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Bismuth-Based Compounds as High-Performance Anode Materials for Sodium-Ion Batteries: Mechanisms, Challenges, and Perspectives

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Abstract. The paper discusses the performance of bismuth anodes in sodium-ion batteries (SIBs) in the context of the increasing demand for renewable sources, which in turn impels the need for cost-effective sodium batteries. It begins by stating that graphite is not suitable for Na^+ ions, while hard carbon usually has poor initial coulombic efficiency. It focuses on three material options that involve Bi, Bi_2O_3, and Bi_2S_3, which use conversion–alloying techniques. In addition, the paper discusses various studies conducted in recent years to improve the performance of these materials by using them as scaffolds, carbon, or heterointerfaces, while describing challenges that impede the performance of SIBs in full-cell batteries. The analysis indicates that the key for the Bi-based anodes to be more competitive in practice is less about the high capacity values of the half-cell and more about how the issues of mechanical degradation and the interphase region can be mitigated under conditions of reasonable electrode loadings and limited sodium mass. For this reason, the importance of scalable processing and relevant cell performance assessment values (efficiency, capacity, and electrode density) for the selection of Bi-based anodes suitable for sodium-ion batteries is promoted.

1 Introduction

Decarbonization and the rapid shift toward the electrification of transport and industry are causing a dramatic increase in the demand for green energy and energy storage systems. Among available energy carriers, electricity offers important advantages in cost and environmental impact. However, battery-based energy storage depends heavily on the available battery technology, and modern requirements include more than energy density alone. Although lithium-ion batteries (LIBs) currently dominate the battery market, concerns about lithium availability and cost have encouraged research into alternatives. Sodium-ion batteries (SIBs) have gained prominence as a supplementary technology to LIBs because sodium is abundant and low-cost, allowing SIBs to be scaled for large-scale energy applications [1]. The most important challenge for SIBs is identifying suitable materials for

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their negative electrodes. Graphitic materials, which serve as negative electrodes in LIBs, do not effectively intercalate sodium ions and therefore cannot be used as conventional SIB anodes [2].

The currently preferred material for SIB anodes is hard carbon, but it has serious drawbacks. During the first cycles, the formation of a solid electrolyte interphase (SEI) film results in much lower initial Coulombic efficiency, which means that capacity loss can consume a large portion of the full-cell capacity depending on the precursors and conditions. This issue, together with challenges in improving electrochemical and processing properties, has driven research toward new anode materials.

Bismuth (Bi) and Bi compounds have attracted intensive attention as potential solutions to those issues, especially because Bi metal has been widely studied as a promising alloy-type anode for sodium- and potassium-ion batteries [3]. The reaction between Bi and Na produces Na3Bi, with a promising theoretical capacity of 385 mAh/g and a high volumetric capacity. In particular, Bi is a metal with intrinsic electrical conductivity. Therefore, Bi-based anodes can reduce the need for conductive fillers, making the anode material easier to design and process [4]. Besides Bi, other Bi compounds such as Bi2O3 and Bi2S3 are also potential anode materials with two-step reaction mechanisms, including a conversion reaction followed by an alloying reaction that produces metallic Bi and then Na3Bi. However, Bi-based anodes face challenges similar to those of other alloy- or conversion-type anodes. The alloying and conversion reactions cause expansion and contraction during cycling. This can lead to material failure and degradation of the electrode structure. The repeated formation of interphase layers on fresh surfaces also consumes sodium ions from the anode and electrolyte, lowering Coulombic efficiency during the initial stages of cycling. In full cells with limited sodium inventory, this effect can be especially harmful [1].

Recent studies show that Bi-containing materials may offer viable performance if their structural issues are controlled. Three strategies have proven useful in improving performance. (1) Nanoscale architecture can enhance diffusion [5]. (2) The use of carbon-containing frameworks, including graphene frameworks, porous carbon shells, and Bi@C nanostructure, would ensure efficient electrical conductivity, even after a large volume contraction [6,10]. (3) The building of heterostructures and related Bi-based composite systems can maximize diffusion channels and enhance reversibility for Bi-containing conversion-type materials [7,9]. Despite this progress, two gaps remain. First, performance models must reflect real-world conditions because results based on unrealistically low mass loading or high conductive-additive content can be misleading. Second, materials science and cell-level optimization must be more closely linked, especially for initial Coulombic efficiency. This work addresses these gaps by comparing Bi compounds as SIB anodes and evaluating their capacities, rate performance, cycling stability, and efficiencies. It also discusses degradation remedies and manufacturing potential through a literature-based analysis of studies published after 2020. The aim of this manuscript is to identify strategies for improving SIB storage performance through carbon-encapsulated Bi and Bi compounds. This report is organized as follows: Section 2 describes Bi-based material cases and common performance features; Section 3 assesses failure modes and compares Bi-compound anodes; and Section 4 summarizes the critical points for each material.

2 Case Description

2.1 Bismuth Metal-Type

Bismuth is a heavy post-transition metal that can store sodium through an alloying reaction. It is selected as a potential anode material for sodium-ion batteries (SIBs) because the Na-Bi alloying reaction provides high capacity. The key advantages of this material are its high electrical conductivity and high volumetric capacity.

2.2 Bismuth (III) oxide (Bi_2O_3)

Bi2O3 is an inorganic bismuth oxide that serves as a conversion-alloying-type anode. It is useful because it can generate Bi in situ as a metal phase upon sodiation and then continue sodium storage through alloying reactions. These reactions provide additional sodium-storage pathways. Its advantages include design flexibility in morphology and composite structures, which can help compensate for volume change, as well as compatibility with conductive structures that improve material utilization.

2.3 Bismuth (III) sulfide (Bi_2S_3)

Bi2S3 is a bismuth sulfide that also follows conversion-alloying behavior, producing Bi during cycling and enabling subsequent Na-Bi alloy formation, often within a sulfur-containing framework. It is used because sulfide-based chemistries can offer favorable kinetics and richer interface-engineering options, including defects, heterointerfaces, and mixed sulfide-carbon architectures, that help regulate reaction pathways and mitigate pulverization. Its advantages include potentially improved rate capability from more facile ion transport, opportunities for engineered heterointerfaces to guide charge transfer, and strong synergy with carbon or hetero-sulfide scaffolds that buffer volume change and preserve electrical connectivity during long cycling.

3 Analysis and challenges

3.1 Bismuth metal-type (Bi)

A binder-free Bi anode based on a one-step electrochemical co-deposition strategy was reported, where three-dimensional Bi nanosheets were co-deposited with a conductive carbon nanotube network to form a hierarchical Bi NS/CNTs array directly on the current collector. In this design, the CNT network served as a continuous electron-conducting scaffold and an anchoring framework, while the nanosheet-like Bi provided abundant active interfaces for Na alloying and dealloying. Because the active phase was integrated with the conductive network during deposition, the electrode architecture avoided the usual binder-mediated weak adhesion and helped keep the Bi phase electrically connected during repeated volume changes. Fig. 1 shows a schematic illustration of the one-step electrochemical co-deposition route used to fabricate binder-free Bi NS/CNTs arrays [6].

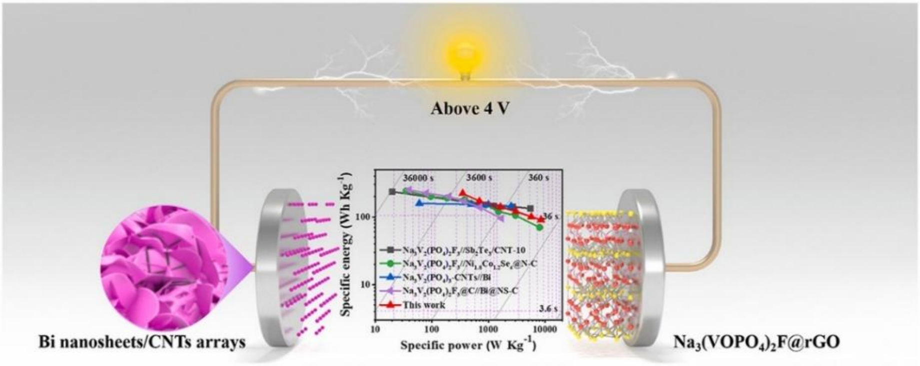

Fig. 1. Schematic illustration of the Bi NS/CNTs array anode [6].

Compared with a sole Bi electrode prepared through the same strategy, the Bi NS/CNTs arrays delivered stronger interfacial adhesion and more stable cycling behavior, which supports the goal of suppressing pulverization and contact loss in alloy-type anodes. The reported capacity remained 383.72 mAh g−1 at 0.1 A g−1 after 200 cycles and 311.68 mAh g−1 at 1 A g−1 after 1000 cycles, showing that the architecture supported long-term reversibility under both moderate- and high-rate conditions. More importantly, when paired with a high-voltage cathode, the resulting full sodium-ion battery operated above 4 V and achieved an energy density of 221.99 Wh kg−1, indicating that metallic Bi can contribute to practical high-voltage SIB configurations when structural stability is addressed [6].

The presence of a carbon nanotube network greatly reduces the main drawbacks of using bismuth alone. By acting as a continuous electron-conducting backbone, CNTs help resist the pulverization normally exhibited by Bi electrodes during repeated volumetric changes. However, the main remaining concern is that many lab-scale studies report performance at relatively low mass loading, which can obscure real cell-level penalties such as poor initial Coulombic efficiency and sodium-inventory loss. In addition, the desired alloy matrix can still be affected by significant expansion and contraction during alloying and dealloying, as shown schematically in the accompanying figure.

3.2 Bismuth (III) oxide (Bi_2O_3)

A representative Bi2O3-based design constructed a heterostructured Bi2O3@rGO composite through a hydrothermal-plus-annealing route [7]. Graphene oxide (GO) was first prepared using the modified Hummers method and ultrasonically dispersed in N,N-dimethylformamide. Then, Bi(NO3)3 5H2O and polyvinylpyrrolidone were introduced to form a precursor dispersion, which was transferred into a Teflon-lined autoclave and heated at 180 ℃ for 8 h. After washing and drying, the precursor was annealed at 300 ℃ for 4 h in air to obtain Bi2O3@rGO. A bare Bi2O3 control was prepared under the same conditions without GO. For electrochemical testing, electrodes were fabricated using an 80/10/10 wt% mixture of active material/Super-P/PVDF, coated on Cu foil, and assembled into CR2032 coin cells with a Na metal counter electrode and 1 M NaClO4 in EC/PC (1:1) electrolyte, with a reported mass loading of around 1 mg cm−2. Fig. 2 shows the Na-ion and electron transfer behavior in Bi2O3@rGO [7].

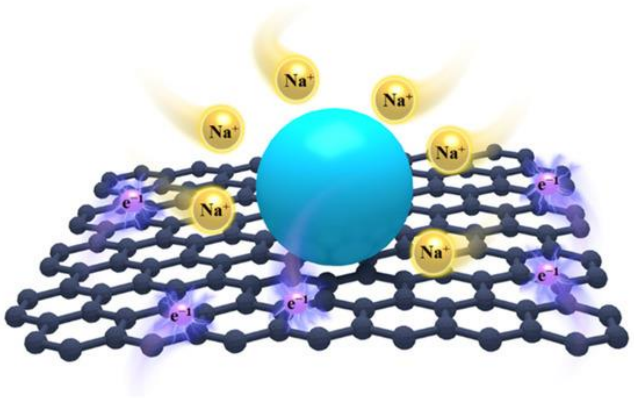

Fig. 2. Schematic of Na-ion and electron transfer in Bi2O3@rGO [7].

The Bi2O3@rGO electrode showed an initial discharge capacity of 421.8 mAh/g at 50 mA/g, reflecting the combined conversion (Bi2O3 to Bi) and subsequent alloying reactions during sodiation [7]. During cycling, the reversible discharge capacity reached 160.9 mAh g−1 after 100 cycles at 50 mA g−1, clearly outperforming bare Bi2O3, which was reported at less than 50 mAh g−1 at the same stage. This result is consistent with rGO suppressing agglomeration and improving charge transfer. The composite also demonstrated better rate behavior, delivering 162, 135, 119, 105, 94, and 83 mAh g−1 at 0.05, 0.1, 0.2, 0.5, 1, and 2 A g−1, and recovering to 141 mAh g−1 when the current returned to 0.05 A g−1. Although the initial Coulombic efficiency was low at 42.51%, it increased rapidly to more than 90% after three cycles and stabilized above 95% after six cycles, whereas bare Bi2O3 required substantially more cycles to approach comparable CE stability [7]. These outcomes support the advantage of carbon-based heterostructuring for maintaining electrical continuity and mitigating particle deformation during repeated conversion and alloying.

While the reduced graphene oxide scaffold helps reduce particle deformation and preserve an electronically conductive pathway, the main problem for Bi2O3-type anode materials remains the high irreversibility of sodium-consuming processes during the early cycles. Despite the benefits offered by an rGO-based heterostructure, an initial Coulombic efficiency of only 42% is a serious concern for full cells because an anode with low ICE directly reduces the sodium reserves of the cathode unless cathode overbalance or pre-sodiation is adopted [7].

3.3 Bismuth (III) sulfide (Bi_2S_3)

A defect-engineered sulfide case reported a carbon-supported Bi2S3-CuS heterostructure with abundant sulfur defects, prepared through a combined calcination and ion-exchange approach [8]. The central idea was to build a mixed-phase sulfide interface, with Bi2S3 coupled with CuS, on a conductive carbon matrix while simultaneously introducing defect sites that could modulate adsorption and diffusion behavior for Na+ storage. Structurally, the heterointerface was intended to provide fast charge-transfer pathways and mechanically buffer reaction strain, while the carbon support maintained continuous electronic conduction under high-rate cycling. Fig. 3 shows a defect-rich Bi2S3-CuS heterostructure anchored on carbon support to accelerate Na+ transport and stabilize cycling [8].

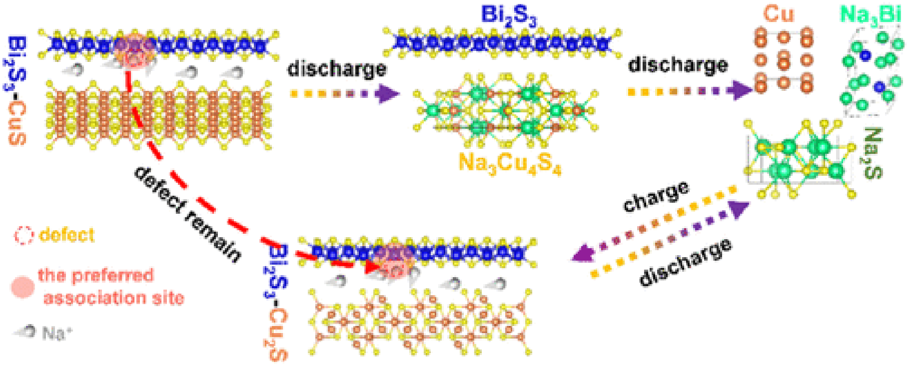

Fig. 3. Mechanism of defective Bi2S3 anchored on CuS/C as an ultrafast and long-life anode for sodium-ion storage [8].

The defect-containing Bi2S3-CuS/C design delivered strong long-life and high-rate performance, including a reported capacity of 592.2 mAh g−1 after 1000 cycles at 8 A g−1. In a full-battery configuration, the system maintained 216 mAh g−1 after 4000 cycles at 10 A g−1, which is a notable data point because many conversion-type sulfides struggle to retain capacity under prolonged high-current operation. Mechanistically, the authors linked this performance to defect and heterointerface synergy: sulfur defects and interfacial coupling were associated with improved reaction kinetics and Na+ transport, supported by electrochemical analysis and density functional theory discussion in the study [8]. Practically, this case suggests that Bi2S3 can move beyond the typical sulfide trade-off of high capacity but fast degradation when interface engineering and defect tuning are applied systematically [8].

The biggest challenge for this kind of sulfide heterostructure is controllability at scale: defect concentration, phase ratio (Bi2S3 vs. CuS), and interfacial uniformity must be reproducible across batches, or performance will vary sharply from cell to cell. Sulfide systems also carry additional side-reaction risks, including surface-driven electrolyte decomposition and unstable interphases, because higher surface activity often increases irreversible consumption and accelerates SEI evolution, especially under high-rate cycling. To make Bi2S3-based heterostructures credible for practical SIBs, future validation should emphasize ICE and gas/impedance evolution tracking, areal-capacity scaling with realistic electrode densities, and electrolyte compatibility screening to reduce parasitic reactions while preserving the high-rate advantage that makes defect-rich sulfides attractive.

4 Summary and suggestions

Based on Table 1, bismuth metal-type (Bi) anodes have the most straightforward profile because their natural electrical conductivity and reversible alloying reaction can be realized once the electrode structure is stabilized. However, long-term stability and high-voltage full-cell operation usually require Bi to be combined with conductive scaffolds that maintain electron transport during repeated alloying and dealloying. As shown in the table, a major issue for Bi anodes is volume expansion, which can lead to electrode breakage, detachment from the current collector, and repeated interphase rebuilding. Bi metal can serve as the best baseline choice when structural reinforcement and early-cycle efficiency are treated as essential design requirements.

Table 1. Comparison of advantages and disadvantages of various Bi-based anodes.

Material	Progress	Challenges
Bismuth Metal-Type (Bi)	-long-term reversibility -high-voltage operation -intrinsic conductivity	-large volume expansion -contact loss and SEI regrowth -low initial efficiency at practical loading
Bismuth (III) oxide (Bi2O3)	-conversion-alloying enables high storage -rGO/carbon improves transport and stability -strong composite/morphology flexibility	-very low initial coulombic efficiency -low intrinsic conductivity of oxide -multistep reaction stress; density penalty from carbon
Bismuth (III) sulfide (Bi2S3)	-fast kinetics potential (engineered interfaces) -strong high-rate durability -tunable interfacial pathways with carbon supports	-defect/phase reproducibility -parasitic reactions and interphase instability -synthesis and scale-up complexity

The table for Bi2O3 points to a different set of trade-offs: high sodium-storage ability through a conversion mechanism followed by alloying, along with strong flexibility in composite and morphology control. Progress on Bi2O3 heavily relies on high-carbon frameworks such as reduced graphene oxide (rGO), since the oxide alone lacks the conductivity needed to maintain charge transfer. The most important issue is the very low initial Coulombic efficiency, which is not only an experimental concern but also a full-cell problem because it decreases usable energy and consumes sodium inventory. Bi2O3 can still play a role if future development uses an ICE-first approach.

For Bi2S3, the central strength in the table is its kinetic potential, especially its ability to support high-rate performance with a conductive carbon matrix and strong durability. Bi2S3 is one of the more attractive research areas for power applications where rapid sodium storage is necessary. The key challenges are defect and phase reproducibility as well as interphase stability. Variability in defect concentration or phase composition directly causes variability in performance. Sulfide surfaces can also increase reactivity if the interfaces are not managed well. Therefore, Bi2S3 offers high potential but also requires strong control over reproducibility and efficiency.

Looking forward, the most promising path involves moving from material-level success to cell-level relevance and scalable processing. For Bi, Bi2O3, and Bi2S3, progress will rely on three common goals: stabilizing volume changes with conductive and mechanical supports, improving early-cycle efficiency to reduce sodium consumption, and testing realistic areal capacity and electrode density. Future studies should standardize the reporting of initial efficiency, areal capacity, electrode density, and full-cell capacity retention. Synthesis methods that can be scaled more easily will become increasingly important. With these standards, research on Bi-based materials can more clearly identify which anodes are likely to move from promising laboratory results to practical sodium-ion batteries.

5 Conclusion

In summary, this paper examined three bismuth-based anode materials for sodium-ion batteries: bismuth (Bi), bismuth oxide (Bi2O3), and bismuth sulfide (Bi2S3). The goal was to evaluate their sodium-storage capability, the benefits created by material development, and the challenges that still limit their use in full-cell batteries. The comparison shows that the practical value of bismuth-based materials depends not only on their intrinsic capacity but also on structural stability, interphase control, and realistic cell-level performance.

Conclusion 1: Bi metal is clearly most advantageous in this regard due to its large volume capacity and natural electrical conductivity. Despite this, another major limiting factor is the expansion that accompanies alloy formation; thus, a mechanically stable material becomes very important. It would appear that a conductive matrix and electrode structure might be required to allow for electrical series continuity and to resist degradation.

Conclusion 2: The Bi_2O_3 material offers a wider design space through conversion and alloying mechanisms, but it experiences severe irreversible capacity loss in the early cycles. The major disadvantage is its low coulombic efficiency during the first cycle, which depletes the sodium resources and limits the usable full-cell capacity. As a result, Bi_2O_3 materials need conductive and controlled interface/formation strategies to ensure high theoretical capacity storage is effectively leveraged.

Conclusion 3: Bi_2S_3 has the greatest ability in respect to rapid kinetic processes if defect engineering and heterogeneous interfaces are utilized. Issues regarding Bi_2S_3 are reproducibility and interphase stability, because if variations in defects and interphases are unmanaged, then it is possible to worsen undesirable side reactions through the active sulfide surface.

According to the results of the experiment, bismuth-anode materials have potential only if "bismuth chemistry" is combined with the battery focus: the key to this will be maintaining conductivity while expanding/contracting the material, protecting interfaces to safeguard the sodium reservoirs, and testing the material under realistic conditions of electrode loading. the next step should be the development of more scaled-up processes for choosing the most efficient base combinations.

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