Potential of Sodium-ion Batteries for Stationary Applications

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Abstract

Sodium-ion batteries (SIBs) present a promising alternative to lithium-ion technologies, particularly for stationary energy storage applications, due to their inherent advantages in cost, resource abundance, and sustainability. However, the cost advantages of stationary SIBs alone are not enough to ensure their commercial success. Compared with lithium ions, sodium ions with large size (0.76 Å for Li and 1.02 Å for Na) and atomic weight (6.94 amu for Li and 22.99 amu for Na) suffer slower ionic transport kinetics and lower energy density. This disadvantage can be compensated by the high-rate capability of sodium containing compounds. Sodium having similar electrochemical properties compared to lithium-ion and a little less potential (-2.71 V vs. SHE) considered as a leading energy storage device for stationary and large-scale energy storage systems. Current SIBs have achieved specific capacities in the range of 100-150 mAh/g, with energy densities of approximately 100-150 Wh/kg. While these figures are lower compared to high-performance lithium-ion batteries, ongoing research is steadily closing this gap. In this review, we outline the current status of SIB technology and industry directions along with a comparison of performance metrics with lithium-ion chemistries used for storage applications.

Keywords: *Sodium-ion Batteries, Stationary Applications, Hard Carbon, Energy Storage Systems*

1. Introduction

In the quest for advancements in energy storage technologies, the spotlight has often shown on Lithium-ion batteries (LIBs) due to their high energy density (200- 250 Wh kg^{-1}), reliability, and established presence in both consumer electronics and large-scale stationary applications. Lithium Iron Phosphate (LFP) graphite and Lithium nickel Cobalt Manganese oxide (NMC)-graphite batteries, in particular, have gained recognition for their robustness, and impressive long cycle life [1, 2]. LFP batteries are renowned for their thermal stability and safety features, achieving energy densities around ~150 Wh/kg [3, 4]. As the demand for sustainable and cost-effective energy solutions continues to rise, Sodium-ion batteries (SIBs) are emerging as a formidable alternative. SIB technology leverages sodium, an abundant and inexpensive resource, to potentially reduce the cost of energy storage systems significantly [5]. Although historically considered less competitive due to lower energy densities compared to lithium-based batteries, recent advancements have demonstrated that SIBs can offer viable alternatives for stationary applications. Modern SIBs are now achieving energy densities in the range of 100-160 Wh/kg, with some advanced prototypes pushing towards 200 Wh/kg [6-7]. This progress is partly attributed to innovations in electrode materials and electrolytes, which have enhanced the performance and longevity of these batteries. For instance, researchers have developed new cathode materials, such as sodium layered oxide, polyanionic frameworks, Prussian blue analogues which have contributed to the improved energy density and cycle stability of SIBs. The practical applications of SIBs are expanding, particularly in stationary energy storage systems [7]. Their lower cost and abundant raw materials make them an attractive option for grid energy storage, peak shaving, and load leveling [8, 9].

Despite their significant potential, the development of

SIBs remains concentrated among a relatively small group of companies, including Faradion (UK), Tiamat (Europe), Altris AB (Europe), HiNa (China), and Natron Energy (USA). These companies do not adhere to a single, uniform approach to sodium battery chemistry. For instance, various types of positive electrodes are utilized, such as layered oxides, Prussian blue analogues, or vanadium-based polyanionic compounds, and these can be paired with either aqueous or non-aqueous electrolytes. This diversity in chemistry not only allows for a range of market applications but also underscores the vast potential for research and innovation in SIB materials, encompassing new developments in positive and negative electrodes as well as electrolytes.

2.Comparative Analysis of Sodium-Ion vs. Lithium-Ion for Stationary Applications.

The growth of SIBs has been extensively accelerated due to the comparable electrochemical properties of sodium and lithium. An examination of the physical properties of sodium and lithium highlights (Table 1) why both elements were once considered equally promising for energy storage.

Table 1. Physical properties of lithium and sodium.

Property	Lithium (Li)	Sodium (Na)
Atomic mass [g mol^{-1}]	6.94	22.99
Electron configuration	[He]$2s^1$	[Ne]$3s^1$
Cationic radius [Å]	0.76	1.02
Density [g cm^{-3}]	0.971	0.534
Standard electrode potential [V]	-3.04	-2.71
Melting point [°C]	180.5	97.7
First ionization energy [kJ mol^{-1}]	520.2	495.8
Theoretical gravimetric capacity [mAh g^{-1}]	3861	1165
Theoretical volumetric capacity [mAh cm^{-3}]	2062	1131

Both lithium and sodium belong to alkali metals in Group 1 of the periodic table, characterized by having a single electron in their valence shell. This commonality makes them highly reactive, with physical properties such as melting point, hardness, conductivity, and first ionization energy decreasing down the group. A crucial factor in comparing these metals is their redox potentials: the standard reduction potential of Na^+/Na is −2.71 V versus the Standard Hydrogen Electrode (SHE), which is approximately 330 mV higher than Li^+/Li at −3.04 V [8]. This difference means that, thermodynamically, the anodic electrode potentials for SIBs will generally be higher than those for LIBs. A comparative analysis of SIBs against well-established lithium-ion technologies, such as LFP is given below.

Energy Density: LFP-based LIBs offer around 150 to 200 Wh/kg [3, 4] while the energy density of SIBs typically ranges from 100 to 150 Wh/kg [6]. Thus, more energy can be delivered and stored by LIBs per unit of weight or volume. On the other hand, SIBs may require larger or heavier systems to store the same amount of energy

Cycle Life: In terms of cycle life, SIBs demonstrate a promising longevity with current technologies offering around 1,500 to 3,000 cycles, making them competitive with LFP, which can achieve between 2,000 and 5,000 cycles. This durability is beneficial for stationary applications that demand long-term reliability and minimal maintenance [1, 6].

Charge/Discharge Rates: SIBs generally support rates of 0.5C to 1C, which are lower compared to LFP batteries that handle up to 1C for charging and 5C for discharging. Although SIBs currently offer slower rates, ongoing advancements are expected to improve these metrics, making them more viable for applications requiring rapid energy storage and delivery [5, 10].

Cost: SIBs have notable cost advantages for stationary applications due to the abundance and lower cost of sodium compared to lithium. For some applications, this cost benefit can make SIBs more appealing, particularly in nations with limited lithium resources like India [11]. Overall, SIBs present a potentially more cost-effective solution for large-scale energy storage, aligning well with the economic constraints of stationary applications.

Safety and Stability: When it comes to safety and stability, SIBs generally offer a robust safety profile due to their stable chemistries, which reduce the risk of thermal runaway and fires [12]. LFP batteries are known

for their safety and thermal stability, which makes them a preferred choice for applications requiring high safety standards. SIBs can be discharged to 0 V and stored and transported in this discharged state unlike LIBs. Nonetheless, all three technologies are considered relatively safe, with SIBs benefiting from ongoing improvements in safety protocols.

Environmental Impact: SIBs have a lower environmental footprint because sodium is widely available, and the extraction process causes less environmental disturbance than lithium. LFP batteries involve the mining and processing of lithium, which have ecological consequences.

To make a true and fair comparison of SIBs and LIBs, that captures the differences in their cell performance as well as the materials costs, LFP//graphite battery would be a suitable reference where both chemistries are cobalt free cell. Figure 1 represents the trend of enhancement in cell-level specific energies of commercially available LIBs compared with Faradion's Na-ion pouch cells [9]. The LFP//graphite system is a good competitor as typically the energy density is similar to that of SIBs as mentioned in Figure 1.

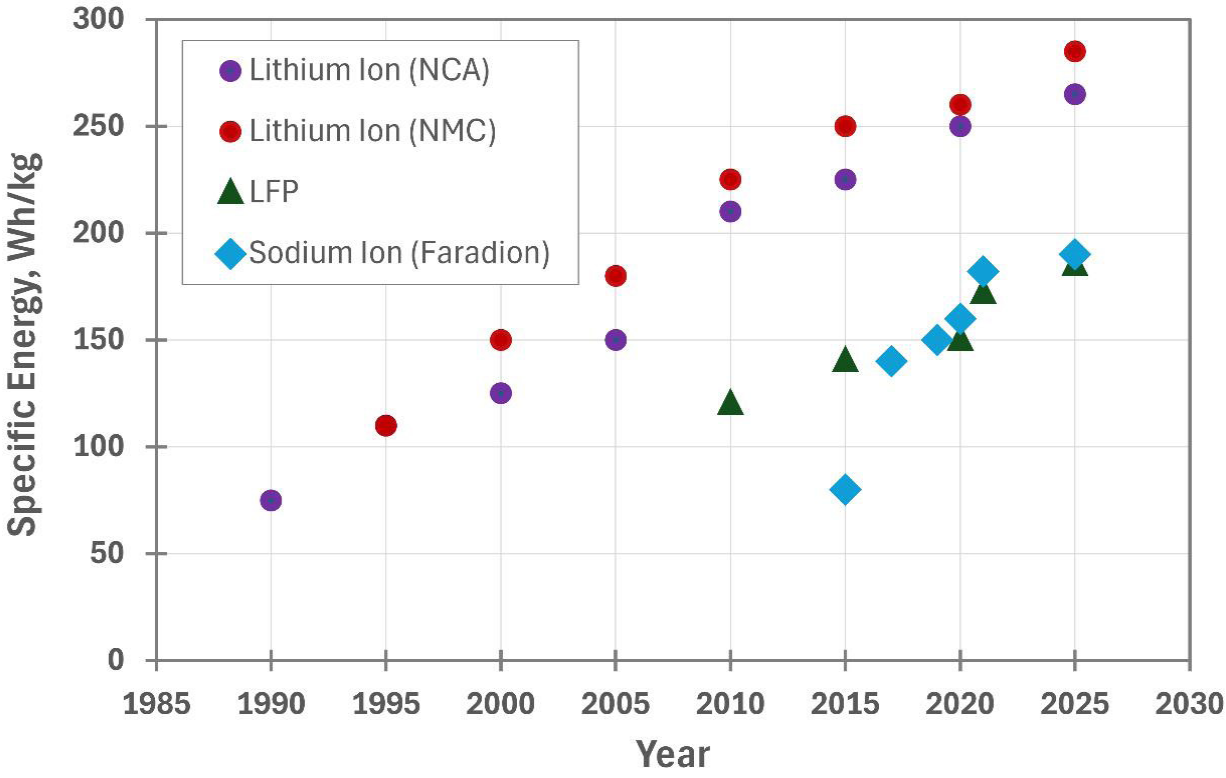


Figure 1: The trend of enhancement in cell-level specific energies of commercially available LIBs compared with Faradion's Na-ion pouch cells [Reproduced with permission from ref. 9, copyright 2025 Royal Society of Chemistry]

For stationary applications, such as grid storage or large-scale energy management systems, SIBs offer potential advantages in terms of cost, resource availability, and environmental impact. However, LIBs currently provide superior energy density and performance, making them more suitable for applications where space and weight are constraints. The choice between the two will depend on specific application needs, cost considerations, and long-term goals related to sustainability and resource management.

3.Electrochemical Mechanism in Electrode Materials

SIBs operate on the electrochemical movement of Na^+ ions between the anode and cathode during charge and discharge cycles. In the discharge process, Na^+ ions move from the anode to the cathode through the

electrolyte, releasing energy as electrons flow through an external circuit. During charging, Na^+ ions return to the anode from the cathode, with electrons flowing back through the circuit. In SIBs electrodes, charge insertion mechanisms are categorized into intercalation, alloying and conversion [5]. Intercalation involves inserting sodium ions into a host material without significant structural changes, typically seen in crystalline compounds. Although sodium ions are larger than lithium ions, causing more strain, intercalation generally results in minimal volume changes. Alloy-type anode materials, generally have high-capacity ~1000 mAh g^{-1}, can be further divided into topotactic and addition reactions. Topotactic alloying involves a solid-solution reaction with no phase changes, while addition reactions involve phase transformations. A major challenge with alloying is managing the substantial volume changes, which can lead to material degradation and poor cycling stability. Conversion-type anodes undergo large volume expansions and significant voltage hysteresis, impacting energy efficiency. However, conversion reactions can achieve very high gravimetric capacities due to their ability to exchange more than one electron per mole of host material [13, 14].

4. Electrode materials and electrolytes

4.1 Anode Materials

4.1.1 Hard Carbon

Hard carbon materials are currently the most popular choice for anodes in SIBs. These materials are derived from oxygen-rich precursors and cannot be converted into graphite, no matter the carbonization temperature. Hard carbons are characterized by a mixture of randomly oriented graphitic domains and disordered carbon regions, resulting in a complex structure with varying interlayer spacing and pore sizes. Although the exact structure of hard carbon remains elusive due to variability in precursor and carbonization conditions, it is known to provide pathways for sodium ion diffusion and storage. One of the primary challenges facing hard carbons is improving their storage capacity to match or exceed that of graphite in LIBs, which is over 372 mAh/g.

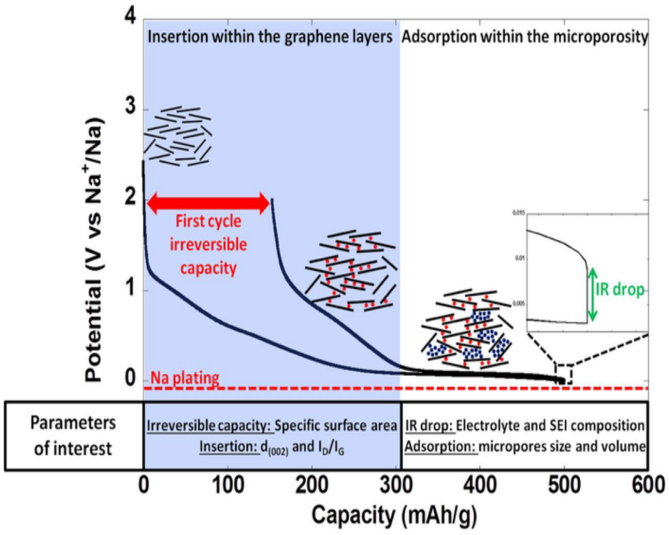


Figure 2. Na^+ storage mechanism into the hard carbon [Reproduced with permission of ref. 15, copyright 2024 IOP Publishing].

Current practical capacities for hard carbons vary from 200 to 450 mAh/g. The complexity of hard carbons, due to their heterogeneous nature and unknown storage mechanisms, complicates the accurate determination of their theoretical energy density. Hard carbon, a non-graphitizable carbon, is synthesized by pyrolyzing carbon-rich precursors such as biomass, lignin, glucose and other organic materials under an inert atmosphere (typically Ar or N_2) at high temperatures, usually around 1000°C. Theories regarding sodium storage mechanisms are evolving, with several models proposed, including intercalation-filling, adsorption-intercalation, adsorption-filling, and three-stage models. New evidence suggests simultaneous adsorption and intercalation during sodiation, with nano-pore filling occurring later. As Figure 2 illustrates, three steps are involved in the Na^+ storage process into the hard carbon: (i) Firstly, Na^+ ions adsorb at defective sites in the slope-voltage region, (ii) Then, Na^+ ions intercalate in the hard carbon lattice, and (iii) Finally, Na^+ ion adsorb at the pore surface in the plateau region.[15] Additionally, recently published articles on hard carbons and theirelectrochemical performance is summarized in Table 2.

Table 2. Summary of electrochemical performance of recently published hard carbons

Materials	Potential Range	ICE	Reversible Capacity	Capacity Retention	Ref.
Cellulose-derived hard carbon	0.0-3.0 V	87.1%	343.3 mAh g^{-1} at 20 mA g^{-1}	86.4% (1000 cycles)	[16]
Nanocrystalline cellulose-derived hard carbon	0.0-2.5 V	90.4%	314 mAh g^{-1} at 0.1 C	87% (100 cycles)	[17]
Phenolic resin-derived hard carbon	0.0-2.5 V	73.6%	304 mAh g^{-1} at 30 mA g^{-1}	87.2% (100 cycles)	[18]
Oxidized cork-derived hard carbon nanosheets	0.0-2.5 V	88%	276 mAh g^{-1} at 20 mA g^{-1}	95% (100 cycles)	[19]
Egg shell membranes-derived hard carbon	0.0-3.0 V	89%	310 mAh g^{-1} at 20 mA g^{-1}	99% (250 cycles)	[20]
Cotton-derived hard carbon	0.01-3.0 V	95%	343 mAh g^{-1} at 20 mA g^{-1}	93.5% (100 cycles)	[21]
Phenolic resin-derived hard carbon	0.0-2.0 V	90.4%	343 mA h g^{-1} at 30 mA g^{-1}	90% (150 cycles)	[22]
Hollow tremella-like carbon sphere	0.0-3.0 V	86%	278 mAh g^{-1} at 100 mA g^{-1}	80.2% (1000 cycles)	[23]
Paper towels-derived hard carbon	0.0-2.0 V	92.05%	336 mAh g^{-1} at 20 mA g^{-1}	95.8% (200 cycles)	[24]
Sucrose and phenolic resin mixture-derived hard carbon	0.0–2.0 V	87%	319 mAh g^{-1} at 100 mA g^{-1}	90% (150 cycles)	[25]
Lignin/epoxy resin-derived hard carbon	0.0-2.0 V	82%	316 mAh g^{-1} at 30 mA g^{-1}	90% (150 cycles)	[26]
Paper towels-derived hard carbon	0.0-2.0 V	94.1%	293.2 mAh g^{-1} at 20 mA g^{-1}	99% (100 cycles)	[27]
Cellulose bitumen-derived hard carbon	0.0-3.0 V	92.7%	241 mAh g^{-1} at 50 mA g^{-1}	92.3% (100 cycles)	[28]
Hard carbon@graphene carbon microspheres	0.0-3.0 V	80.1%	343 mAh g^{-1} at 25 mA g^{-1}	87.2 % (200 cycles)	[29]
Hard carbon microspheres	0.0-2.0 V	86.1%	361 mAh g^{-1} at 20 mA g^{-1}	93.4% (100 cycles)	[30]
Camphor wood residues-derived hard carbon	0.0-2.0 V	82.8%	324.6 mAh g^{-1} at 20 mA g^{-1}	90% (200 cycles)	[31]
Sucrose and phenol formaldehyde resin-derived hard carbon	0.01-2.0 V	85%	310 mAh g^{-1} at 20 mA g^{-1}	93% (100 cycles)	[32]
Hazelnut shell-derived hard carbon	0.0-2.5 V	91%	342 mAh g^{-1} at 20 mA g^{-1}	91% (100 cycles)	[33]
Bamboo-derived hard carbon	0.0-2.5 V	84.1%	348.5 mAh g^{-1} at 30 mA g^{-1}	91.6% (500 cycles)	[34]
Glucose-derived hard carbon	0.0-2.5 V	88%	478 mAh g^{-1} at 25 mA g^{-1}	90% (35 cycles)	[35]

4.1.2 Titanium-based oxides

Titanium-based oxides are promising anode materials for SIBs due to their low cost, ease of processing, and non-toxic nature. They offer safety advantages over carbon-based anodes by operating at higher voltages, thus preventing metallic sodium plating. Key titanium-based oxides include TiO_2, $Na_2Ti_6O_{13}$, and $Na_2Ti_3O_7$. TiO_2, particularly in its nanoscale form, exhibits practical capacities around 155 mAh/g, with anatase being the preferred polymorph [36, 37]. $Li_4Ti_5O_{12}$, known for its zero-strain behavior, provides a reversible capacity of 155 mAh/g. $Na_2Ti_6O_{13}$ features high Na^+ ion diffusion and minimal volume change but has a lower capacity of 49.5 mAh/g [38]. $Na_2Ti_3O_7$ offers the highest energy density in this group, with a specific capacity of 177 mAh/g, but the major challenges for titanium-based oxides, particularly $Na_2Ti_3O_7$, include poor electronic conductivity and sluggish Na^+ ion (de)insertion kinetics, leading to reduced rate performance and cycling stability. $Na_2Ti_3O_7$'s bandgap energy of approximately 3.7 eV makes it an electrical insulator, significantly hindering Na^+ diffusion. Additionally, issues like low initial coulombic efficiency (ICE) and unstable SEI layers further impact performance. Strategies to improve performance include enhancing long-term cycling stability through bulk and surface structural modifications, nanostructuring, and composite fabrication with carbon [38, 39].

4.1.3 Transition metal dichalcogenides

2D transition metal dichalcogenides (TMDs), such as MoS_2, are emerging as promising anode materials for SIBs. Their large interlayer spacings (~6.15 Å for MoS_2), high conductivity (~10^{-3} to 10^{-5} S cm^{-1} for MoS_2) and mechanical flexibility make them well-suited for accommodating the volume expansion that occurs during cycling. TMDs offer high theoretical capacities, like the 670 mAh g^{-1} of MoS_2 [40] and their ability to restack as exfoliated nanosheets enhances structural stability and facilitates efficient Na^+ diffusion. Despite their potential, TMDs face significant challenges. Understanding their charge-storage mechanisms is complex due to phase transitions that occur upon Na^+ intercalation, such as the transformation from semiconducting 2H-MoS_2 to metallic 1T-MoS_2. This phase change, along with structural distortions and lattice modulation, affects performance. Additionally, the formation and behavior of the SEI on TMD anodes remain poorly understood, impacting their overall efficiency and lifespan [41]. To address these challenges, researchers have explored strategies such as incorporating high-conductivity carbon additives (e.g., graphene, carbon nanotubes) to enhance electronic transport and designing novel nanoarchitectures (e.g., hollow structures, heterostructures) to accommodate volume changes and improve structural integrity during cycling [40-41].

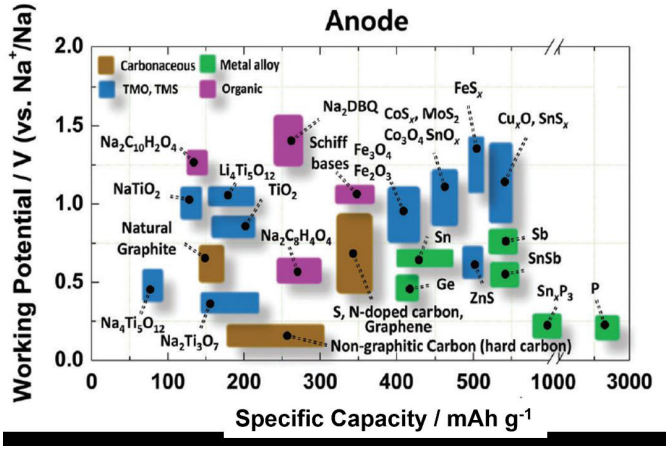


Figure 3: Recent research progress in SIBs Anode; (Reproduced with permission from ref [5]).

4.1.4 Organic electrode materials

Organic electrode materials (OEMs) are gaining attention in rechargeable battery technology due to their potential for sustainability and use of bio-derived or recycled components. Recent research has focused on small redox-active organic molecules, such as disodium terephthalate ($Na_2C_8O_4H_4$), for use in SIBs [42]. These organic systems offer structural diversity and modifiable electronic properties, making them attractive for battery applications. Redox reactions typically involve changes in π-bonds or charge stabilization mechanisms, with functional groups like carboxylates, azo, and imine being explored for their electrochemical performance. Organic anode materials face several challenges, including lower theoretical capacities due to limited redox-active sites

and issues with cycling stability. Organic electrolytes can form inactive side products or lead to solubility problems, reducing coulombic efficiency and complicating practical applications. Additionally, OEMs often have low density and poor electronic conductivity, requiring additives like conductive carbon. The capacity and working potential of various organic groups, such as carbonyl, imine, and azo bonds, also impact overall energy density. Understanding these materials' activity and addressing production costs, scalability, and stability remain critical areas for improvement [43]. These challenges are being tackled using various strategies such as polymerizing small organic molecules or embedding them into covalent organic frameworks (COFs) reduces solubility and enhances structural integrity. Modifying functional groups can stabilize redox activity and optimize voltage. Forming composites with conductive materials like carbon nanotubes improves electron transport, while using solid or gel electrolytes helps prevent material dissolution. These approaches collectively enhance the performance and durability of organic anode materials in sodium-ion batteries [42-43]. Figure 3 provides an overview of the latest advancements in research on anode for SIBs.

4.1.5 Alloy Materials

Alloy materials can store many Na^+ ions in the host structure with a relatively low operating potential (below 1.0 V). Numerous studies have been conducted on metals (Sn, Bi), metalloids (Si, Ge, As, Sb), and polyatomic nonmetal compounds (P) as possible anode materials for SIBs [5, 44]. However, the alloying and dealloying reactions involve a significant number of Na^+ ions, causing the host material to experience substantial volume changes. The repeated volume changes, constrained by the battery casing, create complex mechanical stresses within the active particles, which can eventually result in their fracture or breakdown. Extensive experimental studies on the electrochemical and mechanical behavior of these alloys during Na+ interactions have led to the exploration of optimized architectures and improved electrode designs. Here in this review, we are particularly focusing on the Phosphorous (P) and Tin (Sn) as follows.

Phosphorous (P): Phosphorus, a group 15 nonmetal, has three primary allotropes: white, red, and black. Among these, red phosphorus is relatively stable and may exist in both amorphous and crystalline states. Its potential as an anode material for SIBs with a three-electron redox reaction allowed for a high theoretical capacity of around 2600 mAh g^{-1} [44]. More recently, phosphorus-carbon composites have been investigated to improve their electrochemical performance. However, a key difficulty with phosphorus electrodes is the creation of Na_3P during sodiation, which can emit poisonous and combustible phosphine (PH_3) when exposed to moisture. Despite this constraint, phosphorus electrodes have a lower volume expansion during sodiation than other Na-based alloys. The partial covalent feature of Na_3P reduces sodium's apparent molar volume to 77% and 59% when compared to Na-metal alloys and metallic Na, respectively **[5].** However, a key concern with phosphorus anodes is the breakdown of the electrolyte at the extremely reactive surface of Na_3P. This negatively impacts cycle life. To improve the reversibility of sodium phosphide formation, non-fluorinated binders such as sodium polyacrylate (PANa) and sodium carboxymethyl cellulose (CMCNa), as well as electrolyte additives such as fluoroethylene carbonate (FEC), have been successfully used to improve electrode stability and battery lifespan [5].

Tin (Sn): Sn has been considered as one of the most capable anode materials owing to its high theoretical capacity of 847 mA h g^{-1}, corresponding to the the full sodiation state of $Na_{15}Sn_4$. Based on the theoretical calculations and experiments, there are many reports on multi-stage sodiation of Sn progressed as: Sn → $NaSn_5$ → NaSn → Na_9Sn_4 → $Na_{15}Sn_4$.[5, 45] Sn alloys with elements like silicon, antimony, or iron, if alloyed, can further complement the overall performance by improving the energy density of the battery. However, a few challenges still exist, including the high-volume expansion (up to 300%) during sodiation process, inducing intense mechanical stress that results in electrode cracking, pulverization and eventually capacity decline.[14] To overcome these problems, researchers have been working on several solutions including nanostructuring

Sn to counteract volume expansion effects, as smaller particles are better able to accommodate volume changes and enhancing conductivity by incorporating carbon-based materials such as graphite, graphene, or carbon nanotubes. In addition, hybrid materials that incorporate Sn with more stable elements such as antimony or iron are being created to achieve high capacity in balance with improved structural stability and longer cycling life. Optimization of the electrolyte, such as the creation of more stable SEI layers and enhanced ionic conductivity, also promises to improve the long-term performance of Sn-based anodes. Also, pre-sodiation methods might assist in reducing the initial volume expansion and enhancing the initial cycling efficiency [44]. With future developments in nanotechnology, material hybridization, and electrolyte engineering, Sn alloy anodes will be a central element in the formulation of high-performance, cost-saving, and eco-friendly sodium-ion batteries as a promising alternative to lithium-ion technology [5].

4.2 Cathode Materials

4.2.1 Layered transition Metal Oxides

In transition metal oxides ($Na_{1-x}MO_2$), mainly O3 type and P2 type materials explored as cathodes for SIBs. These crystal structures consist of edge-sharing MO_6 octahedral layers inserted between Na^+ ion layers. The number (O3 and P2) stands for the packing number of Na^+ ion octahedral or prismatic layers in each unit cell. The prime symbol (') denotes monoclinic distortion, so O'3 and P'2 symbolize monoclinic distortion of the O3 and P2 phases, respectively. The electrochemical de-/sodiation of the O3 structure proceeds with reversible structural transformation of O3 ↔ O'3 ↔ P3 ↔ P'3 [5, 46]. When Na^+ ions are partially extracted from the crystal structure, they tend to prefer a prismatic environment. This extraction causes the oxygen to be repelled from the Na layers, resulting in an increase in interlayer distance. Consequently, Na^+ diffusion occurs more rapidly in the P'3 phase due to its larger interlayer spacing compared to O3. These phase transitions are accompanied by the sliding of the MO_2 slab without the breaking of M–O bonds. In contrast, the P2 structure is stable when the Na content is between 0.3 and 0.7 in $Na_{1-x}MO2$, with the average oxidation state of M exceeding +3.3 [51-53]. Also, vacancies in the structure lead to a significant repulsion of oxygen from the Na layers, causing an increase in the interlayer distance. As a result, Na^+ ions occupy prismatic (P) sites due to the larger ionic radius of Na^+ ion [47, 54, 55]. Moreover, a major challenge lies in understanding and managing the structural complexities of both P2 and O3 materials during cycling, as these can influence the performance and longevity of the materials. Current issues involve characterizing the atomic, nano-, and meso-structural changes over many cycles and the effects of subtle substitutions on performance. Additionally, balancing power and capacity optimally remains a challenge. P2 materials offer high power performance, while O3 materials provide better capacity. Developing hybrid P2|O3 materials to meet diverse application requirements and addressing the commercial and technical issues related to these challenges are ongoing concerns [46, 56]. Table 3 summarizes the recent developments in electrochemical performance of potential cathodes for SIBs.

4.2.2 Anion redox layered transition-metal oxides

Oxygen redox reactions in SIBs have gained attention for their potential to provide higher capacity (~250–300 mAh g^{-1}) at elevated voltages (above 4.0 V) compared to traditional transition-metal redox reactions [47]. These reactions involve the overlap of M–O and (M–O)* orbitals, enabling oxygen ion electron removal [57-58]. While initial studies used expensive 4d and 5d metals, current research has shifted to more affordable 3d metals like manganese, often doped to enhance performance. Oxygen redox reactions face issues with reversibility and large hysteresis, caused by structural transformations and cation migration during cycling. High-voltage operation can lead to lattice oxygen loss and electrolyte instability. Techniques to distinguish bulk and surface phenomena in redox activity are limited, complicating the understanding of these processes [58].

4.2.3 Polyatomic anion-based materials

Polyatomic anion insertion compounds offer diverse structural chemistries, enhancing stability and enabling higher operating voltages (above 3.5 V vs. Na^+/Na). Notable examples include vanadium-containing phosphates and fluoride phosphates, such as NASICON $Na_3V_2(PO_4)_3$[59-61], $Na_3V_2(PO_4)_2F_3$[62] and $NaVPO_4F$ [63-66] which provide high ion mobility and tunable voltages. New developments like $Na_3V_2(PO_4)_2FO_2$[67] demonstrate increased energy density by accommodating additional sodium ions. Challenges include controlling polymorphic phases, which affect ionic conductivity and voltage stability. Research is needed to optimize reaction conditions and explore dopants to achieve higher redox potentials. Additionally, replacing expensive vanadium with cheaper alternatives, and addressing sluggish diffusion kinetics in new materials like $NaFeSO_4F$, are ongoing issues [68].

4.2.4 Prussian blue and analogues

Prussian blue analogues (PBAs), with the formula $Na_xM[M'(CN)_6]_{1-y}.zG$, are promising Na-ion battery cathodes due to their low cost, abundant elements, and high porosity. Despite significant progress, challenges remain in achieving high capacity and stability. PBAs show potential with capacities up to 120 mAh g^{-1} for 800 cycles using aqueous electrolytes, though non-aqueous electrolytes can offer higher capacities [69, 70].

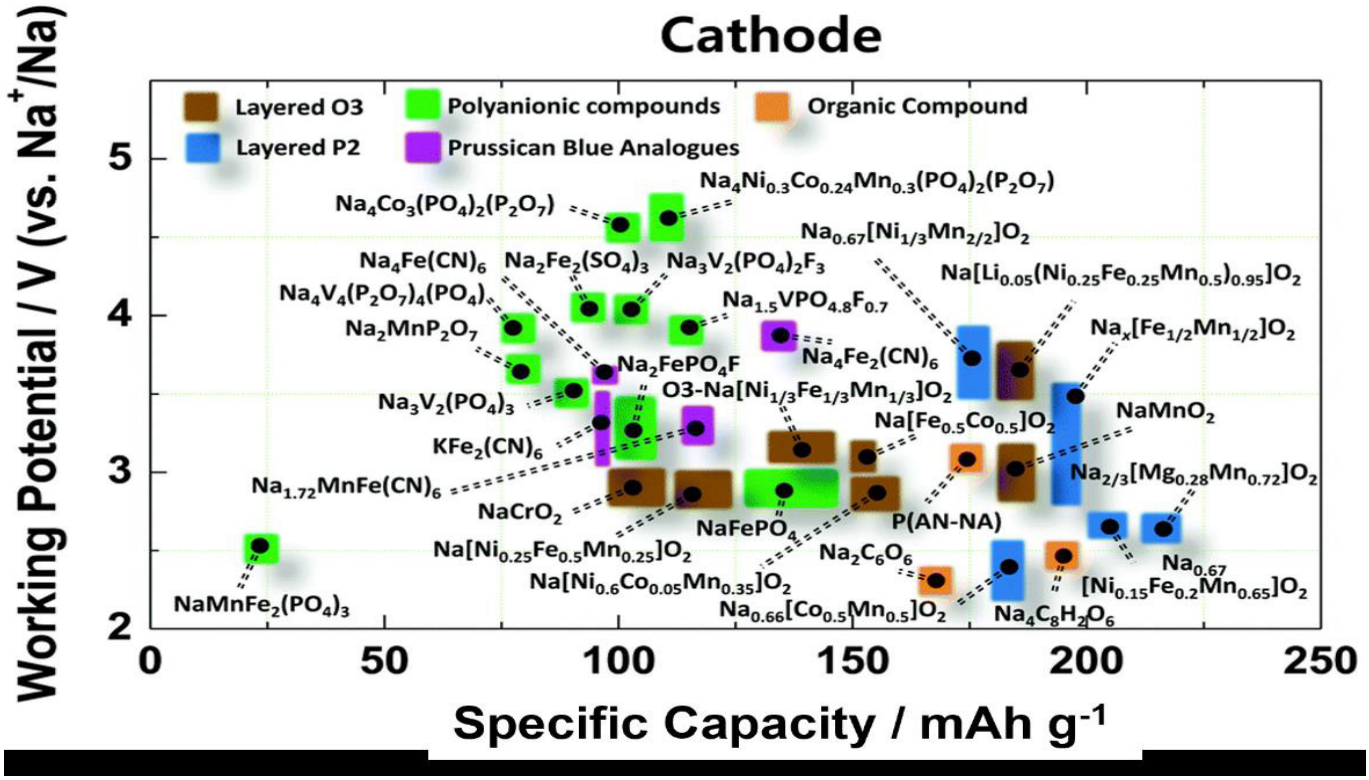


Figure 4: Recent research progress in SIBs cathode (Reproduced with permission of ref [5]).

The primary issue is maintaining structural stability and high capacity during cycling. PBAs face issues with moisture sensitivity and limited reversibility, particularly when cycling more than one sodium ion per formula unit. High vacancy concentrations from synthesis and the presence of water lead to reduced structural stability and capacity fading. Challenges include improving electronic conductivity and preventing phase transitions due to water content. The complexity of electrolyte interactions adds to the difficulty of optimizing PBAs for long-term use [71-73]. Figure 4 provides an overview of the advancements in research on cathodes for SIBs.

Table 3. Summary of electrochemical performance of developing cathodes for SIBs.

Materials	Voltage Range	Reversible Capacity	Capacity Retention	Ref.
$Na_{0.7}CoO_2$	2.0-3.8 V	125 mA h g^{-1} at 5 mA g^{-1}	86% (100 cycles)	[50]
$Na_{2/3}Ni_{1/6}Mn_{2/3}Cu_{1/9}Mg_{1/18}O_2$	2.5-4.15 V	87.9 mA h g^{-1} at 0.5C	81.4% (500 cycles)	[51]
$Na_{0.76}Cu_{0.22}Fe_{0.30}Mn_{0.48}O_2$	2.0-4.0 V	125.5 mA h g^{-1} at 0.1C	79% (300 cycles)	[52]
$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$	1.5-4.0 V	126.3 mA h g^{-1} at 13 mA g^{-1}	75.6% (30 cycles)	[47]
$Na_{2/3}Fe_{0.2}Mn_{0.8}O_2$	1.5-4.2 V	189.81 mA h g^{-1} at 0.1C	72% (50 cycles)	[48]
$Na_{0.78}Ni_{0.23}Mn_{0.69}O_2$	2.0-4.5 V	138 mA h g^{-1} at 0.1C	90% (20 cycles)	[49]
$Na_{2/3}[Mn_{0.7}Zn_{0.3}]O_2$	1.5-4.6 V	190 mA h g^{-1} at 0.1C	80% (200 cycles)	[53]
$Na_{0.55}[Ni_{0.1}Fe_{0.1}Mn_{0.8}]O_2$	1.5-4.3 V	221.5 mA h g^{-1} at 12 mA g^{-1}	75% (100 cycles)	[54]
$Na_{0.44}MnO_2$	1.5-4.0 V	118 mA h g^{-1} at 50 mA g^{-1}	67.8% (140 cycles)	[55]
$Na_{0.44}MnO_2$	2.0-4.0 V	119 mA h g^{-1} at 0.2C	63% (60 cycles)	[56]
$NaFePO_4$	1.5-4.5 V	101.4 mA h g^{-1} at 20 mA g^{-1}	90.6% (250 cycles)	[57]
$NaFePO_4$	2.0-4.5 V	158.5 mA h g^{-1} at 0.1 C	93.4% (5000 cycles)	[58]
$Na_3V_2(PO_4)_3$	2.5-4.0 V	114.5 mA h g^{-1} at 0.1 C	98.2% (2650 cycles)	[59]
$Na_3V_2(PO_4)_3$	2.4-3.8 V	104.7 mA h g^{-1} at 0.1 C	93.12% (500 cycles)	[60]
$Na_3V_2(PO_4)_3$	2.5-4.1 V	115 mA h g^{-1} at 0.1 C	95% (100 cycles)	[61]
$NaVPO_4F$	2.5-4.0 V	133.8 mA h g^{-1} at 0.2 C	94.5% (100 cycles)	[63]
$NaVPO_4F$	2.0-4.3 V	134.1 mA h g^{-1} at 0.1 C	95.1% (100 cycles)	[64]
$NaVPO_4F$	2.0-4.3 V	123.1 mA h g^{-1} at 0.1 C	87.7% (100 cycles)	[65]
$NaVPO_4F$	2.4-4.0 V	120 mA h g^{-1} at 0.1 C	97% (300 cycles)	[66]
$Na_{2-x}FeFe(CN)_6$	2.0-3.8 V	85 mA h g^{-1} at 1 C	98.9% (500 cycles)	[72]
$FeFe(CN)_6$	2.0-4.3 V	110 mA h g^{-1} at 50 mA g^{-1}	ca 64.8% (100 cycles)	[73]

4.3 Electrolytes

4.3.1 Organic electrolytes

The development of organic electrolytes for SIBs closely mirrors the advancements in LIBs, driven by similar operational needs such as high ionic conductivity, low viscosity, and stability across diverse conditions [74]. Essential characteristics include the ability to dissolve salts effectively to facilitate ion transport, as well as high thermal and chemical stability to accommodate various climates and electrode materials. Cost-effectiveness also remains a critical factor, making solvents like linear and cyclic carbonates (e.g., dimethyl carbonate (DMC), ethylene carbonate (EC), and propylene carbonate (PC) and ethers (e.g., diglyme) prominent choices [75-77]. Despite the parallels with LIB technology, SIBs face unique challenges. Linear carbonates, while useful in LIBs for adjusting viscosity and melting points, create unstable SEI layers in SIBs due to their reactions with sodium [78]. Additionally, the use of graphite, common in LIBs, is not feasible for SIBs because it cannot intercalate sodium ions. This necessitates the frequent use of solvents like PC, which are unsuitable for LIBs due to solvent co-interactions with graphite. Sodium salts

interact differently with solvents compared to lithium salts, impacting desolvation dynamics and performance [79].

4.3.2 Ionic liquids

Ionic liquids (ILs) have emerged as a promising alternative electrolyte for SIBs due to their unique properties. ILs are molten salts that are non-flammable and possess a wide electrochemical stability window. These characteristics make them safer compared to traditional organic electrolytes and capable of operating over a broad temperature range [80-83]. Additionally, ILs tend to form a more uniform and stable SEI layer, which is crucial for maintaining battery performance and longevity. This stability helps reduce the corrosion of aluminum current collectors, a common issue with organic solvents. However, the use of ILs in SIBs is not without challenges. One major drawback is their relatively high cost and the complexity of their purification processes. Furthermore, ILs, particularly those based on imidazolium and pyrrolidinium, are hygroscopic, which can introduce complications in battery performance [84-88]. Another issue is the higher viscosity and lower ionic conductivity of ILs compared to conventional organic electrolytes, which can affect the battery's efficiency, especially at room temperature.

4.3.3 Solid and Gel-Type Polymer Electrolytes

Solid and gel polymer electrolytes (SPEs and GPEs) are key components in advancing SIBs due to their potential to enhance battery safety and performance. SPEs, also known as dry solid polymer electrolytes, consist of a polymer matrix that dissolves salt ions, providing mechanical strength. However, the ionic conductivity of traditional SPEs is generally low, ranging from 10^{-2} to 10^{-4} mS cm^{-1} at ambient temperatures, making them less practical for many applications [89, 90]. To address the low conductivity issue, GPEs incorporate a significant amount of liquid electrolytes. These liquid components act as solvents and plasticizers, enhancing the ionic conductivity of the polymer matrix. While GPEs can achieve higher ionic conductivity compared to SPEs, this improvement comes at the expense of mechanical strength and electrochemical stability. In the realm of SIBs, research on gel polymer electrolytes has been more limited. However, studies on PEO-NaTFSI-based SPEs have shown high ionic conductivities, around 1 mS cm^{-1} at 70 °C. Despite these promising results, the relatively modest Na^+ transference number (0.4-0.5) and the need for high operating temperatures pose challenges for sodium-metal based rechargeable batteries, particularly given sodium's low melting point of 97.7 °C [91].

5. Industrial Status and Targets

SIBs are gaining traction as an alternative to LIBs, particularly in stationary energy storage applications. Major players in the industry (as shown in Table 4), such as Faradion, CATL and Natron Energy, are advancing SIB technology for grid storage, renewable energy integration, and backup power solutions [92-96]. These companies have moved from pilot projects to larger-scale commercial deployments, demonstrating the practical viability of SIBs. Current SIBs typically offer specific energies in the range of 100-150 Wh/kg. While this figure is lower than those of LIBs, they are competitive for many stationary applications where high energy density is less critical than cost and safety. The cost of SIBs is currently around $100-$150 per kWh [94] which could significantly reduce over period of time. This cost advantage is particularly appealing for large-scale energy storage solutions. SIBs are being deployed in various pilot projects and early-stage commercial applications. They are increasingly used in grid-scale energy storage, industrial backup power systems, and off-grid renewable energy storage. The technology is also being explored for applications in electric vehicles, although it is still in the early stages compared to LIBs.

Table 4. Current industry players and their future targets:

Company	Cathode	Anode	Cell Form Factor	Current Achievements	Future Targets
Faradion	Prussian Blue or layered oxide	Hard carbon	Pouch cells	140 Wh/kg 204 Wh/L	- Increase energy density to 200 Wh/kg - Reduce cost to $50-$80/kWh - Enhance cycle life to 5,000 cycles
CATL	Layered oxide or polyanionic	Hard carbon	Cylindrical and pouch cells	100-150 Wh/kg	- Achieve energy density of 200 Wh/kg - Lower cost - Improve cycle life and reliability
Natron Energy	Prussian Blue	Hard carbon	Prismatic cells	100-150 Wh/kg	- Increase energy density - Enhance cycle life - Expand application scope
HiNa	Layered oxide	Hard carbon	Pouch cells	120-160 Wh/kg	- Achieve higher energy density - Expand market presence - Enhance cost-efficiency
Northvolt	Prussian White	Hard carbon	Pouch and Prismatic	160 Wh/kg	- Scale up production - Expand market presence - Cost reduction

6. Conclusions and Perspectives

The progress towards the commercialization of SIBs has been substantial, marked by significant advancements in both anode and cathode materials. The discovery of hard carbon as a functional anode material has established it as a leading choice, given its current prominence among the limited options available. Capacities of HCs can be further improved by compositing them with alloy type Sn and P anodes. On the cathode side, a variety of promising materials have emerged, including NASICON structures, layered oxides, and Prussian blue analogs. Tailoring elemental compositions, nanosizing, and carbon coating have proven effective strategies for improving redox potentials, rate capability, and cycle life.

For India, this potential is particularly compelling given the country's abundant sodium resources, as sodium is the sixth most abundant element in the Earth's crust and the need for scalable, economical energy storage solutions to support its growing renewable energy sector. By leveraging sodium-ion technology, India could enhance its energy security, reduce costs, and promote local manufacturing and innovation. However, in order to achieve this, more research and development funding will be needed, together with smart government policy support to promote a strong local sector. Embracing SIBs could not only address critical energy challenges but also position India as a leader in the next generation of energy storage technologies.

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