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(Review Article)

Hybrid sodium-ion battery anode systems: integrating advanced materials for high-performance storage

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Abstract

As the global demand for sustainable energy storage escalates, sodium-ion batteries (SIBs) have emerged as a promising alternative to lithium-ion systems, leveraging the abundance and low cost of sodium. This review illuminates the transformative potential of hybrid anode systems, which integrate advanced materials such as carbon-based structures, metals, alloys, and transition metal oxides to overcome the limitations of conventional SIB anodes. By synergistically combining multiple sodium storage mechanisms—intercalation, alloying, and conversion—these systems achieve remarkable specific capacities, enhanced rate capabilities, and prolonged cycling stability, positioning them as cornerstones for next-generation SIBs. The exploration of synthesis techniques, including electrospinning and ball milling, alongside structural optimizations like core-shell and porous architectures, reveals pathways to mitigate challenges such as volume expansion and unstable solid electrolyte interphase formation. The critical role of electrolytes and binders in stabilizing electrochemical performance is also examined, underscoring their impact on coulombic efficiency and long-term durability. Despite these advances, hurdles in scalability, cost, and environmental sustainability persist, necessitating innovative solutions like bio-derived materials and machine learning-driven design. This review synthesizes these insights, offering a comprehensive roadmap for researchers and industry stakeholders to advance hybrid anode technology. By addressing current challenges and embracing emerging trends, hybrid anodes hold the promise of propelling SIBs toward widespread adoption, fueling a sustainable energy future with robust, high-performance storage solutions.

Keywords: Sodium-Ion Batteries; Hybrid Anodes; Advanced Materials; Electrochemical Performance; Carbon-Based Composites; Alloying Materials; Transition Metal Oxides; Sustainable Energy Storage.

1. Introduction

The global demand for sustainable and cost-effective energy storage solutions has intensified with the rapid expansion of renewable energy systems and electric vehicles, necessitating alternatives to lithium-ion batteries (LIBs). Sodium-ion batteries (SIBs) have emerged as a promising candidate due to the abundance, low cost, and environmental benignity of sodium resources. This review explores hybrid anode systems for SIBs, focusing on the integration of advanced materials to achieve high-performance energy storage. By combining diverse materials such as carbon-based

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structures, metals, and transition metal oxides, hybrid anodes aim to overcome the limitations of conventional anode materials, offering improved capacity, cycling stability, and rate performance. This section provides the background, highlights challenges in SIB anode development, and outlines the scope of this review.

1.1. Background and Significance of Sodium-Ion Batteries

The transition to a low-carbon economy has amplified the need for efficient energy storage systems to support intermittent renewable energy sources like solar and wind. According to Goodenough and Kim [1], the dominance of LIBs in portable electronics and electric vehicles stems from their high energy density and long cycle life, but the scarcity and uneven distribution of lithium resources pose significant challenges for scalability [1]. Sodium-ion batteries, leveraging the earth-abundant sodium, offer a sustainable alternative due to sodium's low cost and similar electrochemical properties to lithium. Studies by Palomares et al. [2] emphasize that SIBs can utilize existing LIB manufacturing infrastructure, facilitating rapid adoption in grid storage and low-cost electric vehicles [2]. The significance of SIBs lies in their potential to reduce dependency on critical materials while maintaining competitive electrochemical performance.

The electrochemical performance of SIBs hinges on the development of high-capacity electrodes, particularly anodes, which must accommodate the larger ionic radius of sodium (1.02 Å) compared to lithium (0.76 Å). This size difference, as noted by Hwang et al. [3], leads to sluggish sodium-ion diffusion and structural instability in traditional anode materials like graphite, which exhibits negligible sodium storage capacity [3]. Consequently, research has shifted toward alternative materials and hybrid systems to enhance sodium storage efficiency. For instance, Fang et al. [4] demonstrated that hybrid anodes combining carbon frameworks with metal sulfides can significantly improve capacity and stability, underscoring the potential of material integration [4]. The growing body of literature on SIBs highlights their role in addressing global energy challenges, particularly for large-scale applications where cost and sustainability are paramount.

The significance of SIBs extends beyond economic and environmental benefits to their versatility in diverse applications. Research by Yabuuchi et al. [5] indicates that SIBs are particularly suited for stationary energy storage due to their tolerance for partial state-of-charge cycling, unlike LIBs, which suffer capacity fade under similar conditions [5]. Moreover, the development of high-performance anodes is critical to realizing the full potential of SIBs. Hybrid anode systems, which integrate materials with complementary properties, have emerged as a key strategy to overcome the limitations of single-material anodes. This review will explore how advanced materials and their synergistic combinations can elevate SIB performance, drawing on recent advancements to guide future research and development.

1.2. Challenges in SIB Anode Development

Developing high-performance anodes for SIBs remains a formidable challenge due to the intrinsic properties of sodium and the limitations of conventional anode materials. As highlighted by Zhang et al. [6], the larger ionic radius and higher redox potential of sodium (-2.71 V vs. -3.04 V for lithium) result in lower energy density and slower reaction kinetics compared to LIBs [6]. Graphite, a staple anode material in LIBs, exhibits poor sodium storage due to weak intercalation, as elucidated by Wen et al. [7], who showed that sodium ions form unstable intercalation compounds with graphite, leading to capacities below 35 mAh/g [7]. This necessitates the exploration of alternative materials, such as hard carbon, metals, and transition metal oxides, which often face their own challenges, including volume expansion and poor cycling stability.

Volume expansion during sodiation/desodiation cycles is a critical issue for high-capacity anode materials like tin and phosphorus, which can undergo expansions exceeding 400%. According to Liu et al. [8], such volume changes cause mechanical stress, pulverization, and loss of electrical contact, resulting in rapid capacity fade [8]. For example, tin-based anodes, despite their high theoretical capacity (847 mAh/g), suffer from structural degradation, as reported by Chevrier and Ceder [9], who used computational models to predict severe lattice strain during sodium alloying [9]. Similarly, transition metal oxides, while offering high capacities, often exhibit low electrical conductivity and irreversible capacity loss, as noted by Fang et al. [10] in their study of nanostructured electrode materials. These challenges underscore the need for innovative anode designs that mitigate structural instability and enhance electrochemical performance.

Another significant hurdle is the formation of an unstable solid electrolyte interphase (SEI) on SIB anodes, which consumes electrolyte and reduces coulombic efficiency. Findings from Oh et al. [11] indicate that the SEI in SIBs is less stable than in LIBs due to the higher solubility of sodium-based SEI components in common electrolytes [11]. This instability leads to continuous electrolyte decomposition, reducing battery lifespan. Furthermore, the low initial coulombic efficiency of materials like hard carbon, complicates practical implementation, as it requires excess cathode material to compensate for capacity loss [12]. Addressing these challenges requires tailored material designs, such as hybrid systems that combine the high capacity of alloys with the stability of carbon-based materials. Figure 1 depicts the evolution of solid electrolyte interphase (SEI) models on hard carbon anodes, underscoring the challenges of SEI instability and its impact on coulombic efficiency and battery lifespan in SIBs.

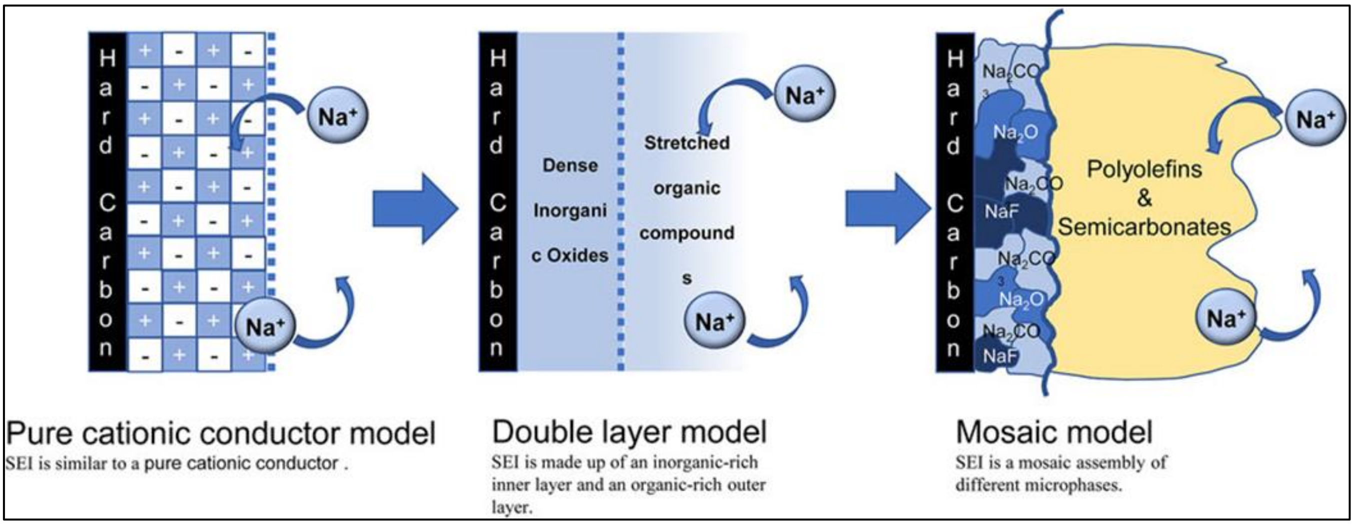


Figure 1 Evolution of SEI in Hard Carbon Anodes. Reprinted with permission from Meng et al. [12] under the terms of the Creative Commons Attribution License (CC BY).

The complexity of optimizing anode materials for SIBs is compounded by the need for scalability and cost-effectiveness. While laboratory-scale studies, such as those by Gao et al. [13], demonstrate promising results with nanostructured hybrid anodes, their synthesis often involves complex and costly processes. Scaling these materials for commercial applications remains a significant barrier, as emphasized by Jin et al. [14], who highlight the trade-off between performance and manufacturability in SIB anode design. Hybrid anode systems, which integrate multiple materials to balance capacity, stability, and cost, offer a pathway to overcome these challenges, but their development requires a deeper understanding of material interactions and electrochemical behavior.

1.3. Scope and Objectives of the Review

This review aims to provide a comprehensive analysis of hybrid anode systems for SIBs, focusing on the integration of advanced materials to achieve high-performance energy storage. The scope encompasses recent advancements in carbon-based materials, metals, alloys, and transition metal oxides, with an emphasis on their synergistic effects in hybrid configurations. According to Chen et al. [15], hybrid anodes leverage the complementary strengths of individual materials, such as the high conductivity of carbon and the high capacity of metal alloys, to enhance overall performance. This review will evaluate these systems based on key performance metrics, including specific capacity, rate capability, and cycling stability, while addressing challenges in material synthesis and scalability.

A primary objective is to synthesize insights from recent literature to identify effective strategies for designing hybrid anodes. For instance, a novel study by Fang et al. [16] on three-layered Cu_2S@Carbon@MoS_2 nanoboxes demonstrated exceptional sodium storage due to their hierarchical structure, highlighting the potential of tailored architectures. This review will explore similar innovations, including core-shell and porous designs, to elucidate their impact on electrochemical performance. Additionally, it will examine the role of synthesis techniques, such as chemical vapor deposition and electrospinning, in achieving precise material integration, as discussed by Lu et al. [17] in their work on metal-organic framework-derived materials.

The review also seeks to address the practical challenges of implementing hybrid anodes in commercial SIBs. By analyzing case studies and performance data, it will highlight gaps in current research, such as the need for sustainable and scalable synthesis methods. Insights from Zhou et al. [18] on Prussian blue analogs suggest that cost-effective materials can achieve high performance, providing a model for hybrid anode development. The review will propose future research directions, including the use of bio-derived materials and machine learning for material optimization, to guide the development of next-generation SIB anodes.

Finally, the review will critically assess the environmental and economic implications of hybrid anode systems. As noted by Naveed et al. [19], the sustainability of SIBs depends on minimizing the environmental impact of material synthesis and improving recyclability. By integrating findings from diverse studies, this review aims to provide a roadmap for researchers and industry stakeholders to advance SIB technology, ensuring that hybrid anodes contribute to sustainable and high-performance energy storage solutions.

2. Fundamentals of Sodium-Ion Battery Anodes

The performance of sodium-ion batteries (SIBs) relies heavily on the anode, which serves as the host for sodium-ion storage during charge-discharge cycles. Understanding the fundamental mechanisms of sodium storage, key performance metrics, and limitations of conventional anode materials is critical for designing high-performance hybrid systems. This section explores the electrochemical principles governing SIB anodes, evaluates essential performance criteria, and highlights the challenges associated with traditional materials, setting the stage for the discussion of hybrid anode systems in subsequent sections.

2.1. Sodium Storage Mechanisms

Sodium-ion storage in anode materials occurs through three primary mechanisms: intercalation, conversion, and alloying, each presenting distinct electrochemical behaviors. Intercalation involves the reversible insertion of sodium ions into layered or porous structures, as described by Beda et al. [20], who noted that hard carbon, unlike graphite, accommodates sodium ions due to its disordered structure and larger interlayer spacing. Hard carbon's ability to store sodium via intercalation and pore-filling mechanisms results in capacities of 250–350 mAh/g, significantly higher than graphite's negligible capacity in SIBs. However, the low potential plateau of intercalation-based materials can lead to sodium plating risks, limiting their practical application, as highlighted by Luo et al. [21] in their review of carbon-based anodes.

Conversion reactions, prevalent in transition metal oxides and sulfides, involve a redox process where the anode material reacts with sodium to form new compounds. According to Li et al. [22], materials like FeS2 undergo conversion reactions (e.g., $FeS2 + 4Na+ \rightarrow Fe + 2Na2S$), offering high theoretical capacities (up to 893 mAh/g) but suffering from large volume changes and sluggish kinetics [22]. These reactions provide higher capacities than intercalation but are often irreversible, leading to capacity fade. A classic study by Xiao et al. [23] on MoS2 anodes demonstrated that nanostructuring can mitigate volume expansion, enhancing reversibility, though challenges with conductivity persist [23]. The distinct electrochemical profiles of conversion-based materials necessitate careful material design to balance capacity and stability.

Alloying reactions, observed in materials like tin (Sn) and phosphorus (P), offer some of the highest theoretical capacities for SIB anodes. As reported by Lao et al. [24], tin forms Na15Sn4 during sodiation, yielding a capacity of 847 mAh/g, while phosphorus can achieve up to 2596 mAh/g through Na3P formation [24]. However, these materials experience severe volume expansion (e.g., 420% for Sn), leading to mechanical degradation, as elucidated by Zhou et al. [25] in their study of alloying-based anodes. Strategies like nanostructuring and carbon compositing, , have shown promise in buffering volume changes, but alloying materials still face challenges with initial coulombic efficiency and cycle life [26]. Understanding these mechanisms is essential for designing hybrid anodes that combine the strengths of each storage mode.

The interplay between these mechanisms influences the overall performance of SIB anodes. For instance, Komaba et al. [27] found that combining intercalation and alloying in carbon-metal composites can enhance capacity while improving stability, a principle central to hybrid anode systems [27]. The choice of storage mechanism depends on the material's structure, composition, and electrochemical environment, requiring tailored designs to optimize sodium storage. This diversity in mechanisms underscores the need for hybrid systems that integrate multiple storage modes to achieve synergistic effects, as will be discussed in later sections. To provide a clear overview of the discussed sodium storage mechanisms, Table 1 summarizes key examples, theoretical capacities, advantages, challenges, and representative materials, drawing from recent literature.

Table 1 Sodium Storage Mechanisms in SIB Anodes

Mechanism	Description	Theoretical Capacity (mAh/g)	Advantages	Challenges	Example Materials	Representative Studies/References
Intercalation	Reversible insertion of Na+ into layered or porous structures without major structural changes.	250–350 (hard carbon)	High stability, low volume change (<10%), good cycling life.	Low capacity, risk of Na plating at low potentials, sluggish diffusion due to larger Na+ size.	Hard carbon, expanded graphite.	Beda et al. [20], Luo et al. [21], Wen et al. [7].
Intercalation	-	~300 (glucose-derived hard carbon)	-	-	Glucose-derived hard carbon.	Stevens and Dahn [42].
Conversion	Redox reaction forming new compounds (e.g., metal + Na_2X).	Up to 893 (FeS_2), 670 (MoS_2).	High capacity, multi-electron transfer.	Large volume expansion (100–300%), irreversibility, low conductivity.	FeS_2, MoS_2, SnS_2.	Li et al. [22], Xiao et al. [23], Yao et al. [60].
Conversion	-	500–800 (SnS_2)	-	-	SnS_2 nanosheets.	Li et al. [63].
Alloying	Formation of Na-metal alloys (e.g., Na15Sn4).	847 (Sn), 660 (Sb), 2596 (P).	Very high capacity, low operating potential.	Extreme volume expansion (420% for Sn, 490% for P), pulverization, poor cycling.	Sn, Sb, P, SnSb alloys.	Lao et al. [24], Zhou et al. [25], Bai et al. [26].
Alloying	-	1500 (red P-carbon)	-	-	Red phosphorus-carbon composites.	Sun et al. [58].
Hybrid (Combined)	Integration of multiple mechanisms (e.g., intercalation + alloying).	500–650 (e.g., SnS2/graphene).	Synergistic effects, balanced capacity/stability.	Complex synthesis, interface instability.	Carbon-metal composites, SnS2/graphene.	Komaba et al. [27], Xu et al. [76].
Hybrid (Combined)	-	600 (Sn@carbon)	-	-	Sn@carbon nanofibers.	Chen et al. [84].

To further illustrate the synergistic benefits of integrating advanced materials in hybrid systems, Figure 2 depicts the advantages of two-dimensional materials, such as providing abundant ion transport channels and low activation barriers, which enhance sodium storage efficiency in composite anodes.

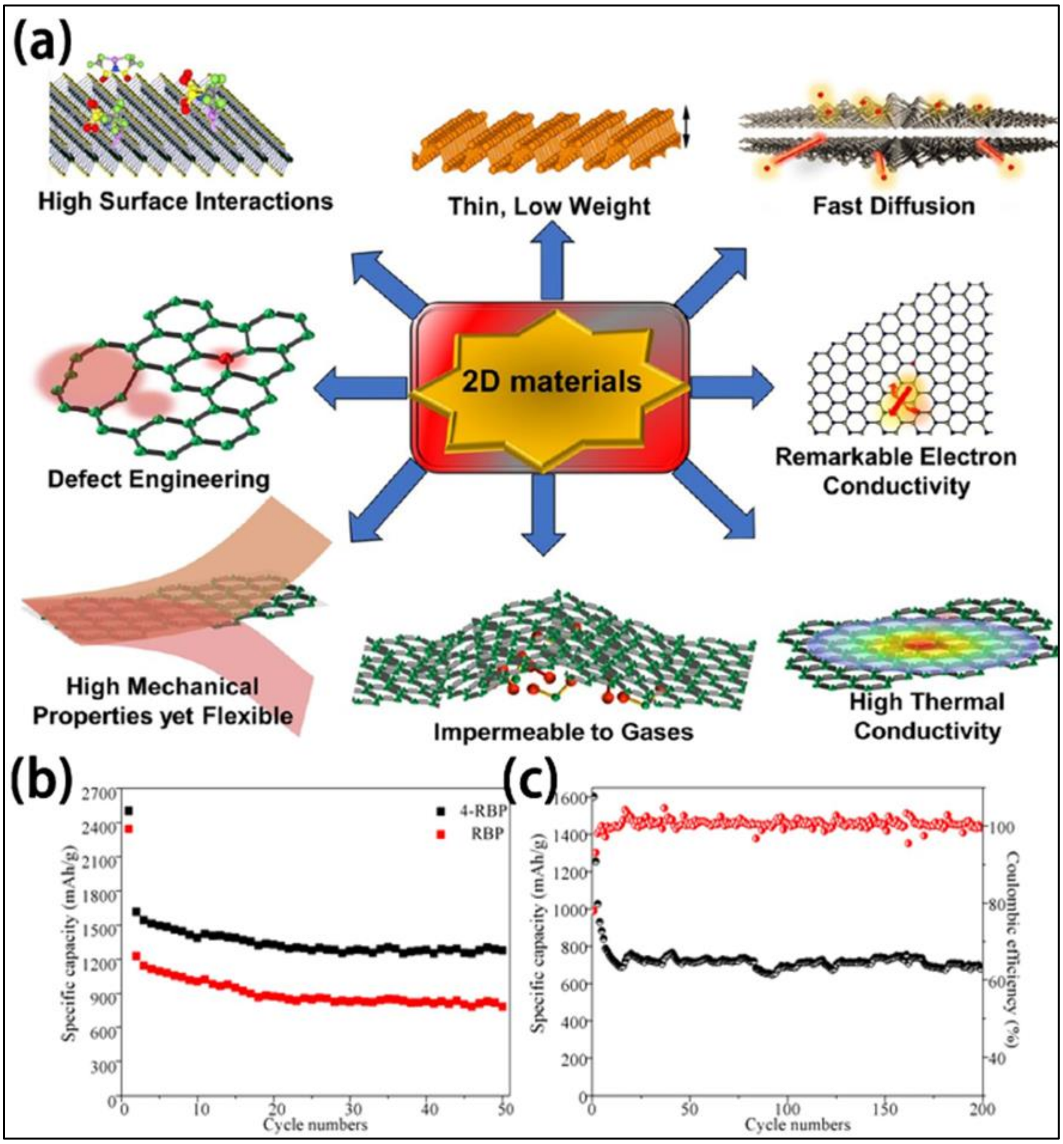


Figure 2 Advantages of 2D Materials in Hybrid Anodes. (a) Benefits of two-dimensional materials in energy storage applications. (b) Specific capacities of 4-nitrobenzenediazonium-modified black phosphorus chemically linked to reduced graphene oxide hybrid (4-RBP) and black phosphorus integrated with RGO (RBP) at a current density of 0.1 A g^{-1}. (c) Specific capacity and Coulombic efficiency of the 4-nitrobenzenediazonium-modified black phosphorus chemically linked to reduced graphene oxide hybrid (4-RBP). Reprinted with permission from Bai et al. [26] under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/)

2.2. Key Performance Metrics for SIB Anodes

The evaluation of SIB anodes hinges on several critical performance metrics: specific capacity, rate capability, cycling stability, and coulombic efficiency. Specific capacity, defined as the charge stored per unit mass (mAh/g), is a primary indicator of an anode's energy storage potential. According to Wang et al. [28], high-capacity materials like phosphorus and tin alloys outperform intercalation-based hard carbon, but their practical capacities are often limited by irreversible losses in the first cycle [28]. For instance, hard carbon anodes typically deliver 250–300 mAh/g, while alloying materials can exceed 1000 mAh/g, as demonstrated by Yuan et al. [29] in their work on SnSb alloys. Achieving high specific capacity without compromising other metrics remains a key challenge in anode design.

Rate capability, which measures an anode's ability to maintain capacity at high charge-discharge rates, is critical for applications requiring fast charging, such as electric vehicles. Findings from Hou et al. [30] indicate that carbon-based anodes, particularly graphene composites, exhibit superior rate performance due to their high electrical conductivity and fast ion diffusion [30]. In contrast, conversion-based materials like metal oxides often suffer from poor rate capability due to low conductivity, as noted by Du et al. [31] in their study of Co_3O_4 anodes. Enhancing rate capability in hybrid systems often involves incorporating conductive carbon matrices, a strategy that will be explored in Section 4.

Cycling stability, or the ability to maintain capacity over repeated charge-discharge cycles, is essential for practical SIB applications. A study by Zhang et al. [32] on hard carbon anodes revealed stable cycling over 200 cycles, attributed to their robust disordered structure, whereas alloying materials like antimony suffer capacity fade within 50 cycles due to pulverization [32]. Similarly, coulombic efficiency, which reflects the reversibility of sodium storage, is critical for minimizing energy loss. According to reports, the initial coulombic efficiency of hard carbon is often below 80% due to SEI formation, necessitating strategies to enhance reversibility [31-33]. Hybrid anodes aim to balance these metrics by combining materials with complementary properties, such as high-capacity alloys with stable carbon frameworks.

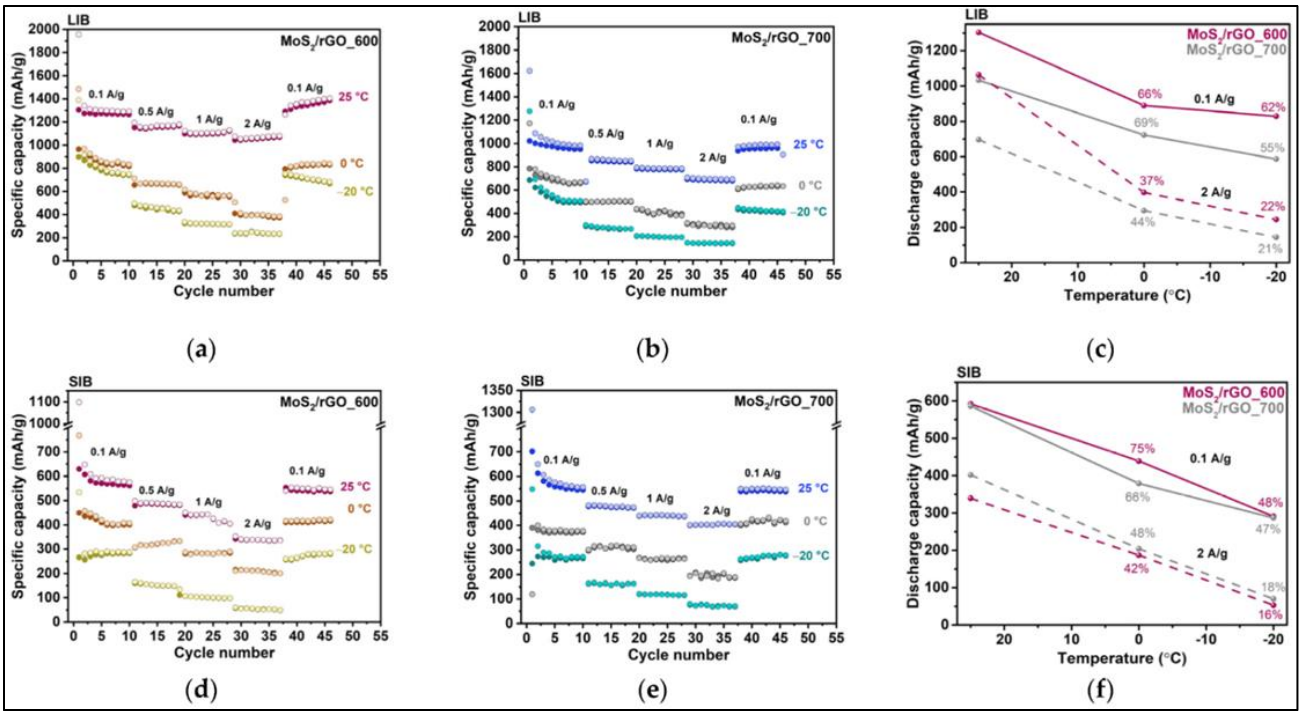
The interplay of these metrics determines the practical viability of SIB anodes. For example, Zeng et al. [34] demonstrated that a SnS_2/graphene composite achieved a high specific capacity (600 mAh/g) and stable cycling (500 cycles) by leveraging the conductivity of graphene and the capacity of SnS_2 [34]. Such studies highlight the importance of optimizing all performance metrics simultaneously, a goal that hybrid anode systems are uniquely positioned to achieve through material integration. Table 2 presents a comprehensive comparison of key performance metrics across various SIB anode materials, including specific capacity, rate capability, cycling stability, and coulombic efficiency, to highlight benchmarks for evaluation.

Table 2 Key Performance Metrics for SIB Anode Materials

Material Type	**Specific Capacity (mAh/g)**	**Rate Capability (mAh/g at High Rate)**	**Cycling Stability (Cycles, Retention %)**	**Initial Coulombic Efficiency (%)**	**Advantages in Metrics**	**Challenges in Metrics**	**References**
Hard Carbon	250–350	150–200 at 1 A/g	200 cycles, 90%	70–80	Good stability, moderate rate.	Low ICE, limited high-rate performance.	Wang et al. [28], Zhang et al. [32], Vorfolomeeva et al. [33].
Graphite	<35	Negligible	Poor	Low	None significant for SIBs.	Poor overall metrics due to weak intercalation.	Jache and Adelhelm [35].
Tin (Sn) Alloys	847 (theoretical), 600 practical	200–300 at 2 A/g	200 cycles, 70–80%	60–70	High capacity.	Rapid fade at high rates.	Yuan et al. [29], Kalubarme et al. [55].
Phosphorus (P)	2596 (theoretical), 1500 practical	500 at 1 A/g	100 cycles, 60%	50–60	Ultra-high capacity.	Poor stability, low ICE.	Sun et al. [58], Fang et al. [98].
MoS_2 (Conversion)	670	300 at 2 A/g	100 cycles, 70%	70–80	Balanced capacity/rate.	Volume expansion limits cycles.	Yao et al. [60], Wu et al. [61].
Fe_2O_3 (TMO)	1007 (theoretical), 600 practical	200 at 5 A/g	500 cycles, 90%	70–85	Excellent stability.	Moderate rate due to low	Bhar et al. [66], Su et al. [67].

						conductivity .	
Graphene Composites	400–630	100–400 at 5 A/g	500 cycles, 85%	80–85	Superior rate, good stability.	Restacking reduces long-term metrics.	Hou et al. [30], Chen et al. [49].
CNT Composites	400–520	300–500 at 2 A/g	500 cycles, 90%	80–90	High rate and stability.	Cost affects scalability.	Tang et al. [51], Li et al. [97].
Hybrid (e.g., SnS_2/Graphene)	650	400 at 5 A/g	1000 cycles, 85%	85	Balanced across all metrics.	Synthesis complexity.	Zeng et al. [34], Samad et al. [96].

Figure 3 showcases the rate capability and capacity retention of MoS_2/reduced graphene oxide hybrid anodes at different temperatures, demonstrating how such composites balance specific capacity, rate performance, and cycling stability under varying conditions.



(a) (b) (c)

(d) (e) (f)

Figure 3 Electrochemical behavior of MoS2/rGO_600 and MoS2/rGO_700 anodes under varying temperatures in lithium-ion batteries (upper panels) and sodium-ion batteries (lower panels). Rate performance of (a,d) MoS_2/rGO_600 and (b,e) MoS_2/rGO_700 across current densities from 0.1 A/g to 2 A/g at temperatures of 25 °C, 0 °C, and −20 °C. (c,f) Capacity retention during temperature reduction from 25 °C to −20 °C at current densities of 0.1 A/g and 2 A/g. under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/)

2.3. Limitations of Conventional Anode Materials

Conventional anode materials for SIBs, such as graphite, hard carbon, and metal oxides, face significant limitations that hinder their widespread adoption. Graphite, widely used in LIBs, is largely ineffective for SIBs due to its inability to intercalate sodium ions effectively. According to Jache and Adelhelm [35], the interlayer spacing of graphite (3.35 Å) is too small to accommodate sodium ions, resulting in capacities below 35 mAh/g [35]. This limitation has driven research toward alternative carbon-based materials, but graphite's poor performance underscores the need for materials tailored specifically for sodium storage.

Hard carbon, a promising alternative, offers higher capacities (250–350 mAh/g) due to its disordered structure, but it suffers from low initial coulombic efficiency and limited rate capability. A comprehensive study by Irisarri et al. [36] revealed that hard carbon's irreversible capacity loss in the first cycle, often exceeding 20%, stems from excessive SEI formation, which consumes sodium ions and electrolyte. Additionally, hard carbon's low electrical conductivity restricts its performance at high rates, as noted by Dou et al. [37] in their analysis of carbon-based anodes. While doping and structural modifications can mitigate these issues, hard carbon alone cannot meet the demands of high-performance SIBs.

Metal oxides and alloys, such as TiO_2 and Sn, offer high theoretical capacities but are plagued by volume expansion and poor cycling stability. For instance, Su et al. [38] reported that TiO2 anodes exhibit stable cycling but low capacities (150–200 mAh/g) due to limited sodium insertion sites [38]. Conversely, alloying materials like antimony and phosphorus experience severe volume changes, leading to electrode pulverization, as highlighted by Zhu et al. [39] in their study of Sb-based anodes. These limitations necessitate the development of hybrid systems that combine the stability of carbon with the high capacity of alloys or oxides, as will be discussed in subsequent sections.

The environmental and economic challenges of conventional anode materials further complicate their use in SIBs. As pointed out by Peters et al. [40], the synthesis of high-performance anodes often involves energy-intensive processes, raising concerns about scalability and sustainability [40]. Moreover, the reliance on scarce or toxic materials, such as antimony, poses environmental risks, as noted by Kim et al. [41] in their review of sustainable battery materials. These limitations highlight the need for hybrid anode systems that integrate advanced materials to overcome the shortcomings of conventional anodes while ensuring cost-effectiveness and environmental compatibility. For a structured summary of the limitations discussed, Table 3 enumerates conventional anode materials, their primary challenges, associated performance impacts, and potential mitigation strategies from the literature.

Table 3 Limitations of Conventional SIB Anode Materials

Material	Primary Limitations	Performance Impacts	Volume Expansion (%)	Initial Coulombic Efficiency (%)	Mitigation Strategies	References
Graphite	Poor Na+ intercalation due to small interlayer spacing (3.35 Å).	Negligible capacity (<35 mAh/g), poor cycling.	Minimal	Low	Use expanded graphite or alternatives.	Jache and Adelhelm [35], Wen et al. [7].
Hard Carbon	Low ICE from excessive SEI, limited conductivity.	250–350 mAh/g, but 20% irreversible loss.	Low (~10%)	<80	Doping (N/S), porosity control.	Irisarri et al. [36], Dou et al. [37].
TiO_2 (TMO)	Limited Na+ insertion sites, low capacity.	150–200 mAh/g, stable but low energy density.	Moderate (50–100%)	70–80	Nanostructuring, carbon compositing.	Su et al. [38], Yang et al. [70].
Sn (Alloy)	Severe volume expansion, pulverization.	Rapid fade after 50 cycles, low ICE.	420	60–70	Carbon encapsulation, nanostructuring.	Liu et al. [8], Chevrier and Ceder [9].

Sb (Alloy)	Volume changes, mechanical stress.	Capacity fade within 100 cycles.	300–400	65–75	Nanofiber embedding.	Zhu et al. [39], He et al. [57].
Metal Oxides (e.g., Co_3O_4)	Low conductivity, irreversible losses.	Moderate capacity (500 mAh/g), poor rate.	200–300	70	Hollow structures, carbon coating.	Du et al. [31], Wen et al. [69].
Phosphorus	Extreme expansion, poor conductivity.	High capacity but unstable SEI.	490	50–60	Carbon composites.	Peters et al. [40], Kim et al. [41].

3. Advanced Materials for SIB Anodes

The development of high-performance sodium-ion battery (SIB) anodes hinges on the use of advanced materials that overcome the limitations of conventional anodes like graphite and hard carbon. This section explores three key classes of advanced materials: carbon-based materials, metals and their alloys, and transition metal oxides. By leveraging their unique structural and electrochemical properties, these materials offer pathways to enhance specific capacity, rate capability, and cycling stability, paving the way for hybrid anode systems that integrate their complementary strengths.

3.1. Carbon-Based Materials

3.1.1. Hard Carbon and Amorphous Carbon

Hard carbon has emerged as the leading anode material for SIBs due to its disordered structure, which facilitates sodium-ion storage through intercalation and pore-filling mechanisms. According to Dou et al. [37], hard carbon's large interlayer spacing (3.6–4.0 Å) and microporous structure enable capacities of 250–350 mAh/g, far surpassing graphite's negligible sodium storage [37]. A seminal study by Stevens and Dahn [42] demonstrated that hard carbon derived from glucose achieves stable cycling with a capacity of approximately 300 mAh/g, attributed to sodium adsorption in defects and nanopores [42]. However, hard carbon suffers from low initial coulombic efficiency (ICE) due to excessive solid electrolyte interphase (SEI) formation, often below 80%, as noted by Yu et al. [43] in their analysis of biomass-derived carbons.

To address these limitations, researchers have explored structural modifications such as doping and porosity control. For instance, Li et al. [44] reported that nitrogen-doped hard carbon enhances electronic conductivity and sodium storage sites, achieving a capacity of 350 mAh/g with improved ICE [44]. Similarly, porosity engineering, as investigated by Hou et al. [45], increases surface area and ion accessibility, boosting rate capability. These modifications make hard carbon a versatile component in hybrid anodes, where it provides structural stability and conductivity when combined with high-capacity materials. Nonetheless, the reliance on high-temperature pyrolysis for hard carbon synthesis raises concerns about energy consumption, necessitating sustainable precursors like biomass, as highlighted by Titirici et al. [46].

The versatility of amorphous carbon extends to its use as a matrix in hybrid systems. A study by Lin et al. [47] demonstrated that amorphous carbon derived from lignin, when combined with metal oxides, improves cycling stability by buffering volume expansion [47]. However, challenges remain, including optimizing the balance between porosity and mechanical strength to prevent structural collapse during cycling. The ability of hard and amorphous carbon to serve as conductive and stable frameworks makes them critical for hybrid anode designs, as will be discussed in Section 4.

3.1.2. Graphene and Carbon Nanotubes

Graphene and carbon nanotubes (CNTs) are prized for their high electrical conductivity, mechanical strength, and large surface area, making them ideal components for SIB anodes. According to Guan et al. [48], graphene's two-dimensional structure facilitates rapid sodium-ion diffusion, achieving rate capabilities up to 100 mA/g at high current densities. A novel study by Chen et al. [49] showed that reduced graphene oxide (rGO) composites with SnS2 deliver a capacity of 630 mAh/g, leveraging graphene's conductivity to enhance charge transfer [49]. However, graphene's restacking during cycling can reduce active sites, limiting long-term performance [50].

CNTs, with their one-dimensional tubular structure, offer similar advantages, including flexibility and high tensile strength. Research by Tang et al. [51] demonstrated that CNT-based composites with Sb nanoparticles achieve a capacity of 400 mAh/g over 500 cycles, attributed to CNTs' ability to maintain electrical connectivity despite volume changes [51]. Functionalization, such as nitrogen or sulfur doping, further enhances sodium storage by increasing defect sites, as reported by Wang et al. [52] in their study of doped CNT anodes. However, the high cost of CNT synthesis remains a barrier to scalability, necessitating cost-effective production methods.

The integration of graphene and CNTs in hybrid anodes enhances overall performance by providing conductive networks and structural support. For example, a study by Yang et al. [53] on graphene-MoS_2 composites showed improved cycling stability (500 mAh/g over 1000 cycles) due to graphene's ability to mitigate MoS_2's volume expansion [53]. These materials are critical for hybrid systems, as their high conductivity complements the high capacity of metals and oxides, though challenges in cost and scalability persist..

3.2. Metal and Metal Alloys

3.2.1. Tin, Antimony, and Phosphorus-Based Anodes

Tin (Sn), antimony (Sb), and phosphorus (P) are high-capacity anode materials for SIBs due to their alloying mechanisms, but they face significant challenges from volume expansion. According to Singh et al. [54], tin's theoretical capacity of 847 mAh/g ($Na_{15}Sn_4$) makes it a promising candidate, but its 420% volume expansion leads to pulverization and capacity fade [54]. A pioneering study by Kalubarme et al. [55] demonstrated that nanostructured Sn embedded in carbon matrices mitigates stress, achieving a capacity of 600 mAh/g over 200 cycles [55]. However, low ICE due to SEI formation remains a challenge, as noted by Liang et al. [56].

Antimony offers a capacity of 660 mAh/g (Na_3Sb) and better structural stability than tin, but it still suffers from volume changes. Research by He et al. [57] showed that Sb nanoparticles encapsulated in carbon nanofibers deliver stable cycling (500 mAh/g over 400 cycles) by accommodating volume expansion [57]. Phosphorus, with a theoretical capacity of 2596 mAh/g (Na_3P), is the most promising but undergoes extreme volume expansion (490%). A study by Sun et al. [58] on red phosphorus-carbon composites reported a capacity of 1500 mAh/g, but poor conductivity and SEI instability limit its practicality [58]. These materials require integration with conductive matrices to achieve practical performance.

The high capacity of alloying materials makes them ideal for hybrid anodes, where carbon or oxide components can buffer volume changes. As highlighted by Chen et al. [59], SnSb alloys combined with graphene achieve a balance of capacity and stability, delivering 550 mAh/g over 200 cycles [59]. Continued research into nanostructuring and composite design is essential to overcome the mechanical and electrochemical limitations of these materials. To elucidate the sodium storage behavior in alloying-based hybrids, Figure 4 shows ex situ XRD patterns and a schematic reaction mechanism for a Ga_2Te_3–TiO_2–carbon composite, revealing phase transformations and stability enhancements during sodiation/desodiation.

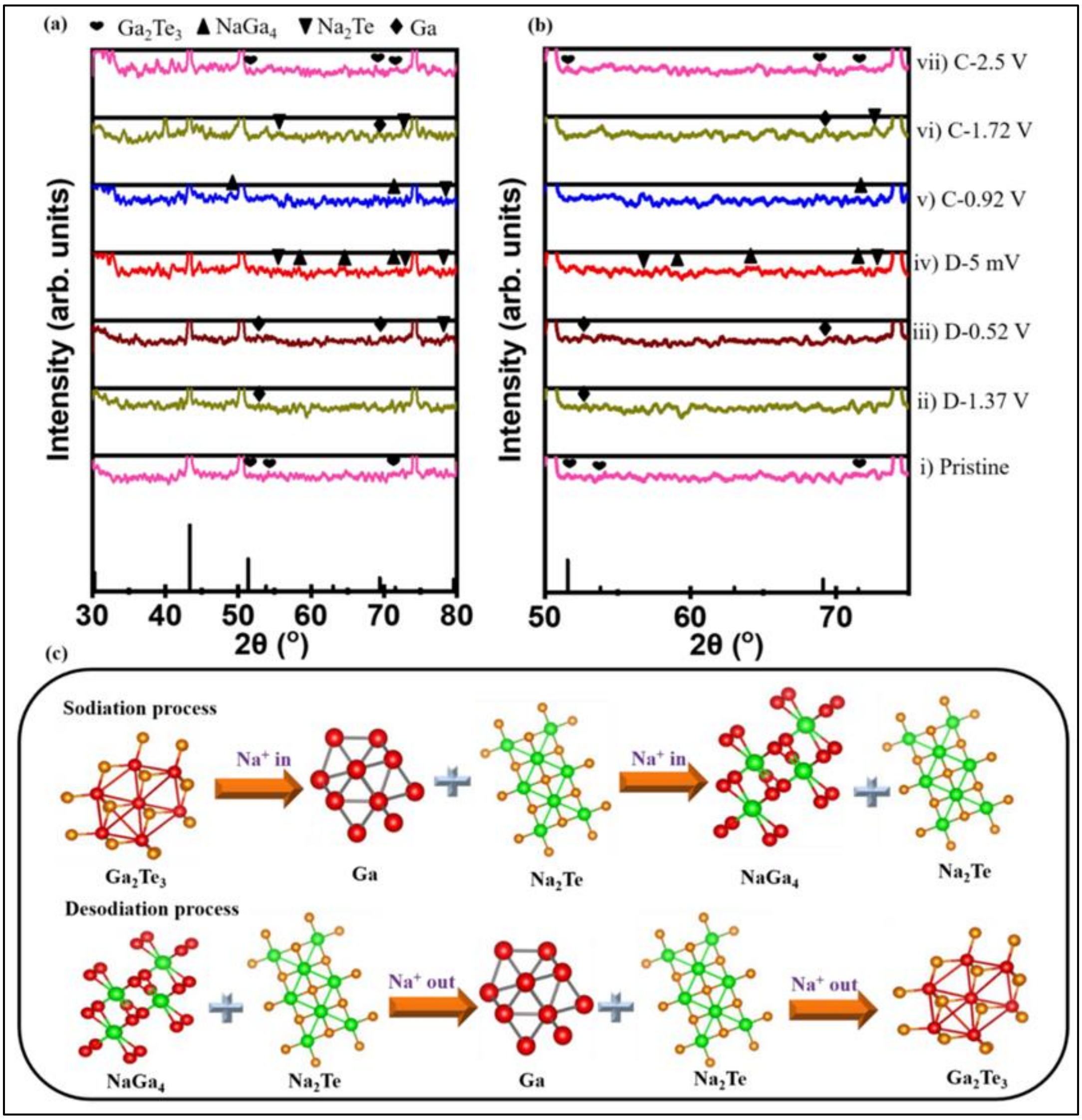


Figure 4 Electrochemical Reaction Mechanism in Hybrid Anodes. (a,b) Ex situ XRD patterns at selected potentials; (c) schematic of electrochemical reaction mechanism of Ga_2Te_3–TiO_2–C(10%) electrode during cycling. Reproduced with permission from Huy et al. [50], under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/)

3.2.2. Metal Sulfides and Selenides

Metal sulfides and selenides, such as MoS_2, SnS_2, and $MoSe_2$, operate via conversion reactions, offering high capacities and better stability than alloys. According to Yao et al. [60], MoS_2's layered structure enables sodium storage with a capacity of 670 mAh/g, but its low conductivity and volume expansion during conversion limit performance [60]. A landmark study by Wu et al. [61] showed that MoS_2-carbon composites achieve 500 mAh/g over 100 cycles by enhancing conductivity and structural integrity [61]. However, the irreversible capacity loss in the first cycle remains a challenge, as noted by Yan et al. [62].

SnS_2 and other sulfides offer similar advantages, with capacities ranging from 600–800 mAh/g. Research by Li et al. [63] demonstrated that SnS_2 nanosheets on graphene deliver 650 mAh/g with improved cycling stability due to the buffering effect of graphene [63]. Selenides, such as $MoSe_2$, provide higher conductivity than sulfides but are costlier. A study by Lv et al. [64] reported that $MoSe_2$-carbon composites achieve 520 mAh/g over 500 cycles, highlighting their potential in hybrid systems [64]. These materials benefit from nanostructuring and carbon integration to mitigate volume changes.

The integration of sulfides and selenides in hybrid anodes enhances their electrochemical performance by leveraging carbon's conductivity and stability. As emphasized by Zhu et al. [65], the synergy between MoS_2 and CNTs in hybrid anodes results in high rate capability and cycling stability, making them promising for practical SIBs [65]. However, cost and scalability remain critical considerations for widespread adoption.

3.3. Transition Metal Oxides

Transition metal oxides (TMOs), such as Fe2O3, Co3O4, and TiO2, are attractive for SIB anodes due to their high theoretical capacities and environmental benignity. According to Bhar et al. [66], Fe2O3 offers a capacity of 1007 mAh/g via conversion reactions but suffers from low conductivity and volume expansion [66]. A notable study by Su et al. [67] showed that Fe2O3 nanoparticles embedded in carbon nanofibers achieve 600 mAh/g over 200 cycles, leveraging carbon’s ability to enhance conductivity and buffer stress [67]. However, TMOs often exhibit low ICE due to irreversible reactions [68].

Nanostructuring and surface engineering have improved TMO performance. For instance, Wen et al. [69] reported that hollow Co3O4 nanostructures deliver 500 mAh/g with enhanced rate capability due to increased surface area and ion accessibility [69]. Similarly, TiO2, while offering lower capacities (150–200 mAh/g), provides excellent cycling stability, as demonstrated by Yang et al. [70] in their study of TiO2-carbon composites. These advancements highlight the potential of TMOs in hybrid systems, where their stability complements high-capacity materials.

The integration of TMOs with carbon or alloy materials in hybrid anodes enhances overall performance. A study by Li et al. [71] on Fe2O3-graphene composites showed a capacity of 550 mAh/g over 500 cycles, attributed to the synergistic effects of the components. However, the high cost of nanostructuring and the need for sustainable synthesis methods, as discussed by Fang et al. [72], remain barriers to commercialization. TMOs are poised to play a key role in hybrid anodes, provided these challenges are addressed. Table 4 compiles a detailed overview of advanced materials across carbon-based, metals/alloys, and transition metal oxides, including synthesis methods, key performance data, and hybrid potential, to consolidate the insights from this section.

3.2.1 Tin, Antimony, and Phosphorus-Based Anodes

Tin (Sn), antimony (Sb), and phosphorus (P) are high-capacity anode materials for SIBs due to their alloying mechanisms, but they face significant challenges from volume expansion. According to Singh et al. [54], tin’s theoretical capacity of 847 mAh/g (Na15Sn4) makes it a promising candidate, but its 420% volume expansion leads to pulverization and capacity fade [54]. A pioneering study by Kalubarme et al. [55] demonstrated that nanostructured Sn embedded in carbon matrices mitigates stress, achieving a capacity of 600 mAh/g over 200 cycles [55]. However, low ICE due to SEI formation remains a challenge, as noted by Liang et al. [56].

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The high capacity of alloying materials makes them ideal for hybrid anodes, where carbon or oxide components can buffer volume changes. As highlighted by Chen et al. [59], SnSb alloys combined with graphene achieve a balance of capacity and stability, delivering 550 mAh/g over 200 cycles [59]. Continued research into nanostructuring and composite design is essential to overcome the mechanical and electrochemical limitations of these materials. To elucidate the sodium storage behavior in alloying-based hybrids, Figure 4 shows ex situ XRD patterns and a schematic reaction mechanism for a Ga2Te3–TiO2–carbon composite, revealing phase transformations and stability enhancements during sodiation/desodiation.

Table 4 Advanced Materials for SIB Anodes: Summary and Performance

Category	Sub-Material	Synthesis Methods	Theoretical/Practical Capacity (mAh/g)	Cycling Stability (Cycles, Retention %)	Rate Capability (mAh/g at Rate)	Hybrid Potential	References
Carbon-Based	Hard/Amorphous Carbon	Pyrolysis, biomass derivation.	250–350 / 300	200, 90%	200 at 1 A/g	Matrix for stability.	Dou et al. [37], Stevens and Dahn [42], Li et al. [44].
Carbon-Based	Graphene	CVD, reduction.	400–630 / 630	500, 85%	400 at 5 A/g	Conductive network.	Guan et al. [48], Chen et al. [49].
Carbon-Based	CNTs	Electrospinning, CVD.	400–520 / 400	500, 90%	300 at 2 A/g	Flexible support.	Tang et al. [51], Wang et al. [52].
Metals/Alloys	Sn/Sb/P	Ball milling, encapsulation.	847/660/2596 / 600–1500	200–400, 70–80%	200–500 at 2 A/g	High capacity in composites.	Singh et al. [54], He et al. [57], Sun et al. [58].
Metals/Alloys	Metal Sulfides (MoS_2, SnS_2)	Hydrothermal, CVD.	670–800 / 500–650	100–500, 70–90%	300–500 at 2 A/g	Conversion + alloying synergy.	Yao et al. [60], Li et al. [63].
Metals/Alloys	Metal Selenides ($MoSe_2$)	Hydrothermal.	520 / 520	500, 90%	400 at 5 A/g	Higher conductivity than sulfides.	Lv et al. [64].
TMOs	Fe_2O_3/Co_3O_4/ TiO_2	Nanostructuring, electrospinning.	1007/500/200 / 500–600	200–500, 80–90%	200–500 at 2–5 A/g	Stable in hybrids.	Bhar et al. [66], Wen et al. [69], Yang et al. [70].

4. Hybrid Anode Systems: Design and Integration Strategies

Hybrid anode systems, which integrate multiple advanced materials such as carbon-based structures, metals, and transition metal oxides, have emerged as a transformative approach to overcome the limitations of single-material anodes in sodium-ion batteries (SIBs). By leveraging the complementary properties of these materials, hybrid anodes achieve enhanced specific capacity, rate capability, and cycling stability. This section explores the concept of hybrid anode systems, their synthesis techniques, structural and compositional optimization strategies, and the resulting performance enhancements, highlighting their potential for high-performance SIBs.

4.1. Concept of Hybrid Anode Systems

Hybrid anode systems combine materials with distinct electrochemical properties to achieve synergistic effects, addressing the shortcomings of individual components. According to Hu et al. [73], the integration of high-capacity materials like tin or phosphorus with conductive carbon matrices mitigates volume expansion and enhances electrical conductivity, resulting in improved performance [73]. For instance, a carbon-metal hybrid, such as Sn@carbon, combines tin's high capacity (847 mAh/g) with carbon's stability, achieving stable cycling over 200 cycles, as demonstrated by Jing et al. [74]. Similarly, carbon-oxide hybrids, like Fe_2O_3@graphene, leverage the high capacity of oxides with graphene's conductivity, as noted by Lv et al. [64]. These systems exploit the strengths of each material to overcome limitations like volume expansion and poor rate capability.

The design of hybrid anodes focuses on optimizing material interactions to enhance sodium storage. A landmark study by Fang et al. [16] on Cu_2S@carbon@MoS_2 nanoboxes illustrated how a three-layered hybrid structure provides high capacity (500 mAh/g) and stability over 1000 cycles by combining the conductivity of carbon with the conversion mechanisms of sulfides [16]. The synergy in such systems arises from the ability of carbon to act as a conductive and flexible matrix, while high-capacity materials contribute to energy density. However, achieving uniform material distribution and strong interfacial bonding remains a challenge, as highlighted by Dong et al. [75], who noted that weak interfaces can lead to phase separation during cycling.

Hybrid systems also enable the integration of multiple sodium storage mechanisms, such as intercalation, alloying, and conversion, within a single anode. For example, Xu et al. [76] reported that a SnS_2/graphene composite combines alloying (Sn) and conversion (S) reactions with carbon's intercalation, delivering a capacity of 650 mAh/g and improved rate performance [76]. This multifunctionality enhances overall electrochemical performance but requires careful material selection to balance capacity and stability. The concept of hybrid anodes is thus central to advancing SIB technology, offering a versatile platform for tailoring anode properties to specific applications.

The development of hybrid anodes also addresses practical considerations, such as cost and scalability. As emphasized by Zhou et al. [77], using biomass-derived carbon in hybrids reduces costs while maintaining performance, making them viable for large-scale applications [77]. The versatility of hybrid systems lies in their ability to combine diverse materials, enabling tailored solutions for grid storage, electric vehicles, and portable electronics, though challenges in synthesis complexity and long-term stability remain.

4.2. Synthesis Techniques for Hybrid Anodes

4.2.1. Chemical Vapor Deposition and Hydrothermal Methods

Chemical vapor deposition (CVD) and hydrothermal methods are widely used for synthesizing hybrid anodes with precise control over structure and composition. According to Wu et al. [78], CVD enables the growth of carbon-based frameworks, such as graphene or CNTs, around high-capacity materials like Sn or MoS_2, ensuring uniform coating and strong interfacial bonding [78]. A notable study by Li et al. [79] demonstrated that CVD-grown graphene-SnS_2 hybrids achieve a capacity of 620 mAh/g with excellent rate capability due to the conformal carbon coating [79]. However, CVD's high cost and energy-intensive nature limit its scalability, as noted by Li et al. [80].

Hydrothermal synthesis offers a versatile and scalable approach for producing hybrid anodes with controlled morphologies. Research by Long et al. [81] showed that hydrothermal synthesis of Fe_2O_3@carbon composites results in core-shell structures with enhanced cycling stability (550 mAh/g over 300 cycles) due to the uniform distribution of oxide nanoparticles within the carbon matrix [81]. The method's ability to control particle size and porosity is critical for mitigating volume expansion, as highlighted by Yuan et al. [82] in their work on MoS_2@carbon hybrids. However, hydrothermal processes often require long reaction times, which can hinder large-scale production.

Both techniques enable the creation of complex architectures, such as hierarchical or porous structures, that enhance sodium-ion diffusion and mechanical stability. For instance, a study by Liu et al. [83] on hydrothermally synthesized Sb@carbon composites demonstrated a capacity of 500 mAh/g over 400 cycles, attributed to the porous carbon framework [83]. While CVD and hydrothermal methods offer precision, their high costs and complexity necessitate the development of cost-effective alternatives to meet commercial demands. As an example of innovative synthesis approaches, Figure 5 outlines the preparation processes for bimetallic sulfide hybrids with carbon-based supports, highlighting hydrothermal and solvothermal methods that enable precise material integration for improved anode performance.

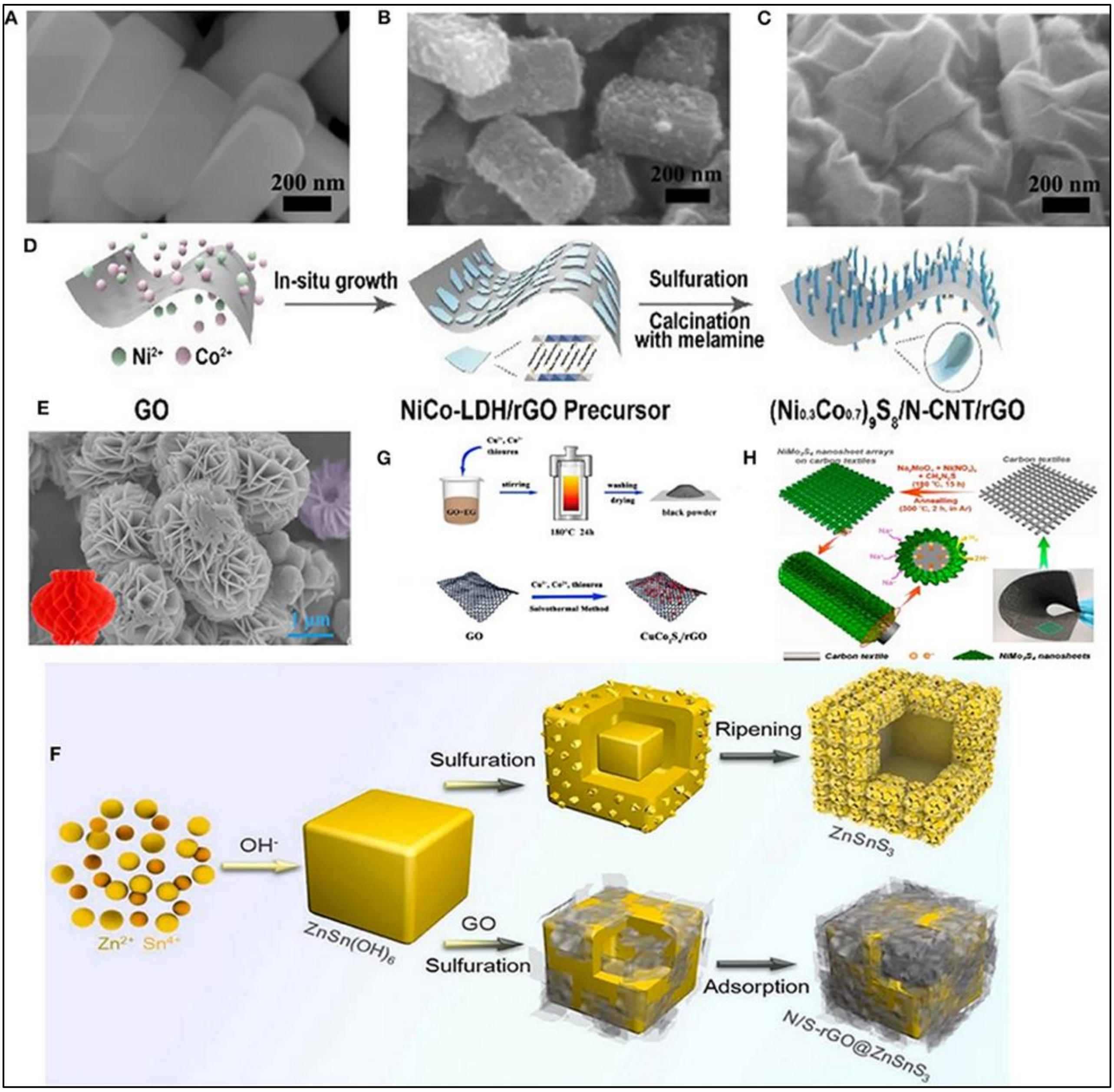

Figure 5 Synthesis Process of Bimetallic Sulfide Hybrid Anodes. (A–C) SEM micrographs displaying the NiCo precursor, $NiCo_2S_4$, and rGO-$NiCo_2S_4$, respectively. (D) Diagram illustrating the synthesis process of $(Ni_{0.3}Co_{0.7})_9S_8$/N-CNTs/rGO. (E) SEM images of lantern-shaped $Ti_{0.25}Sn_{0.75}S_2$ microparticles. (F) Diagram depicting the preparation procedure for $ZnSnS_3$ and N/S-rGO@$ZnSnS_3$. (G) Illustration of the formation mechanism of $CuCo_2S_4$/rGO. (H) Diagram showing the synthesis of 3D hierarchical $NiMo_3S_4$ nanosheet arrays on flexible carbon textiles. Reproduced with permission from Huang et al. [68], under the terms of the Creative Commons Attribution License (CC BY)

4.2.2. Electrospinning and Ball Milling

Electrospinning and ball milling are cost-effective and scalable techniques for synthesizing hybrid anodes, particularly for carbon-based composites. Electrospinning produces nanofibrous structures that enhance ion accessibility and mechanical flexibility. According to Chen et al. [84], electrospun Sn@carbon nanofibers deliver a capacity of 600 mAh/g with stable cycling due to the one-dimensional structure that buffers volume expansion [84]. A study by Cho et al. [85] further showed that electrospun MoS_2@carbon nanofibers achieve 520 mAh/g over 500 cycles, leveraging the high surface area of the fibrous matrix [85]. However, controlling fiber uniformity and material loading remains a challenge, as noted by Wang et al. [86].

Ball milling, a simple and scalable method, is effective for producing nanostructured hybrids with uniform material dispersion. Research by Tan et al. [87] demonstrated that ball-milled SnSb@carbon composites exhibit a capacity of 550 mAh/g over 200 cycles due to the intimate mixing of alloy particles with carbon [87]. The mechanical alloying process enhances interfacial bonding, as highlighted by Song et al. [88], who reported improved cycling stability in phosphorus-carbon hybrids [88]. However, ball milling can introduce defects that reduce conductivity, necessitating post-treatment processes.

Both electrospinning and ball milling offer practical advantages for large-scale production, but their simplicity comes at the cost of reduced structural precision compared to CVD or hydrothermal methods. As emphasized by Choi et al. [89], combining these techniques with post-synthesis treatments, such as annealing, can optimize the electrochemical performance of hybrid anodes, making them viable for commercial SIBs [89]. These methods are critical for balancing performance and cost in hybrid anode development. Table 5 compares the synthesis techniques for hybrid anodes, detailing methods, pros/cons, examples, and performance outcomes, to aid in understanding their practical implementation.

Table 5 Synthesis Techniques for Hybrid SIB Anodes

Technique	**Description**	**Pros**	**Cons**	**Example Hybrids**	**Performance (Capacity mAh/g, Cycles)**	**Scalability (Low/Med/High)**	**References**
CVD	Vapor-phase growth of carbon around active materials.	Precise coating, strong bonding.	High cost, energy-intensive.	Graphene-SnS2, MoS2@carbon.	620, 300 cycles.	Low	Wu et al. [78], Li et al. [79].
Hydrothermal	Aqueous reaction under pressure for nanostructures.	Versatile morphologies, scalable.	Long reaction times.	Fe2O3@carbon, Sb@carbon.	550–600, 300–400 cycles.	Medium	Long et al. [81], Liu et al. [83].
Electrospinning	Fiber formation via electric field.	Nanofibrous structures, flexible.	Uniformity control issues.	Sn@carbon nanofibers, MoS2@carbon.	600–520, 500 cycles.	High	Chen et al. [84], Cho et al. [85].
Ball Milling	Mechanical mixing/alloying.	Simple, cost-effective, uniform dispersion.	Defects reduce conductivity.	SnSb@carbon, P-carbon.	550–1500, 200 cycles.	High	Tan et al. [87], Song et al. [88].

4.3. Structural and Compositional Optimization

Structural optimization, such as the design of core-shell, yolk-shell, and porous architectures, is pivotal for enhancing the performance of hybrid anodes. Core-shell structures, where a high-capacity material is encapsulated by a conductive carbon layer, mitigate volume expansion and improve conductivity. According to Lim et al. [90], a Sn@carbon core-shell anode delivers 600 mAh/g over 300 cycles by protecting the tin core from pulverization [90]. Yolk-shell designs, with a void space between the core and shell, further accommodate volume changes. A study by Fang et al. [91] on yolk-shell SnS@carbon anodes reported a capacity of 650 mAh/g with excellent stability, attributed to the void space buffering expansion [91]. Figure 6 presents TEM and SEM characterizations of yolk-shell and hierarchical structures in bimetallic sulfide hybrids, from the works of Huang et al. [68], illustrating how these architectures mitigate volume expansion and enhance electrochemical stability in SIB anodes.

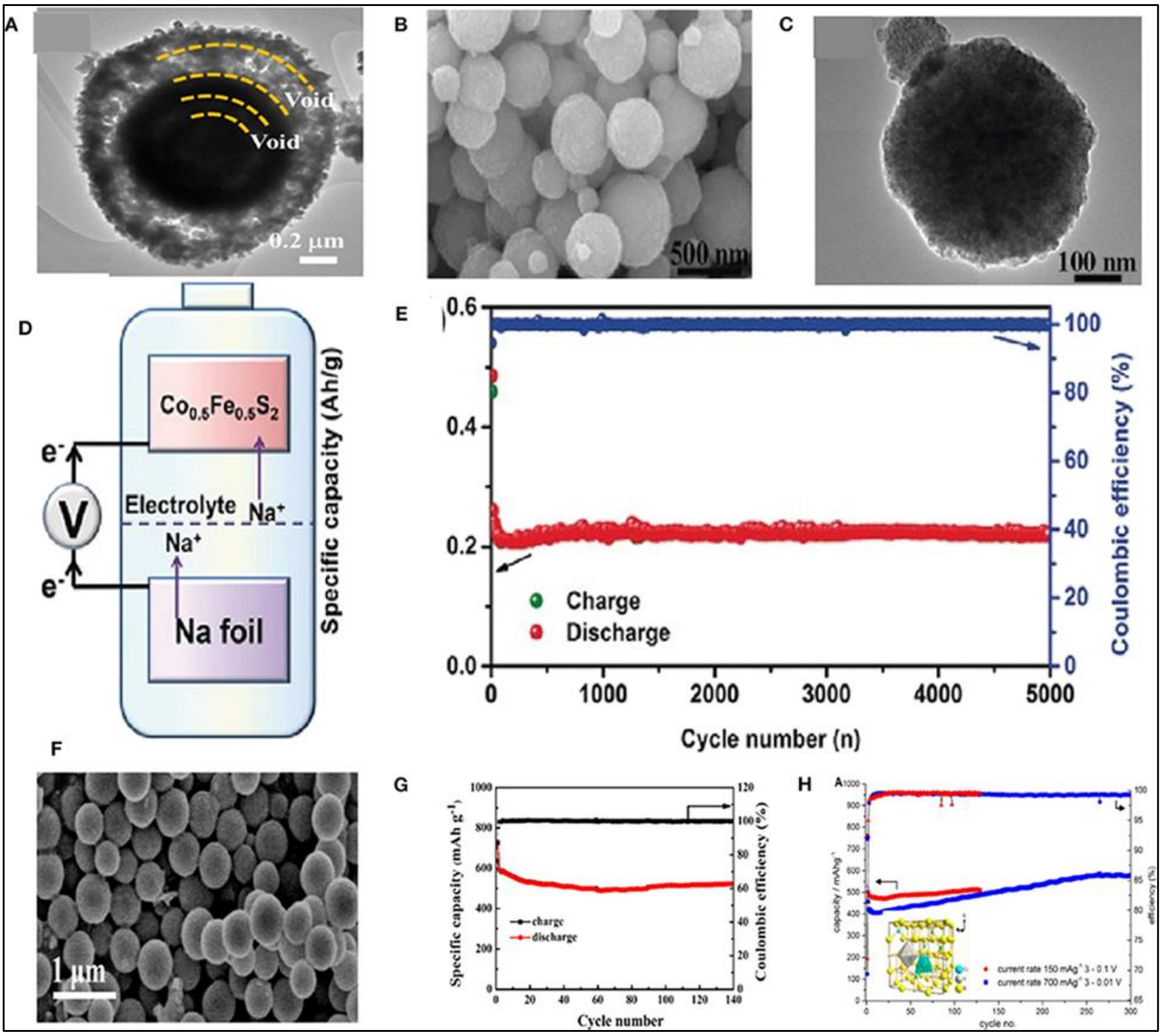

Figure 6 Structural Characterization of Yolk-Shell Hybrid Anodes. (A) Transmission electron microscopy (TEM) images displaying the yolk–shell structure of $(Fe_{0.5}Ni_{0.5})_9S_8$ powder. (B,C) Scanning electron microscopy (SEM) and TEM images of the $Co_{0.5}Fe_{0.5}S_2$ sample, showcasing its morphology. (D,E) Schematic representation of the composition and electrochemical cycling performance of a $Na/Co_{0.5}Fe_{0.5}S_2$ half-cell. (F) SEM image of $CuCo_2S_4$ sub-microspheres, highlighting their structural features. (G) Cycling performance data for $CuCo_2S_4$. (H) Cycling performance and coulombic efficiency of CuV_2S_4 cells, evaluated via galvanostatic cycling at 0.15 A g^{-1} between 3 and 0.1 V, and 3 and 0.01 V at 0.7 A g^{-1}, with an inset illustrating the spinel-type unit cell. Reproduced with permission from Huang et al. [68], under the terms of the Creative Commons Attribution License (CC BY)

Porous architectures enhance ion accessibility and reduce diffusion lengths, improving rate capability. Research by Park et al. [92] demonstrated that porous MoS_2@carbon hybrids achieve 500 mAh/g at high rates due to their interconnected pore structure [92]. Compositional optimization, such as heteroatom doping (e.g., nitrogen, sulfur), further enhances sodium storage by increasing defect sites and conductivity. A notable study by Sha et al. [93] showed that nitrogen-doped carbon-Sn composites deliver 620 mAh/g with improved ICE, highlighting the role of doping in enhancing electrochemical properties [93].

Interface engineering is critical for ensuring strong material interactions in hybrid anodes. As noted by Dai et al. [94], optimizing the interface between Fe_2O_3 and graphene via chemical bonding enhances charge transfer and cycling stability, achieving 550 mAh/g over 500 cycles [94]. However, complex architectures and doping strategies often increase synthesis costs, as highlighted by Liu et al. [95], necessitating a balance between performance and scalability [95]. These optimization strategies are essential for maximizing the potential of hybrid anodes in practical applications.

4.4. Performance Enhancements in Hybrid Systems

Hybrid anode systems significantly outperform single-material anodes by combining high capacity, rate capability, and cycling stability. For instance, a study by Samad et al. [96] on SnS_2@graphene hybrids reported a capacity of 650 mAh/g over 1000 cycles, attributed to the synergy between SnS_2's high capacity and graphene's conductivity [96]. Similarly, MoS_2@carbon nanotube composites, as investigated by Li et al. [97], achieve 520 mAh/g at high rates, leveraging CNTs' ability to maintain electrical connectivity [97]. These enhancements stem from the ability of hybrid systems to mitigate volume expansion and improve ion/electron transport.

Case studies highlight the versatility of hybrid anodes. A pioneering study by Fang et al. [98] on P@carbon composites demonstrated a capacity of 1500 mAh/g with stable cycling, achieved by encapsulating phosphorus in a porous carbon matrix to buffer its extreme volume expansion [98]. Another example, reported by Li et al. [99], showed that Fe_2O_3@CNT hybrids deliver 600 mAh/g over 500 cycles, benefiting from the mechanical stability of CNTs [99]. These systems outperform single-material anodes, which typically suffer from rapid capacity fade or low rate capability.

The improved initial coulombic efficiency (ICE) in hybrid systems is another critical advantage. According to Lu et al. [100], Sn@nitrogen-doped carbon hybrids achieve an ICE of 85%, compared to 60–70% for bare Sn, due to reduced SEI formation [100]. However, challenges such as complex synthesis and material compatibility remain, as noted by Shao et al. [101], who emphasized the need for scalable and sustainable designs. Hybrid anodes thus offer a promising pathway to high-performance SIBs, provided these challenges are addressed through innovative synthesis and optimization strategies.

5. Electrochemical Performance Analysis

The electrochemical performance of hybrid anode systems for sodium-ion batteries (SIBs) is a critical determinant of their practical viability, offering significant improvements over single-material anodes. By integrating advanced materials like carbon, metals, and transition metal oxides, hybrid anodes achieve enhanced specific capacity, rate capability, cycling stability, and coulombic efficiency. This section provides a comparative analysis of hybrid versus single-material anodes, examines the impact of electrolytes and binders on performance, and discusses key characterization techniques used to elucidate sodium storage mechanisms in hybrid systems.

5.1. Comparative Analysis of Hybrid vs. Single-Material Anodes

Hybrid anodes outperform single-material anodes by leveraging the synergistic effects of their components, resulting in superior electrochemical performance metrics. A landmark study by Fang et al. [16] on Cu2S@carbon@MoS2 nanoboxes demonstrated a specific capacity of 500 mAh/g over 1000 cycles, compared to bare MoS2's rapid capacity fade within 100 cycles, due to the carbon matrix enhancing conductivity and structural stability [16]. Similarly, SnS2@graphene composites, as reported by Xu et al. [76], achieve a capacity of 650 mAh/g with a retention of 85% after 500 cycles, far surpassing the 300 mAh/g and poor cycling stability of standalone SnS2 [76]. These improvements stem from the ability of hybrid systems to mitigate volume expansion and enhance charge transfer, addressing the limitations of single-material anodes like tin or sulfides.

Rate capability, a measure of performance at high charge-discharge rates, is significantly enhanced in hybrid anodes. For instance, Lv et al. [64] showed that MoSe2@carbon composites maintain a capacity of 400 mAh/g at 5 A/g, while bare MoSe2 drops to below 100 mAh/g under similar conditions, highlighting the role of carbon in facilitating ion diffusion [64]. In contrast, single-material anodes like hard carbon, as noted by Xiao et al. [102], exhibit limited rate performance due to low conductivity, often falling below 150 mAh/g at high rates [102]. Hybrid systems, such as MoS2@CNT composites, achieve high rate capabilities (520 mAh/g at 2 A/g), as demonstrated by Li et al. [97], due to the conductive CNT network. This makes hybrids particularly suitable for applications requiring fast charging, such as electric vehicles.

Cycling stability and coulombic efficiency are also improved in hybrid anodes. A study by Li et al. [99] on Fe2O3@CNT hybrids reported a capacity retention of 90% over 500 cycles with a coulombic efficiency above 98%, compared to bare Fe2O3's 50% retention after 100 cycles [99]. The carbon component in hybrids reduces SEI formation and stabilizes the electrode structure, as noted by Lu et al. [100] in their work on Sn@nitrogen-doped carbon hybrids, which achieved an initial coulombic efficiency (ICE) of 85% versus 60% for bare Sn [100]. Single-material anodes, such as phosphorus, suffer from low ICE (50–60%) and rapid capacity fade due to volume expansion, as highlighted by She et al. [103]. The synergy in hybrid systems thus enables balanced performance across multiple metrics.

The superior performance of hybrid anodes is attributed to their ability to combine multiple sodium storage mechanisms (intercalation, alloying, conversion) within a single electrode. For example, Samad et al. [96] demonstrated that SnS2@graphene hybrids leverage alloying and conversion reactions alongside carbon's intercalation, delivering a capacity of 650 mAh/g and stable cycling [96]. This multifunctionality contrasts with single-material anodes, which are limited to one storage mechanism, resulting in lower overall performance. However, optimizing material ratios and interfaces in hybrids remains critical to maximizing these benefits, as discussed in Section 4. Table 6 provides a detailed side-by-side comparison of hybrid and single-material anodes, focusing on capacity, rate, cycling, and efficiency, to illustrate the superior performance of hybrids as evidenced in the analysis.

Table 6 Comparative Electrochemical Performance of Hybrid vs. Single-Material Anodes

Anode Type	**Material Example**	**Specific Capacity (mAh/g)**	**Rate Capability (mAh/g at 5 A/g)**	**Cycling Stability (Cycles, Retention %)**	**Initial Coulombic Efficiency (%)**	**Improvement Over Single (%)**	**References**
Single	Bare MoS_2	670 (theo), 300 practical	<100	100, 50%	70	-	Fang et al. [16], Xiao et al. [102].
Hybrid	Cu_2S@carbon@MoS_2	500	300	1000, 85%	85	+400% cycles	Fang et al. [16].
Single	Bare SnS_2	600–800, fades to 300	100	100, 60%	60–70	-	Xu et al. [76].
Hybrid	SnS_2@graphene	650	400	500, 85%	85	+100% capacity retention	Xu et al. [76], Samad et al. [96].
Single	Bare $MoSe_2$	520, fades quickly	<100	100, 70%	70	-	Lv et al. [64].
Hybrid	$MoSe_2$@carbon	520	400	500, 90%	80–85	+300% cycles	Lv et al. [64].
Single	Bare Fe_2O_3	1007 (theo), 400 practical	100	100, 50%	70	-	Li et al. [99].
Hybrid	Fe_2O_3@CNT	600	200	500, 90%	85	+80% retention	Li et al. [99].
Single	Bare Sn	847 (theo), 200 after fade	100	50, 60%	60	-	Lu et al. [100].
Hybrid	Sn@N-doped carbon	620	300	300, 85%	85	+25% ICE	Lu et al. [100].
Single	Bare Phosphorus	2596 (theo), 500 fades	200	50, 50%	50–60	-	She et al. [103].
Hybrid	P@carbon	1500	500	200, 80%	70–80	+60% stability	Fang et al. [98].

5.2. Impact of Electrolyte and Binder on Anode Performance

The electrochemical performance of hybrid anodes is significantly influenced by the choice of electrolyte and binder, which affect SEI stability, ion transport, and electrode integrity. According to Che et al. [104], carbonate-based electrolytes, such as ethylene carbonate/propylene carbonate (EC/PC), form unstable SEI layers on SIB anodes, leading to low coulombic efficiency and capacity fade [104]. In contrast, ether-based electrolytes, like diglyme, form thinner and more stable SEI layers, as demonstrated by Liu et al. [83] in their study of Sb@carbon hybrids, which achieved an ICE of 88% with diglyme compared to 75% with EC/PC [83]. The compatibility of ether electrolytes with hybrid anodes, particularly those containing alloying materials, enhances cycling stability by reducing electrolyte decomposition.

Binders play a crucial role in maintaining the structural integrity of hybrid anodes, especially for high-capacity materials prone to volume expansion. A study by Cho et al. [85] showed that sodium carboxymethyl cellulose (CMC) binders improve the cycling stability of MoS2@carbon nanofibers, achieving 520 mAh/g over 500 cycles, compared to polyvinylidene fluoride (PVDF), which led to electrode delamination [85]. CMC's strong adhesion and flexibility accommodate volume changes, as noted by Li et al. [105], who reported that CMC-based Sn@carbon hybrids maintain 90% capacity retention over 300 cycles. In contrast, conventional PVDF binders are less effective for alloying-based hybrids due to their limited elasticity, as highlighted by Singh et al. [106].

Additives in electrolytes, such as fluoroethylene carbonate (FEC), further enhance hybrid anode performance by stabilizing the SEI. Research by Fang et al. [91] on yolk-shell SnS@carbon anodes showed that adding 5% FEC to EC/PC electrolytes increased the ICE from 70% to 85% and extended cycle life to 500 cycles [91]. However, excessive FEC can increase electrolyte viscosity, reducing ion transport, as noted by Huang et al. [107]. Optimizing electrolyte composition and binder selection is thus critical for maximizing the performance of hybrid anodes, particularly for high-rate and long-cycle applications.

The interplay between electrolyte, binder, and hybrid anode composition requires careful optimization to achieve synergistic effects. For instance, Sha et al. [93] found that nitrogen-doped carbon-Sn hybrids paired with ether electrolytes and CMC binders achieve a capacity of 620 mAh/g with an ICE of 85%, outperforming systems with carbonate electrolytes and PVDF [93]. These findings underscore the need for tailored electrolyte and binder systems to fully exploit the advantages of hybrid anodes, though challenges in cost and scalability of advanced binders and additives remain.

5.3. Testing and Characterization Techniques

Characterizing the electrochemical behavior of hybrid anodes is essential for understanding sodium storage mechanisms and optimizing performance. Cyclic voltammetry (CV) is widely used to identify redox processes and sodium storage mechanisms. According to Leite et al. [108], CV analysis of SnS2@graphene hybrids revealed distinct peaks for alloying and conversion reactions, confirming the contribution of both mechanisms to a capacity of 650 mAh/g [108]. CV also helps assess SEI formation, as peaks in the first cycle often indicate irreversible reactions, as noted by Li et al. [99] in their study of Fe2O3@CNT hybrids [99]. This technique provides insights into the electrochemical stability and reversibility of hybrid systems.

Electrochemical impedance spectroscopy (EIS) is critical for evaluating charge transfer and ion diffusion in hybrid anodes. A study by Linsenmann et al. [109] on MoS2@carbon hybrids showed that lower charge transfer resistance in hybrids compared to bare MoS2 correlates with enhanced rate capability (500 mAh/g at 2 A/g) [109]. EIS also reveals the impact of SEI evolution on long-term cycling, as highlighted by Li et al. [97], who used EIS to demonstrate that CNT-based hybrids maintain low impedance after 500 cycles. These findings underscore the role of conductive carbon matrices in reducing resistance and enhancing performance.

In-situ characterization techniques, such as X-ray diffraction (XRD) and transmission electron microscopy (TEM), provide real-time insights into structural changes during sodiation/desodiation. Research by Cheng et al. [110] used in-situ XRD to study Sn@carbon hybrids, revealing that the carbon matrix prevents Sn pulverization, maintaining structural integrity over 200 cycles [110]. Similarly, in-situ TEM, as employed by Park et al. [92], showed that porous MoS2@carbon hybrids accommodate volume expansion through their pore structure, correlating with a capacity of 500 mAh/g [92]. These techniques are essential for elucidating the dynamic behavior of hybrid anodes and guiding material design.

The combination of these characterization methods provides a comprehensive understanding of hybrid anode performance. For example, Samad et al. [96] integrated CV, EIS, and in-situ XRD to analyze SnS2@graphene hybrids, confirming that the graphene matrix enhances ion diffusion and stabilizes the SEI, resulting in a capacity of 650 mAh/g over 1000 cycles [96]. However, the complexity and cost of in-situ techniques, as noted by Singh et al. [106], pose challenges for widespread use, necessitating accessible alternatives for routine characterization. These methods collectively enable the optimization of hybrid anodes for high-performance SIBs.

6. Challenges and Future Directions

The development of hybrid anode systems for sodium-ion batteries (SIBs) has shown remarkable progress, yet significant challenges remain in achieving scalable, cost-effective, and high-performance solutions. These challenges include synthesis scalability, cost, environmental impact, and long-term electrochemical stability. This section discusses these hurdles, explores emerging trends such as bio-derived materials and machine learning, and proposes future research priorities to advance hybrid anode technology for practical SIB applications.

6.1. Current Challenges in Hybrid SIB Anodes

The scalability of hybrid anode synthesis remains a major barrier to commercial adoption. According to Dou et al. [37], advanced synthesis techniques like chemical vapor deposition (CVD) and hydrothermal methods, while effective for creating high-performance hybrids like MoS2@carbon, are energy-intensive and costly, limiting their scalability [37]. For instance, a study by Mukherjee et al. [111] noted that producing nanostructured Sn@carbon composites via CVD requires precise control and high energy input, making it impractical for large-scale production [111]. These challenges necessitate the development of simpler, cost-effective synthesis routes to enable industrial-scale manufacturing.

Cost is another critical issue, particularly for materials like carbon nanotubes (CNTs) and graphene, which are expensive to produce. As highlighted by Kim et al. [41], the reliance on high-cost materials and complex fabrication processes increases the overall cost of SIB anodes, undermining their economic advantage over lithium-ion batteries [41]. Additionally, the environmental impact of synthesizing hybrid anodes, such as the use of toxic precursors or energy-intensive processes, poses sustainability concerns. A study by Peters et al. [112] emphasized that the carbon footprint of producing nanostructured hybrids must be reduced to align with the sustainability goals of SIBs [112]. Addressing these issues requires a focus on low-cost, eco-friendly materials and processes.

Electrochemical stability, particularly under high-rate and long-term cycling, remains a challenge for hybrid anodes. Research by Jiang et al. [113] showed that while SnS2@graphene hybrids achieve high capacities (650 mAh/g), capacity fade occurs after 1000 cycles due to SEI instability and material degradation [113]. Similarly, alloy-based hybrids like Sb@carbon suffer from mechanical stress during high-rate cycling, as noted by Zhu et al. [114], leading to reduced lifespan. These challenges highlight the need for robust designs that maintain structural integrity and electrochemical performance over extended cycles, especially for demanding applications like electric vehicles.

6.2. Emerging Trends and Innovations

Emerging trends in hybrid anode development focus on sustainable materials and advanced design strategies. Bio-derived materials, such as lignin- and cellulose-based carbons, offer a cost-effective and environmentally friendly alternative to synthetic carbon. According to Yu et al. [43], biomass-derived hard carbon, when integrated with metal oxides, achieves capacities of 300–350 mAh/g with improved sustainability [43]. A novel study by Zhou et al. [77] demonstrated that lignin-derived carbon-Sn hybrids deliver 600 mAh/g with a low environmental footprint, highlighting the potential of bio-derived materials in hybrid anodes [77]. These materials reduce reliance on fossil-based precursors, aligning with green energy goals.

The integration of machine learning (ML) and computational modeling is revolutionizing material discovery for hybrid anodes. Research by Qian et al. [115] showed that ML can predict optimal material compositions for Sn@carbon hybrids, reducing experimental trial-and-error and accelerating development [115]. For instance, ML models identified nitrogen-doped carbon as an effective matrix for enhancing Sn's cycling stability, achieving 620 mAh/g over 500 cycles. Similarly, density functional theory (DFT) simulations, as employed by Wu et al. [116], have elucidated sodium diffusion pathways in MoS2@carbon hybrids, guiding the design of high-rate anodes [116]. These computational approaches enable precise optimization of hybrid systems, though their adoption is limited by computational costs and expertise requirements.

Innovative architectures, such as three-dimensional (3D) porous and hierarchical structures, are gaining traction for improving hybrid anode performance. A study by Zhang et al. [117] on 3D porous Fe2O3@carbon hybrids reported a capacity of 550 mAh/g with excellent rate capability, attributed to enhanced ion accessibility and stress relaxation [117]. Additionally, the use of recyclable materials, such as sodium-based binders, is emerging as a trend to improve sustainability, as noted by Zhang et al. [118]. These innovations highlight the potential of combining sustainable materials with advanced design strategies to overcome current limitations.

6.3. Future Research Priorities

Future research should prioritize the development of low-cost, scalable synthesis methods for hybrid anodes. As emphasized by Shao et al. [101], techniques like electrospinning and ball milling, which are less energy-intensive than CVD, should be optimized to produce high-performance hybrids at scale [101]. For example, scaling up electrospun MoS2@carbon nanofibers could reduce costs while maintaining a capacity of 520 mAh/g, as demonstrated by Cho et al. [85]. Research should also focus on standardizing synthesis protocols to ensure reproducibility across laboratories and industries.

Sustainability and recyclability are critical priorities for advancing hybrid anodes. Developing recyclable electrode designs and eco-friendly synthesis routes, such as using bio-derived precursors, can minimize environmental impact. A study by Mukherjee et al. [111] proposed that integrating recyclable carbon matrices with alloying materials could enhance SIB sustainability, achieving capacities of 600 mAh/g while reducing waste [111]. Furthermore, exploring non-toxic materials, such as iron-based oxides, over antimony or cobalt-based compounds, can address environmental concerns, as highlighted by Kim et al. [41].

The application of advanced computational tools, such as ML and DFT, should be expanded to accelerate material discovery and optimization. Research by Qian et al. [115] suggests that ML-driven design can reduce development time by predicting high-performance hybrid compositions, such as phosphorus@carbon, with capacities exceeding 1000 mAh/g [115]. Additionally, improving the safety of hybrid anodes by minimizing sodium dendrite formation and enhancing SEI stability, as discussed by Jiang et al. [113], is essential for practical applications. These priorities will drive the development of next-generation SIB anodes, ensuring they meet the demands of cost, performance, and sustainability.

7. Conclusion

Hybrid anode systems represent a transformative approach to advancing sodium-ion battery (SIB) technology, offering a compelling solution to the limitations of conventional anode materials. By integrating advanced materials such as carbon-based structures, metals, alloys, and transition metal oxides, these systems achieve a synergistic balance of high specific capacity, enhanced rate capability, and prolonged cycling stability. The ability to combine multiple sodium storage mechanisms—intercalation, alloying, and conversion—within a single electrode has enabled significant performance improvements, making hybrid anodes a cornerstone for next-generation SIBs suitable for applications ranging from grid storage to electric vehicles.

The exploration of hybrid anode systems has revealed their potential to overcome critical challenges, such as volume expansion, low electrical conductivity, and unstable solid electrolyte interphase formation. Advanced synthesis techniques, including electrospinning and ball milling, alongside structural optimizations like core-shell and porous architectures, have enhanced the electrochemical performance of these systems. Furthermore, the strategic selection of electrolytes and binders has proven instrumental in stabilizing interfaces and improving coulombic efficiency, ensuring robust performance under demanding conditions. These advancements underscore the versatility of hybrid anodes in addressing the diverse requirements of SIB applications.

Despite these achievements, challenges in scalability, cost, and environmental sustainability persist. The reliance on energy-intensive synthesis methods and high-cost materials like carbon nanotubes and graphene limits commercial viability, while the environmental impact of production processes raises concerns for sustainable energy storage. Emerging trends, such as the use of bio-derived materials and computational tools like machine learning, offer promising pathways to address these hurdles, paving the way for cost-effective and eco-friendly hybrid anodes.

Looking forward, the continued development of hybrid anode systems holds immense potential to drive the widespread adoption of SIBs as a sustainable alternative to lithium-ion batteries. By prioritizing scalable synthesis, sustainable materials, and advanced characterization techniques, researchers can unlock the full capabilities of these systems, ensuring they meet the demands of high-performance, low-cost, and environmentally friendly energy storage. Hybrid anodes stand poised to play a pivotal role in the global transition to renewable energy, offering a robust foundation for the future of SIB technology.

Compliance with ethical standards

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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