodium terephthalate and sodium rhodizonate, offer high capacities and stable cycling performance. Research aims to address their solubility and conductivity challenges.

Polyaniline (PANI): PANI and its derivatives have shown promise due to their good conductivity and capacity. Efforts are directed toward improving their structural stability and sodium storage capabilities.

Organic materials present a promising avenue for developing sustainable and high-performance anodes for sodium-ion batteries. Their structural diversity, tunability, and environmental benefits make them attractive candidates for future energy storage solutions. Addressing challenges related to conductivity, stability, and solubility through innovative molecular design, polymerization, composite formation, and electrolyte optimization will be key to unlocking the full potential of organic anode materials in SIBs. With continued research and development, organic anodes could play a significant role in advancing the field of sodium-ion batteries.[42]

CATHODE MATERIALS

The cathode materials in SIBs are crucial for determining the battery's overall energy density and stability.[43] Key cathode materials include:[44]

1. Layered Transition Metal Oxides:

Materials such as $NaCoO_2$, $NaNiO_2$, and $NaFeO_2$ are widely studied due to their high capacity and good cycling performance. They operate through intercalation/deintercalation mechanisms of sodium ions.[45]

Layered transition metal oxides are among the most promising cathode materials for sodium-ion batteries (SIBs) due to their high capacity, structural versatility, and electrochemical performance.[46] These materials, characterized by their layered crystal structures, facilitate the efficient intercalation and deintercalation of sodium ions during charge and discharge cycles. Compounds such as Na_xCoO_2, Na_xNiO_2 and Na_xFeO_2 have been extensively studied, demonstrating significant potential in achieving high energy densities.[47] The layered configuration allows for reversible sodium ion storage, contributing to the stability and longevity of the battery. Furthermore, the ability to tailor the composition by doping with various metals (e.g., manganese, nickel, cobalt) enhances the electrochemical properties and cycling stability of these cathodes. Despite their promising attributes, challenges such as phase transitions and structural degradation during cycling remain. Ongoing research focuses on optimizing the structural integrity and improving the electrochemical performance through advanced synthesis techniques and surface modifications.[48] Overall, layered transition metal oxides are at the forefront of cathode material development for SIBs,[45] offering a pathway to high-performance, sustainable, and cost-effective energy storage solutions.[49]

Na_xCoO_2 (Sodium Cobalt Oxide)

Na_xCoO_2 offers a theoretical capacity of approximately 120-160 mAh/g. This material has a well-defined layered structure that facilitates the intercalation and deintercalation of sodium ions. Sodium cobalt oxide exhibits relatively high electronic conductivity, which contributes to its electrochemical performance. The average operating voltage is around 3.0-3.4 V versus Na/Na^+, which is beneficial for achieving high energy density. Na_xCoO_2 cathodes demonstrate good cycling stability, although capacity retention can be an issue over prolonged cycles. This material shows decent rate capability, but performance may decrease at high current densities. Challenges include phase transitions and potential structural degradation during cycling, which can impact long-term performance.[20]

Na_xNiO_2 (Sodium Nickel Oxide)

Na_xNiO_2 provides a theoretical capacity of about 150-180 mAh/g. Similar to Na_xCoO_2, Na_xNiO_2 has a layered structure conducive to sodium ion intercalation. The average operating voltage is around 3.0-3.5 V versus Na/Na^+, offering high energy density. Sodium nickel oxide exhibits good thermal and electrochemical stability. Na_xNiO_2 cathodes generally show good cycling performance, but like Na_xCoO_2, they can suffer from capacity fading over time. This material exhibits good rate performance, with rapid sodium ion diffusion through the layered structure. Ongoing research is focused on mitigating issues related to phase transitions and improving the overall stability during extended cycling.[50]

Na_xFeO_2 (Sodium Iron Oxide)

Iron is abundant and inexpensive, making Na_xFeO_2 a cost-effective cathode material. Na_xFeO_2 offers a theoretical capacity of approximately 140-160 mAh/g (moderate capacity). Sodium iron oxide is environmentally benign compared to cobalt and nickel-based oxides. It also has a layered structure, which supports sodium ion intercalation. Na_xFeO_2 cathodes display good cycling stability, but their capacity retention can be lower compared to cobalt and nickel oxides. The average operating voltage is around 2.5-3.0 V versus Na/Na^+, which is slightly lower than Na_xCoO_2 and Na_xNiO_2. Sodium iron oxide generally has a lower rate capability compared to its cobalt and nickel counterparts, but efforts are being made to improve this through material modifications and nanostructuring.[39]

Na_xCoO_2, Na_xNiO_2 and Na_xFeO_2 are all promising cathode materials for sodium-ion batteries, each with unique properties and performance characteristics. While Na_xCoO_2 and Na_xNiO_2 offer higher capacities and operating voltages, Na_xFeO_2 stands out for its abundance, low cost, and environmental benefits. Research continues to address challenges such as phase transitions, structural stability, and rate performance to optimize these materials for practical applications in energy storage.[51]

2. Polyanionic Compounds:

Compounds like sodium iron phosphate ($NaFePO_4$) and sodium vanadium phosphate ($Na_3V_2(PO_4)_3$) are known for their structural stability and high voltage operation. They store sodium ions through intercalation.[52]

Polyanionic compounds have emerged as a highly promising class of cathode materials for sodium-ion batteries (SIBs), primarily due to their robust structural stability and high operating voltage.[53] These materials include phosphates, sulfates, and fluorophosphates, characterized by their polyanion frameworks (e.g. PO_4^{3-}, SO_4^{2-}, and POF_4^{2-}).[54] The inherent strength of the polyanionic groups significantly contributes to the stability of the structure during sodium ion intercalation and deintercalation processes.[55] One of the most well-known polyanionic compounds is sodium iron phosphate ($NaFePO_4$), which operates at a relatively high voltage of around 3.4 V versus Na/Na^+, providing a theoretical capacity of approximately 154 mAh/g. The high voltage results from the inductive effect of the polyanion, which stabilizes the Fe^{3+}/Fe^{2+} redox couple, thereby enhancing the overall energy density of the battery.[51]

In addition to $NaFePO_4$, other notable polyanionic compounds include sodium vanadium phosphate ($Na_3V_2(PO_4)_3$) and sodium iron fluorophosphate (Na_2FePO_4F). $Na_3V_2(PO_4)_3$ offers a theoretical capacity of about 117 mAh/g and operates at a high voltage of 3.4 V, while Na_2FePO_4F combines the advantages of both phosphate and fluoride ions, resulting in high thermal stability, safety, and a high operating voltage of 3.3 V.[56] These materials also exhibit excellent rate capability and cycling stability due to the rigid polyanionic frameworks that effectively suppress volume changes during cycling.[57] Furthermore, the presence of multiple redox-active sites within these compounds allows for multi-electron transfer processes, potentially increasing the capacity and energy density.[56]

Research into polyanionic compounds as cathode materials for SIBs continues to advance, focusing on optimizing the synthesis methods and exploring new compositions to further enhance their electrochemical performance. Techniques such as doping,[58] nanostructuring, and surface coating are being employed to improve conductivity, rate capability, and cycling stability.[57] Moreover, the use of advanced characterization tools helps in understanding the sodium storage mechanisms at a fundamental level, guiding the design of next-generation cathode materials. With their combination of high voltage, stability, and safety, polyanionic compounds hold great promise for the development of efficient and sustainable sodium-ion batteries, making them suitable for a wide range of applications, including grid storage and electric vehicles.[54]

3. Prussian Blue Analogs (PBAs):

PBAs such as $Na_2Fe(CN)_6$ are attractive due to their open framework structure, which allows for fast sodium ion diffusion. They also offer good thermal stability and high capacity.[59]

Prussian Blue Analogs (PBAs) have gained significant attention as promising cathode materials for sodium-ion batteries (SIBs) due to their open framework structure and high theoretical capacity. PBAs are a class of coordination compounds with a general formula of $A_2M[M'(CN)_6]_7.zH_2O$, where A represents an alkali metal ion (such as Na^+), M and M' are transition metals, and CN is the cyanide group. The open framework structure of PBAs facilitates fast sodium ion diffusion and provides multiple insertion sites, which contribute to their high capacity and excellent rate capability. Notably, PBAs such as $Na_{1.9}Fe[Fe(CN)_6].0.1H_2O$ and $Na_{1.9}Mn[Fe(CN)_6].0.1H_2O$ have demonstrated capacities of around 150mAh/g with good cycling stability.[59]

One of the primary advantages of PBAs is their high operating voltage, typically in the range of 3.0-3.5 V versus Na/Na^+, which is conducive to achieving high energy density. The robust and stable cubic framework of PBAs ensures minimal structural changes during the sodium intercalation and deintercalation processes, resulting in excellent cycling performance. Moreover, the presence of multiple transition metals in PBAs allows for multi-electron redox reactions, further enhancing their capacity and energy density. The tunability of the metal sites in PBAs provides a versatile platform for optimizing their electrochemical properties, making them suitable for various applications.[60]

Despite their promising attributes, PBAs face challenges related to their synthesis and purity. The presence of water molecules within the structure can lead to issues such as phase instability and capacity fading. However, recent advancements in synthesis techniques, such as controlled dehydration processes and the use of high-purity precursors, have significantly improved the performance and stability of PBAs. Additionally, coating PBAs with conductive polymers or carbon materials can enhance their electronic conductivity and overall electrochemical performance. With ongoing research and development, PBAs are poised to become a key component in the next generation of high-performance, cost-effective, and environmentally friendly sodium-ion batteries.[55]

4. Organic Compounds:

Similar to anodes, organic cathode materials are being explored for their environmental benefits and structural diversity. Organic compounds have emerged as a promising class of cathode materials for sodium-ion batteries (SIBs) due to their abundance, environmental friendliness, and structural diversity. These materials typically consist of conjugated systems with functional groups that can undergo reversible redox reactions, allowing for sodium ion storage. Common organic cathode materials include quinones, imides, and conjugated carbonyl compounds. For instance, quinones such as 1,4-benzoquinone and anthraquinone can store sodium ions through multiple electron redox reactions, providing high theoretical capacities. The flexibility in designing organic molecules enables fine-tuning of their electrochemical properties to achieve desired performance metrics.[61]

One of the key advantages of organic cathode materials is their sustainability. Derived from renewable resources, organic compounds offer a more environmentally friendly alternative to traditional inorganic cathodes. Additionally, the synthesis of organic materials often involves simpler and less energy-intensive processes, potentially lowering production costs. The lightweight nature of organic compounds can also contribute to higher specific energy densities in SIBs. Moreover, the structural flexibility of organic materials can accommodate the larger ionic radius of sodium ions, leading to better cycling stability and reduced mechanical strain during charge and discharge cycles.[61]

However, there are challenges associated with using organic compounds as cathode materials. One significant issue is their generally lower electronic conductivity compared to inorganic materials, which can limit rate performance. To address this, researchers are developing composite materials that incorporate conductive additives, such as carbon nanotubes or graphene, to enhance conductivity.[39] Another challenge is the solubility of some organic compounds in electrolytes, which can lead to capacity fading over time. Strategies to mitigate this include designing polymeric structures or using cross-linked networks that are insoluble in the electrolyte. Despite these challenges, ongoing research is making significant strides in improving the performance and stability of organic cathode materials. With continued innovation, organic compounds hold the potential to play a crucial role in the development of sustainable and high-performance sodium-ion batteries.[46]

ELECTROLYTES

The electrolyte in SIBs serves as the medium for sodium ion transport between the anode and cathode. The electrolyte chemistry significantly affects the battery's performance, safety, and stability.[62] Common types of electrolytes include:

1. Liquid Electrolytes:

Organic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), and dimethyl carbonate (DMC) are commonly used solvents. Sodium salts like $NaPF_6$, $NaClO_4$, and NaTFSI are dissolved in these solvents to provide ionic conductivity.[63]

The most commonly used solvents in SIB electrolytes are organic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), and dimethyl carbonate (DMC). These solvents are chosen for their ability to dissolve sodium salts and their electrochemical stability.[62]

The choice of sodium salt is crucial for optimizing ionic conductivity and electrochemical stability. Common salts include sodium hexafluorophosphate ($NaPF_6$), sodium perchlorate ($NaClO_4$), sodium bis(trifluoromethanesulfonyl)imide (NaTFSI), and sodium tetrafluoroborate ($NaBF_4$).[64]

2. Solid Electrolytes:

Solid-state electrolytes, including ceramic materials like NASICON[8] and polymer-based electrolytes like polyethylene oxide (PEO) with sodium salts, offer improved safety and thermal stability.[41]

Ceramic Electrolytes: Materials such as NASICON (Na superionic conductor)[65] and β-alumina are prominent due to their high ionic conductivity and stability. They are particularly suitable for high-temperature applications and all-solid-state SIBs.

Polymer Electrolytes: These are flexible and can be used in solid-state batteries. Polyethylene oxide (PEO) combined with sodium salts is a common choice, providing good ionic conductivity at elevated temperatures.[41]

3. Ionic Liquid Electrolytes:

Ionic liquids are non-flammable and thermally stable, making them attractive for high-temperature applications.[66] They provide high ionic conductivity and electrochemical stability.[67]

Ionic liquids, which are salts in the liquid state at room temperature, are used to enhance the safety and thermal stability of SIBs. They have low volatility and high ionic conductivity, making them attractive for high-temperature applications.[67,68]

Chemistry of SIB Electrolyte

The electrolyte is a critical component in sodium-ion batteries (SIBs), serving as the medium through which sodium ions (Na+) move between the anode and cathode during charge and discharge cycles. The chemistry of the electrolyte significantly influences the battery's overall performance, including its capacity, cycle life, thermal stability, and safety. Here, we explore the key aspects and recent advances in the chemistry of SIB electrolytes.

Mechanisms

1. Intercalation/Deintercalation:

In this mechanism, sodium ions are reversibly inserted and removed from the host material's lattice structure without significant structural changes. This process is common in both anode and cathode materials.

2. Conversion Reactions: Conversion reactions involve the formation and decomposition of new phases during the cycling process. Transition metal oxides/sulfides typically operate through this mechanism, offering high capacities but facing challenges with volume changes.

3. Alloying/Dealloying: This mechanism involves the formation of alloys between sodium and the host material, such as tin or antimony. These reactions provide high capacity but also lead to significant volume expansion and contraction.

High ionic conductivity is essential for efficient ion transport between the electrodes. Liquid electrolytes generally offer higher ionic conductivity compared to solid electrolytes, but advances in solid-state materials are closing this gap.

The electrolyte must remain stable over a wide voltage range to prevent decomposition during the battery’s operation. Additives such as fluoroethylene carbonate (FEC) are often used to enhance the stability and form a robust solid electrolyte interface (SEI).

Thermal Stability: The electrolyte must withstand various temperature conditions without degrading. This is particularly important for applications in electric vehicles and large-scale energy storage, where temperature fluctuations are common.

Non-flammability and low toxicity are critical for the safe operation of SIBs. Ionic liquids and certain solid electrolytes provide enhanced safety features compared to conventional liquid electrolytes.

Recent Advances

Electrolyte Additives:

Additives such as FEC, vinylene carbonate (VC), and various ionic liquids have been researched to improve the formation of stable SEI layers, enhancing the longevity and safety of the batteries.

Hybrid Electrolytes:

Combining solid and liquid electrolytes, or different types of solid electrolytes, can optimize the properties of each to enhance overall battery performance.[69]

Novel Electrolytes:

Research into new compounds and formulations, including highly fluorinated solvents and advanced ionic liquids, continues to push the boundaries of SIB electrolyte chemistry, aiming for higher performance and greater safety.

CHALLENGES AND FUTURE DIRECTIONS

There are few areas that pose challenges to researchers for designing and development of materials for sodium ion batteries. These includes: 1. Compatibility with Electrodes: As for any new materials design, it is necessary to ensure the compatibility of electrolyte with both the anode and cathode materials to prevent unwanted side reactions.[70] 2. Cost Reduction: It is always a market development challenge by a cost-effective electrolyte material and scalable manufacturing processes. 3. Low-Temperature Performance: For wider applicability and reach of developed sodium ion battery design, it is necessary to improve the ionic conductivity and stability of electrolytes at low temperatures for broader application in various climates and environments,[71] including electric vehicles and grid storage in cold climates. 4. Cycling Stability: Ensuring long-term cycling stability, particularly for anode materials that undergo significant volume changes, remains a challenge. 5. Energy Density: Increasing the energy density of SIBs to match or exceed that of LIBs is a key research focus, particularly through the development of high-capacity materials. 6. Safety: Improving the safety of SIBs, especially in terms of preventing dendritic growth and enhancing thermal stability, is essential for their widespread adoption.[70,72]

CONCLUSION

In conclusion, the chemistry of sodium-ion batteries involves a complex interplay of materials and mechanisms that collectively determine their performance. Advances in anode and cathode materials, electrolyte formulations, and understanding of the underlying electrochemical processes are driving the development of next-generation SIBs with improved capacity, stability, and safety. The chemistry of sodium-ion battery electrolytes is a dynamic field of research that holds the key to unlocking the full potential of SIBs. Advances in this area will pave the way for more efficient, safe, and economically viable energy storage solutions.

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CONFLICT OF INTEREST STATEMENT

Author do not have conflict of interest for this review work.

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