RESEARCH ARTICLE

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Unlocking the Potential of Sodium Ion Batteries: A Comprehensive Review

Agniv Chandra [a,*]

[a] Institute of Natural Sciences and Applied technology, Kolkata-700032, India

* Corresponding Author: punkniv93@gmail.com

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Abstract: Sodium ion batteries (SIBs) have recently emerged as a promising alternative to lithium-ion batteries (LIBs) due to their abundance, cost-effectiveness, and similar electrochemical properties. This review provides an in-depth analysis of the science behind it and the technology to explore, the scope for commercialization, prospects, advantages, and disadvantages of SIBs in the realm of energy storage technology. Through a critical examination of current research and developments, this article elucidates the potential of SIBs in revolutionizing the energy storage landscape.

Keywords: Sodium ion Battery, Pouch cell, Prussian Blue Analogues, Faradion

1. Introduction

In recent years, the escalating demand for energy storage solutions has propelled extensive research into alternative battery technologies. Sodium ion batteries (SIBs) have garnered significant attention as a viable contender to lithium-ion batteries (LIBs) owing to the abundant global reserves of sodium and their analogous electrochemical properties. This review aims to delve into the scope, prospects, advantages, and disadvantages of SIBs, shedding light on their transformative potential in addressing energy storage challenges. Sodium-ion batteries, abbreviated as NIBs, SIBs, or Na-ion batteries, are a class of rechargeable batteries that utilize sodium ions (Na^+) as their charge carriers. While their operational principles and cell architecture in some cases mirror those of lithium-ion batteries (LIBs), they substitute lithium with sodium as the intercalating ion. Sodium, being a member of the same group in the periodic table as lithium, shares similar chemical properties. However, it's important to note that certain variations, such as aqueous Na-ion batteries, exhibit notable distinctions from Li-ion batteries.

The interest in SIBs surged within academic and commercial circles during the 2010s and early 2020s, primarily driven by concerns over the uneven geographical distribution, environmental impact, and costliness of lithium. Sodium boasts a significant advantage in its abundant presence, particularly in saltwater sources. Furthermore, many sodium-ion battery variants do not necessitate cobalt, copper, or nickel, opting instead for more readily available iron-based materials, such as $NaFeO_2$ featuring the Fe^{3+}/Fe^{4+} redox pair. This choice stems from the substantial difference in ionic radius between Na^+ (116 pm) and Fe^{2+}/Fe^{3+} (69–92 pm, depending on spin state), whereas the similarity in ionic radius between Li^+ and Fe^{2+}/Fe^{3+} leads to their mixing in cathode material during battery cycling, resulting in loss of cyclable charge. However, the larger ionic radius of Na^+ contributes to slower intercalation kinetics of sodium-ion electrode materials [1-4].

The exploration of Na+ batteries commenced in the 1990s, and after three decades of development, they stand on the brink of commercialization. Various companies such as HiNa, CATL in China, Faradion in the United Kingdom acquired by India's Reliance group, Tiamat in France, Northvolt in Sweden, and Natron Energy in the US are nearing the commercial deployment of NIBs, focusing on utilizing sodium layered transition metal oxides (Na_xTMO_2), Prussian white (an analogue of Prussian blue), or vanadium phosphate as cathode materials.

Although electric vehicles powered by sodium-ion battery packs have not yet hit the market, significant progress has been made. CATL, the world's largest lithium-ion battery manufacturer, announced the commencement of mass production of SIBs in 2022. In February 2023, the Chinese company HiNA Battery Technology Company, Ltd. successfully integrated a 140 Wh/kg sodium-ion battery into an electric test car for the first time, while energy storage manufacturer Pylontech obtained the initial sodium-ion battery certification from TÜV Rheinland. This paper is focused on the basic understanding of the science and technology behind Sodium ion battery and the present and future economic aspects for this technology.

2. Operational Mechanism and Materials

SIB cells comprise a cathode constructed from a sodium-derived substance, an anode (which may not necessarily be sodium-based), and a liquid electrolyte containing dissociated sodium salts dissolved in polar protic or aprotic solvents. When charging, sodium ions migrate from the cathode to the anode, while electrons flow through the external circuit. Conversely, during discharge, this process is reversed.

While dealing with electrochemistry we often use a term mAh/g (or mA-h/g). To get an idea of this quantity the following explanation might be useful. The term mA-h/g stands for milliampere-hours per gram mass. However, it's important to note that mA-h refers to milliampere-hours, indicating the provision of a specified current over a specified duration. Consequently, it cannot be directly compared with watts, which is a unit of power. Comparing mA-h and W is akin to comparing apples and barium. For instance, an automobile lead-acid battery might be labeled as 12 V at 60,000 mA-h (or 60 A-h), signifying its capability to deliver approximately 20 amperes for 3 hours or 10 A for 6 hours. This equates to 12 V * 60 A-H = 720 watt-hours (W-h). Despite each of the six cells in the battery having the same current rating, they operate at just 2 VDC, with each cell storing 120 W-h [5-6]. In figure 1 the various electrode structures in Sodium ion battery has been shown.

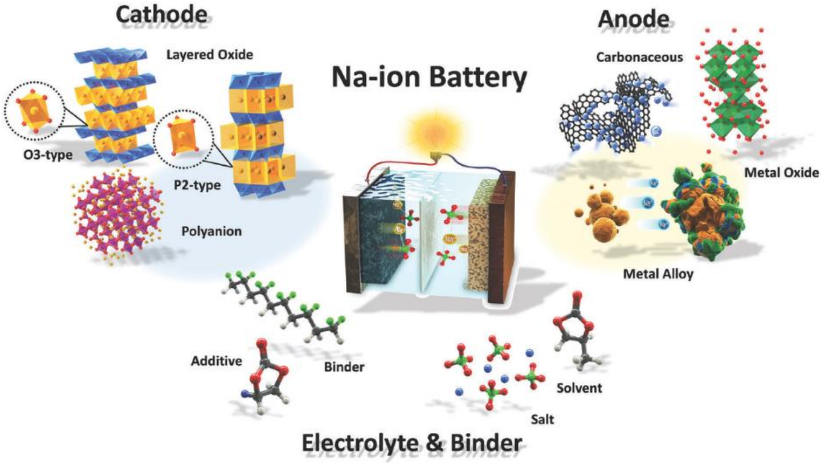

Figure 1. Different electrode structures in sodium-ion batteries (Picture credit: Creative Commons)

Because of the distinct electrochemical and physical attributes of sodium, sodium ion batteries necessitate the utilization of materials distinct from those employed in lithium ion batteries.

2.1 Cathode Materials

2.1.1 Transition Metal Oxides

When reduced, sodium ions can intercalate reversibly in a variety of layered transition metal oxides. In comparison to other cathode materials like phosphates, these oxides usually show lower electrical resistance and higher tap density values. Cation mixing between Na^+ and first row transition metal ions is generally avoided due to the larger size of the Na^+ ion (116 pm) compared to the Li^+ ion (90 pm). Consequently, it has been discovered that cheaper iron and manganese oxides can be used with Na-ion batteries, but more costly cobalt and nickel oxides are required with Li-ion batteries. There are many intercalation stages with varying voltages and kinetic rates as well as slower intercalation kinetics due to the bigger size of the Na^+ ion in comparison to Li^+ ions. Produced from abundant iron and manganese resources, an oxide of P2-type $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ may reversibly store 190 mAh/g at an average discharge voltage of 2.75 V versus Na/Na^+, matching or surpassing the performance of commercial lithium-ion cathodes like $LiFePO_4$ or $LiMn_2O_4$. Its low salt content, however, leads to a lower energy density. Extensive attempts have therefore been made to create oxides that are high in sodium. One example is a 2015 mixed P3/P2/O3-type $Na_{0.76}Mn_{0.5}Ni_{0.3}Fe_{0.1}Mg_{0.1}O_2$ battery, which demonstrated a 140 mAh/g capacity at an average discharge voltage of 3.2 V versus Na/Na^+. Furthermore, a series of doped

Ni-based oxides with the stoichiometric formula $Na_aNi_{(1-x-y-z)}Mn_xMg_yTi_zO_2$ achieved 157 mAh/g in a sodium-ion "full cell" with a hard carbon anode at an average discharge voltage of 3.2 V using the Ni2+/4+ redox couple. The O3-type $NaNi_{1/4}Na_{1/6}Mn_{2/12}Ti_{4/12}Sn_{1/12}O_2$ oxide can deliver 160 mAh/g at an average voltage of 3.22 V vs Na/Na+. When compared to commercial lithium-ion systems, this performance is on par with or even greater in a complete cell design. Furthermore, using just plentiful components, a $Na_{0.67}Mn_{1-x}Mg_xO_2$ cathode material demonstrated a discharge capacity of 175 mAh/g for $Na_{0.67}Mn_{0.95}Mg_{0.05}O_2$. In addition, copper-substituted cathode materials $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ have better capacity retention and a high reversible capacity, although they cost more than their copper-free counterparts.

2.2.2 Prussian Blue and Analogues

Various research groups have investigated the use of Prussian blue and different analogues as cathodes for Na-ion batteries. The optimal composition for a released substance is $Na_2M[Fe(CN)_6]$, with an anticipated capacity of roughly 170 milliampere-hours per gram, distributed across two voltage stages each accommodating a single electron. However, achieving such high specific charges is rare, especially in samples with a low number of structural defects. For example, rhombohedral $Na_2MnFe(CN)_6$ has displayed a capacity of 150–160 mAh/g and an average discharge voltage of 3.4 V, while rhombohedral Prussian white $Na_{1.88(5)}Fe[Fe(CN)_6]\cdot 0.18(9)H2O$ exhibited an initial capacity of 158 mAh/g, retaining 90% capacity after 50 cycles. While Titanium, Manganese, Iron, and Cobalt based PBAs exhibit a two-electron electrochemistry, Ni PBA demonstrates only single electron behavior. PBAs like $Na_2Mn^{II}[Mn^{II}(CN)_6]$ which does not contain iron (Fe) is also known, offers quite a large reversible capacity of 209 mAh/g at C/5, albeit with a low voltage (1.8 V versus Na+/Na). Structure of Prussian Blue is given in Figure 2.

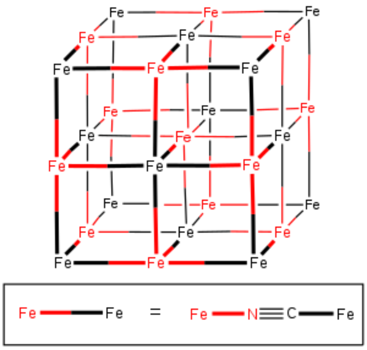

Figure 2. The basic structure of Prussian blue consists of fully occupied unit cells. However, approximately one-fourth of the $Fe(CN)_6$ groups depicted will be randomly absent, resulting in an average of 18 cyanide ions (instead of the depicted 24) and three ferrous iron atoms. (Picture credit: Smokefoot)

2.1.3 Oxoanions

Studies have also investigated cathodes utilizing oxoanions, which provide lower tap density and energy density than oxides. However, the robust covalent bonding of the polyanion contributes positively to cycle longevity, safety, and cell voltage. Within polyanion-based cathodes, sodium vanadium phosphate and fluorophosphate have shown remarkable cycling durability, with the latter displaying a satisfactory capacity (~120 milliampere-hours per gram) at elevated average discharge voltages (~3.6 volts versus Na/Na+). Additionally, sodium manganese silicate has shown the ability to deliver a very high capacity of more than 200 mAh/g with impressive cycling stability. Startups such as TIAMAT and SgNaPlus are actively developing and commercializing cathode materials based on sodium-vanadium-phosphate-fluoride ($Na_3V_2O_{2x}(PO4)_2F_{3-2x}$, where $0 < x < 1$) and sodium-iron-phosphate ($Na_3Fe_3(PO_4)_4$), respectively, both showing promising cycling stability and performance.

2.2 Anode materials

2.2.1 Carbon-based Materials

Anodic materials play a crucial role in sodium-ion batteries (NaIBs), contributing significantly to their performance and efficiency. Among these materials are various carbon-based substances, each offering unique characteristics and capabilities. Hard carbon, for instance, stands out for its disordered, non-crystalline, and amorphous nature. First recognized for its ability to absorb sodium in 2000, hard carbon has since been proven effective in delivering a capacity of 300 mAh/g. Its potential profile typically slopes above 0.15 V vs Na/Na+, with about half of its capacity being achieved at a flat top potential profile below this threshold. These capacities rival those observed in lithium-ion batteries with graphite anodes. Notably, hard carbons doped with nitrogen exhibit even greater specific capacities, showcasing stability across numerous cycles. Graphite, another carbon-based material, has been explored in sodium-ion cells, particularly when co-intercalated with sodium in ether-based electrolytes. However, one limitation of carbonaceous materials is their relatively negative intercalation potentials, restricting their use to non-aqueous systems.

2.2.2 Graphene

Researchers have also investigated graphene Janus particles to enhance energy density in sodium-ion batteries. These particles feature distinct interaction sites on one side and ensure inter-layer separation on the other, resulting in promising energy densities. One side of these particles provides interaction sites, while the other ensures inter-layer separation, resulting in an energy density of 337 mAh/g. In this regard Janus two-dimensional materials (2DMs) need to be elaborated for the non-specialised reader. They represent an innovative category of 2DMs where either the two sides of the material are functionally distinct or are subjected to varying local environments.

2.2.3 Carbon arsenide

Carbon arsenide (AsC_5) has garnered attention due to its high specific gravity, low expansion, and ultra-low diffusion barrier, indicating rapid charge/discharge cycling capabilities. Studies have shown that AsC_5 retains structural stability even after sodium adsorption, suggesting a lengthy cycle life.

2.2.4 Metals and metal alloys

Metals and metal alloys are also being explored for their potential as anodic materials. While stable alloys can form with sodium at room temperature, challenges such as volume change and material pulverization after a few cycles need to be addressed. For instance, sodium forms an alloy with tin ($Na_{15}Sn_4$) with a high specific capacity, but the significant volume change limits its cycling stability [7-8].

2.2.5 Oxides and Sulphides

Certain sodium titanate phases and molybdenum disulfide have also shown promise as anodic materials. Sodium titanate phases deliver capacities at low working potentials, albeit with limited cycling stability. Meanwhile, molybdenum disulfide, with its layered structure, presents opportunities for improved performance, although challenges such as capacity fade persist [9-10].

While these materials show potential, some have yet to overcome challenges such as poor electrochemical kinetics and limited cycling stability. Nonetheless, ongoing research aims to address these issues and unlock the full potential of sodium-ion batteries for various applications. Other materials, such as mercury, electroactive polymers, and sodium terephthalate derivatives, have been explored in laboratories but have yet to gain commercial interest.

2.3. Electrolytes

Sodium-ion batteries have the flexibility to utilize both aqueous and non-aqueous electrolytes. However, the limited electrochemical stability window of water leads to lower voltages and restricted energy densities. To extend the voltage range, non-aqueous carbonate ester polar aprotic solvents are employed. These solvents encompass ethylene carbonate, dimethyl carbonate, diethyl carbonate, and propylene carbonate. The prevalent salts utilized in non-aqueous electrolytes typically include NaClO4 and sodium hexafluorophosphate (NaPF6), which are dissolved in a blend of these solvents. It is widely acknowledged that these carbonate-based electrolytes possess flammability, raising safety concerns for large-scale applications. A glyme-based electrolyte variant, utilizing sodium tetrafluoroborate as the salt, has been demonstrated to be non-flammable. Additionally, emerging salts such as NaTFSI (TFSI = bis(trifluoromethane)sulfonimide), NaFSI (FSI = bis(fluorosulfonyl)imide), NaDFOB (DFOB = difluoro(oxalato)borate), and NaBOB (bis(oxalato)borate) anions have garnered attention. Furthermore, the incorporation of electrolyte additives can also be employed to enhance performance metrics [11-12].

3. Scope of Sodium Ion Batteries

SIBs encompass a diverse array of applications spanning portable electronics, electric vehicles (EVs), stationary storage systems, and grid-level energy storage. With the rising need for sustainable energy solutions, SIBs offer a compelling option for storing intermittent renewable energy sources such as solar and wind power. Their scalability and versatility make them suitable for both small-scale and large-scale applications, facilitating the transition towards a cleaner energy future.

3.1 Prospects of Sodium Ion Batteries

The prospects of SIBs are buoyed by their abundance, cost-effectiveness, and environmental sustainability. Sodium resources are more widely distributed geographically compared to lithium, mitigating concerns regarding resource depletion and geopolitical dependencies. Furthermore, the lower cost of sodium-based materials and the potential for leveraging existing manufacturing infrastructure offer a competitive edge for SIBs in commercial markets. As advancements in electrode materials and electrolytes continue to enhance the performance and cycle life of SIBs, their widespread adoption appears increasingly feasible. A comparative table for different types of batteries is given in the following table.

3.2 Advantages of Sodium Ion Batteries

1. Abundance and Cost-Effectiveness: Sodium is abundantly available globally, with reserves far surpassing those of lithium, ensuring a stable and affordable supply chain for battery production [Figure 3].
2. Environmental Sustainability: SIBs alleviate environmental concerns associated with lithium extraction and disposal, offering a greener alternative with reduced ecological footprint.
3. Similar Electrochemical Properties to LIBs: SIBs exhibit electrochemical characteristics akin to LIBs, enabling seamless integration into existing battery technologies and infrastructure.

4. Compatibility with Existing Manufacturing Infrastructure: Leveraging established manufacturing processes for LIBs, SIBs can be produced at scale without significant capital investment, fostering rapid commercialization.
5. Scalability and Versatility: SIBs are suitable for a wide range of applications, from consumer electronics to grid-level energy storage, facilitating the transition towards renewable energy integration and decarbonization.

3.3. Disadvantages of Sodium Ion Batteries

1. Lower Energy Density: Compared to LIBs, SIBs typically exhibit lower energy density, resulting in reduced specific energy and overall performance in certain applications.
2. Limited Electrode and Electrolyte Options: The relatively nascent stage of SIB research has constrained the availability of high-performance electrode materials and electrolytes, impeding optimization efforts.
3. Challenges in Material Synthesis and Stability: Developing sodium-based electrode materials with superior stability, rate capability, and cyclability remains a formidable challenge, necessitating continued research into novel synthesis methods and chemistries.
4. Temperature Sensitivity: SIBs may experience performance degradation at extreme temperatures, limiting their suitability for certain operating conditions and climates.
5. Competition from Established LIBs: Despite their potential advantages, SIBs face stiff competition from well-established LIBs in terms of performance, reliability, and market penetration, posing barriers to widespread adoption.

Figure 3. A salt plant with abundance of Sodium Chloride (Picture credit: Creative commons)

Table 1. Comparative analysis of NIB with LIB or Pb-Acid battery

	Sodium-ion battery	**Lithium-ion battery**	**Lead–acid battery**
Temperature range	−20 °C to 60 °C	Acceptable:−20 °C to 60 °C. Optimal: 15 °C to 35 °C	−20 °C to 60 °C
Materials	Abundant in earth	Scarce	Toxic
Direct current round-trip efficiency	up to 92%	85–95%	70–90%
Energy density (Gravimetric)	75–200 W·h/kg, (expected as per prototype)	120–260 W·h/kg	35–40 Wh/kg
Energy density (Volumetric)	250–375 W·h/L(expected as per prototype)	200–683 W·h/L	80–90 W·h/L
Cycles at 80% depth of discharge	Hundreds to thousands.	3,500	900
Cost per kW-h	\$40–77 (theoretical in 2019)	\$137 (average in 2020).	\$100–300
Safety	Low risk for aqueous batteries, high risk for Na in carbon batteries	High risk	Moderate risk
Cycling stability	High (due to negligible self-discharge)	High (due to negligible self-discharge)	Moderate (high self-discharge)

4. Commercial aspects: India and the World

4.1 Faradion Limited

A subsidiary of India's Reliance Industries, this company employs the technology using a hard carbon as anodic material, an oxide based cathode and liquid electrolyte in the design of their cells. Their pouch style cells exhibit gravimetric energy densities comparable to that of commercial Lithium ion batteries (160 Wh/kg at the cell level) along with good rate performance up to 3C and cycle lives ranging from 300 (at 100% depth of discharge) to over 1,000 cycles (at

80% depth of discharge). Faradion has demonstrated the safe transportation of sodium-ion cells in a shorted state (at 0 V) and has partnered with AMTE Power plc.

4.2 KPIT Technologies

KPIT Technologies introduced India's first sodium-ion battery technology, developed in collaboration with Pune's Indian Institute of Science Education and Research over nearly a decade. This technology aims to reduce the cost of batteries for electric vehicles by 25-30% and offers benefits such as a longer lifespan, faster charging, and resistance to below-freezing temperatures, with energy densities ranging from 100 to 170 Wh/kg.

4.3. Altris AB

Established in 2017 as a spin-off from Uppsala University, Sweden, Altris AB was founded by Associate Professor Reza Younesi, Ronnie Mogensen (a former PhD student), and Associate Professor William Brant. The company emerged from research endeavors conducted at the Ångström Advanced Battery Centre under the leadership of Prof. Kristina Edström. Altris is a leader in sodium-ion battery technology and provides hard carbon as the anode material and a patented iron-based Prussian blue counterpart for the positive electrode in non-aqueous sodium-ion batteries. Prussian white cathode, cell manufacture, and nonflammable fluorine-free electrolytes including NaBOB in alkyl-phosphate solvents are all patented by Altris. Collaborating with Clarios, Altris is involved in the production of batteries utilizing its technology.

4.4. BYD

A prominent Chinese electric vehicle and battery manufacturer, BYD Company invested $1.4 billion USD in 2023 to construct a sodium-ion battery plant in Xuzhou, capable of producing 30 GWh annually.

4.5 CATL

CATL, a leading Chinese battery manufacturer, announced plans in 2021 to introduce a sodium-ion-based battery to the market by 2023. Their battery design incorporates a Prussian blue analogue (PBA) for the positive electrode and porous carbon for the negative electrode, boasting a specific energy density of 160 Wh/kg in their first-generation battery. CATL also intends to manufacture hybrid battery packs incorporating both sodium-ion and lithium-ion cells.

4.6 HiNA Battery Technology Company

HiNa Battery Technology Co., Ltd, a spin-off from the Chinese Academy of Sciences (CAS), leverages research conducted by Prof. Hu Yong-sheng's group at the Institute of Physics at CAS. Their batteries utilize Na-Fe-Mn-Cu-based oxide cathodes and anthracite-based carbon anodes. HiNa partnered with JAC to introduce the Sehol E10X, the first electric car equipped with a sodium-ion battery. They also offer various sodium-ion products with different energy densities.

4.7 Natron Energy

An offshoot of Stanford University, Natron Energy employs Prussian blue analogues for both cathodic as well as anodic materials with an aqueous electrolyte. Like Altris AB Natron too have collaborated with Clarios, and is involved in producing batteries using its technology.

4.8 Northvolt

Europe's only large homegrown electric battery maker, Northvolt, has developed a sodium-ion battery with an energy density exceeding 160 watt-hours per kilogram. Initially designed for electricity storage plants, this battery could potentially be used in electric vehicles in the future.

4.9 TIAMAT

TIAMAT spun off from the CNRS/CEA and a H2020 EU-project called NAIADES, focusing on the development of cylindrical cells based on polyanionic materials. Their technology targets applications requiring fast charge and discharge rates, boasting energy densities between 100 Wh/kg to 120 Wh/kg, power densities between 2 and 5 kW/kg, and a lifetime exceeding 5,000 cycles to 80% of capacity.

5. Conclusion

In conclusion, sodium ion batteries represent a compelling alternative to lithium-ion batteries, offering a tantalizing combination of abundance, cost-effectiveness, and environmental sustainability. While facing certain challenges and limitations, ongoing research and technological advancements hold the key to unlocking the full potential of SIBs in revolutionizing the energy storage landscape. With continued innovation and investment, SIBs are poised to play a pivotal role in driving the transition towards a cleaner, more sustainable energy future.

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