

Anode-Free Solid-State Rechargeable Batteries: Mechanisms, Challenges, and Design Strategies

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Anode-free solid-state alkali metal batteries (AFSSAMBs) have emerged as promising high-performance battery systems, attracting significant scientific interest due to their exceptional safety, high theoretical energy density, and cost-effectiveness. Recently, extensive research efforts have focused on addressing the key issues impeding their practical deployment, primarily centered around severe dendrite growth, unstable electrolyte-electrode interface, and low Coulombic efficiency. Despite this progress, a comprehensive framework for the fundamental

understanding of AFSSAMBs is still lacking. This paper presents a comprehensive concept, outlining detailed construction, mechanisms, challenges, and strategies of AFSSAMBs. First, the basic configuration and internal mechanisms of AFSSAMBs are summarized. Subsequently, we discuss the existing challenges hindering the cycling lifespan of AFSSAMBs, offering several promising approaches to overcome these obstacles. In the end, insightful perspectives and viewpoints are briefly proposed on the further developments of AFSSAMBs.

Introduction

Considering the accelerating demand for innovative technologies and energy resources, rechargeable batteries with high energy density, superior electrochemical performance under practical conditions, low cost, and environmental friendliness are crucial for optimizing energy storage systems.^[1,2] Metal-ion batteries (MIBs) have risen to become a predominant energy storage system, which has been universally used across various applications.^[3–5] Given that the limited energy density of ion batteries cannot meet the evolving demands of modern applications, alkali metal anodes, such as lithium and sodium, possess a high theoretical specific capacity (Li: 3860 mAh g⁻¹, Na: 1166 mAh g⁻¹) and a low reduction potential ($E_{\text{Li/Li}^+}$: -3.04 V, $E_{\text{Na/Na}^+}$: -2.73 V vs. standard hydrogen electrode), consequently alkali metal batteries (AMBs) was chosen as one of the most appealing candidates for high-energy batteries.^[6–8] However, the development of AMBs faces significant challenges due to poor alkali metal plating/stripping performance, low Coulombic efficiency (CE), limited lifespan, and serious safety concerns.^[9] These challenges primarily stem from the uncontrolled process of highly reactive alkali metal which produces severe dendrite growth, unstable solid electrolyte interface (SEI), and needless parasitic reactions. In addition, the excessive use of alkali metal foils can cause an increase in costs and safety risks.^[10] Hence, from a theoretical perspective, a new concept of anode-free or anode-less rechargeable batteries at the anode side without any excess lithium/sodium can induce unparalleled higher gravimetric and volumetric energy densities.

In recent years, anode-free alkali metal batteries (AFAMBs) have garnered significant attention as an effective solution to the aforementioned issues in AMBs.^[11] This type of battery only keeps a bare metal current collector, which lacks alkali hosts compared to traditional energy storage battery systems.^[12,13] During the first charging process, the metal ion source is mainly extracted from the cathode which subsequently is electrodeposited at the surface of the anode current collector. Apart from the initial charging procedure, the following charge-discharge cycles exhibit a high degree of similarity to the operational modalities of conventional metallic batteries. The construction of AFAMBs, which uses bare metal foils as the anode current collector, can significantly reduce the weight and thickness of the battery, thereby maximizing energy density. Furthermore, avoiding the use of alkali metal for cell production means lower cost, energy, and technological requirements associated with anode production. Several challenges, however, hampered the practical application of AFAMB so far due to no additional anode material, such as the uncontrolled Li dendrite and electrically isolated dead Li, the unstable SEI, and the large volumetric expansion.^[14] Despite considerable scientific efforts to address these challenges, the results have been limited. AFAMBs using liquid electrolytes often experience poor electrochemical performance, leading to cell failure due to the uncontrolled growth of dendritic alkali metal during cycling.^[15] In the case of common liquid electrolytes, such as ester-based and ether-based electrolytes, the former reacts strongly with Na metal, leading to the continuous emission of flammable gases and the formation of an uneven, brittle, and thick SEI layer. On the other hand, the latter easily oxidizes the surface of positive electrode materials due to the ether groups' active chemical nature.^[16,17]

Conversely, solid-state electrolytes (SSEs) exhibit several advantageous properties, including high modulus, a broad electrochemical stability window, exceptional thermal stability, and impressive ionic conductivity under room temperature conditions.^[18] The incorporation of solid-state electrolytes

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represents a promising strategy for the commercialization of AFAMBs under practical conditions, thereby facilitating the development of anode-free solid-state alkali metal batteries (AFSSAMBs). Figure 1 showcases a streamlined schematic, incorporating the aforementioned cell configurations, with lithium as a representative example within the realm of alkali metals. Meanwhile, there are clear differences in their specific densities and energy densities. Specifically, the anode-free architecture with solid-state electrolyte attains the highest density compared to all other battery configurations.^[19] AFSSAMBs, by replacing the liquid electrolyte of conventional AFLMBs with SSEs, significantly mitigate safety concerns such as the release of toxic gases and thermal runaway.^[20] What's more, SSEs exhibit the capability of functioning as a robust physical barrier to suppress dendrite growth, which restricts metal expansion to a two-dimensional, planar contact zone.^[21,22] It is important to note that this capacity to inhibit dendrite growth is relative to battery systems utilizing liquid electrolytes. In practice, AFSSAMBs still face challenges with dendrite growth and require further optimization and validation before widespread commercialization or application. The anode-free architecture not only addresses the challenges associated with the employment of Li metal anode but also surprisingly enhances the energy densities of the battery system.^[23] However, the practical deployment of this innovative battery architecture faces numerous challenges, particularly regarding unsatisfactory interface contact between the electrolyte and the electrodes.^[20] Recently, many scientists have devoted themselves to developing and optimizing AFSSAMBs, achieving remarkable outcomes in terms of performance and safety.^[24,25] Actually, numerous excellent reviews have emerged to provide guidance for the development of AFAMBs. Recently, various reviews have also introduced advancements, current issues, and challenges related to anode-free solid-state lithium metal batteries. However, these reviews are primarily focused on lithium metal batteries and there is a relative scarcity of information on general alkali metal solid-state batteries with an anode-free configuration. Therefore, this paper presents a comprehensive overview that discusses the configuration and mechanisms, challenges, and strategies and provides insightful perspectives on AFSSAMBs.

In this concept, we start by discussing the configuration and internal mechanisms for AFSSAMBs. Importantly, we then emphasize the foremost challenges affecting the electrochemical performance of AFSSAMBs while concurrently presenting



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the current state-of-the-art design strategies from diverse perspectives. In the end, insightful viewpoints are proposed to research more comprehensive AFSSAMBs in the future. We hope that this concept will help people to better comprehend these rising AFSSAMBs and explore more effective strategies to address the current unresolved challenges.

The Configuration and Mechanisms of AFSSAMBs

The concept of a metal-host-free current collector presents a promising approach for future battery designs, enabling higher energy capacity and reduced costs. The first anode-free solid-state lithium battery, developed by B. J. Neudecker in 2000, used a solid lithium electrolyte (Lipon) and achieved a cycle life exceeding 1000 cycles (Figure 2). The brief timeline mainly illustrates the recent advancements in the field of lithium and sodium metal solid-state batteries featuring an anode-free configuration. Lithium metal batteries with this configuration have advanced significantly. However, research on sodium batteries with an anode-free solid-state structure remains limited. Recently, Grayson Deysher et al. demonstrated a breakthrough with an anode-free solid-state sodium battery, achieving stable cycling performance over several hundred cycles. This accomplishment stems from the integration of the stable sodium borohydride solid electrolyte, formed from the pelletized aluminum current collector, achieving near-perfect contact that enhances overall performance.^[21,22,26–31] AFSSAMBs consist of cathode current collector|cathode material interlayer|separator|anode current collector.^[19] It is generally acknowledged that replacing the liquid electrolyte in AFAMB with a solid-state electrolyte is beneficial.

Although the manufacturing technique, electrolyte type, and safety of AFSSAMB are different from AFAMB built on liquid electrolytes, their reaction mechanism remains analogous throughout the charging and discharging sequence. Figure 3 illustrates the charging and discharging mechanisms of an anode-free solid-state lithium battery, providing a clear visual representation of its operation. In the absence of an anode, the cathode serves as the sole reservoir of alkali ions during the operation of AFSMB. To elaborate, alkali ions extracted from alkali-rich cathode (like LiFePO₄ in lithium cell, NaCrO₂ in sodium cell, etc.) via an electrolyte/separators are electroplated onto the anode current collector's surface, coming into being the transient anode with an electrochemically SEI during the time of charging.^[2] Following the initial charging procedure, the alkali ions are extracted from the transient anode and migrate into the solid-state electrolyte, ultimately inserting themselves into the corresponding cathode material. During subsequent charge-discharge cycles, the AFSSAMB functions similarly to a traditional metal battery. It becomes evident that AFSSAMBS represent the extreme case among the conventional alkali solid-state batteries, which don't possess the residual lithium/sodium sources for the following cycles. In the overall charge-discharge process, the ion migration mode of AFSSAMB

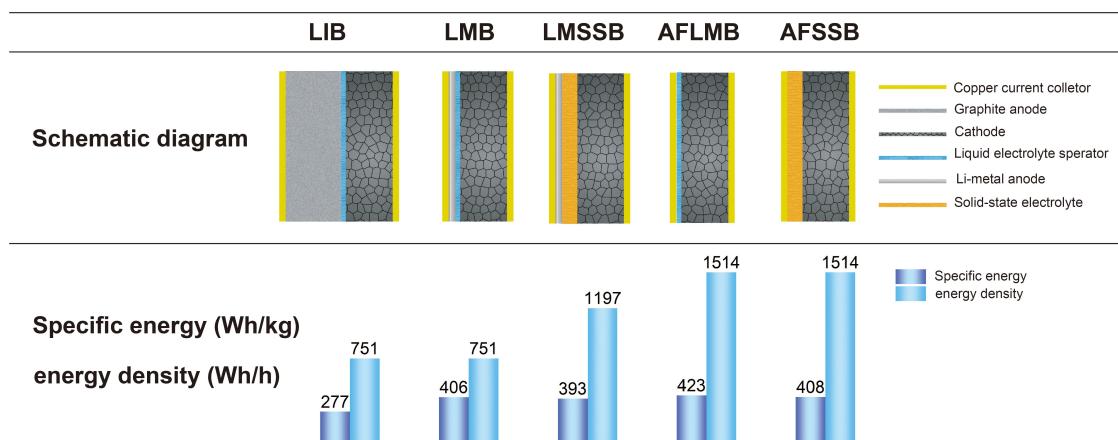


Figure 1. Schematic of various cell configurations, including Li-ion battery (LIB), Li metal battery (LMB), Li metal solid-state battery (LMSSB), anode-free Li metal battery (AFLMB), and anode-free solid-state battery (AFSSB). Accompanying these configurations is a presentation of their respective specific density and energy density.^[19]

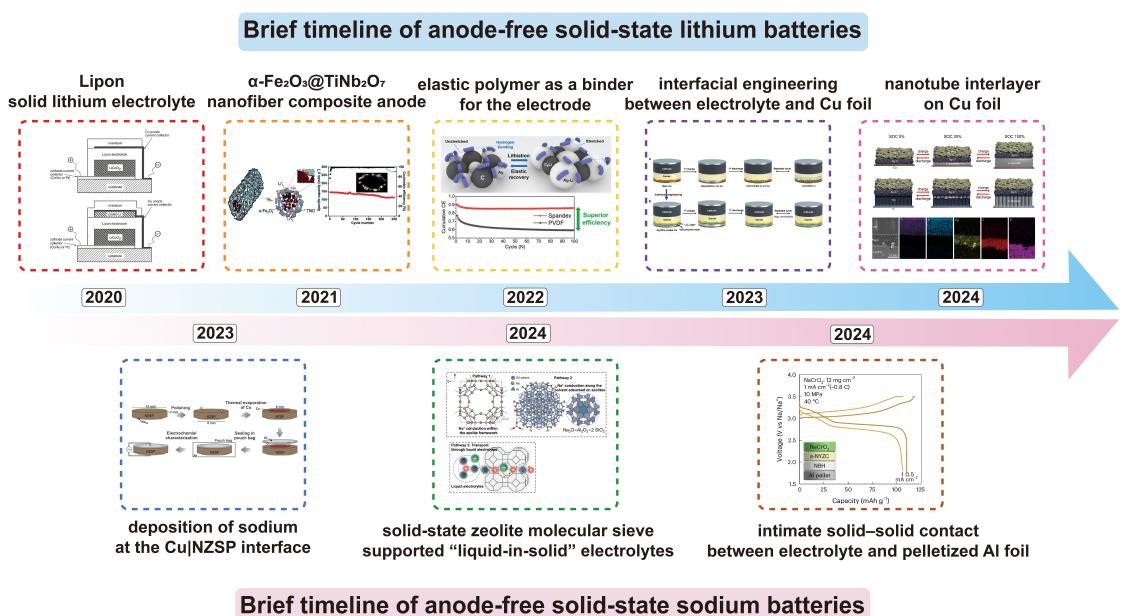


Figure 2. A brief timeline for the development of anode-free solid-state lithium metal batteries and anode-free solid-state sodium metal batteries. Lipon solid lithium electrolyte. Reproduced with permission.^[30] Copyright 2000, The Electrochemical Society. $\alpha\text{-Fe}_2\text{O}_3@\text{TiNb}_2\text{O}_7$ nanofiber composite anode. Reproduced with permission.^[29] Copyright 2021, Royal Society of Chemistry. Elastic polymer as a binder for the electrode. Reproduced with permission.^[26] Copyright 2022, American Chemical Society. Interfacial engineering between electrolyte and Cu foil. Reproduced with permission.^[28] Copyright 2023, Wiley-VCH. Nanotube interlayer on Cu foil. Reproduced with permission.^[31] Copyright 2024, Springer Nature. Deposition of sodium at the Cu|NZSP interface. Reproduced with permission.^[21] Copyright 2023, Wiley-VCH. Solid-state zeolite molecular sieve supported "liquid-in-solid" electrolytes. Reproduced with permission.^[27] Copyright 2024, Wiley-VCH. Intimate solid-solid contact between electrolyte and pelletized Al foil. Reproduced with permission.^[22] Copyright 2024, Springer Nature.

generally resembles that of an anode-free architecture employing a liquid electrolyte. The primary distinction lies in the type of electrolyte through which the ions penetrate. However, in the AFSSAMB configuration, ionic mobility is significantly influenced by the inherent limitations of solid materials. Even so, both systems face common challenges: the direct deposition of alkali metal onto the anode-side current collector and the irreversible consumption of alkali metal. The architecture of only available alkali sources also becomes a standard feature of anode-free battery systems, affecting correlative the power and energy density, costs, and use safety in energy cell systems.^[14]

In reality, the electrochemical performance of the AFSSAMB is almost entirely constrained by the efficiency of alkali metal plating and stripping, as there is no excess alkali metal. Furthermore, the direct deposition of alkali metal onto the bare current collector plays a pivotal role in its long-term cycling capability. Consequently, the AFSSAMB design is affected by a greater number of factors contributing to cell failure compared to traditional alkali metal batteries, such as irreversible alkali metal loss that fails to meet the operational requirements of the cell, uneven alkali metal plating and dendrite formation on the current collector that compromise cycling stability, and the

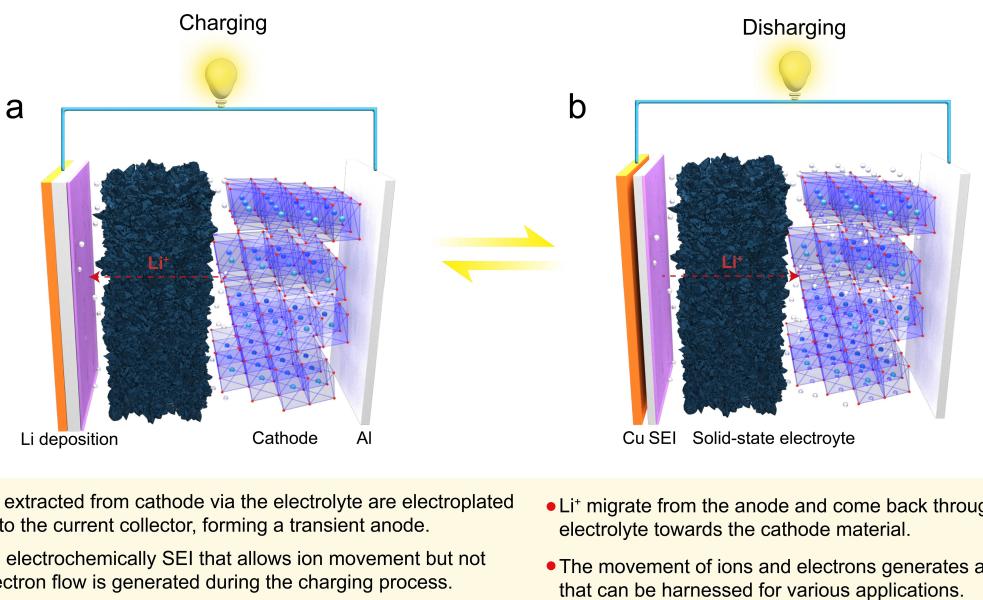


Figure 3. Mechanism illustration of (a) Charging and (b) Discharging for anode-free solid-state lithium battery.

highly unstable interlayer contact between the solid-state electrolyte and the bare current collector, which is crucial for ensuring normal battery operation.

The extensive opportunities associated with solid electrolytes necessitate an in-depth exploration of AFSSAMBs, given their exceptional chemical stability, superior mechanical properties, high modulus, and heightened safety. However, the primary impediment to further advancing AFSSAMBs compared to those with liquid electrolytes is the poor interface compatibility between the electrode and solid electrolyte, leading to high interfacial resistance. In terms of structural forms, solid-state batteries are categorized as semi-solid, quasi-solid, and full-solid. Based on chemical composition, electrolytes can be divided into polymer solid-state electrolytes and inorganic solid-state electrolytes.^[32] Currently, AFSSAMBs primarily employ lithium sources, utilizing garnet-based electrolytes (LLZTO).^[19,28] These full-solid electrolytes exhibit relatively high ionic conductivity, exceptional chemical stability, and favorable physical properties, maintaining stability without excess lithium sources during charging and discharging. In some research, sulfide-based electrolytes and polymer solid electrolytes are also utilized in anode-free configurations.^[13,26] In contrast, studies on batteries with sodium sources are relatively limited. For sodium sources, the primary trend is the use of NAtrium Superlonic CONductors (NASICON) electrolytes, which offer high ionic conductivity, chemical stability, and superior reversible sodiation/de-sodiation capabilities, making them broader in scope for AFSSAMBs exploration.^[21,22] Recently, a “liquid-in-solid” electrolyte has been designed for high-voltage anode-free rechargeable sodium batteries.^[27] This electrolyte consists of a Na-containing solid-state zeolite molecular sieve that supports “liquid-in-solid” electrolytes (Na-SSZE) by confining liquid ether electrolytes within zeolite molecular sieves that inherently possess ionic conductivity. This approach provides material and

conceptual innovations for creating novel solid-state electrolytes that meet the stringent requirements for practical anode-free batteries. Regardless of the type of solid-state electrolyte, a stable electrode-electrolyte interface is crucial, particularly on the anode side with the bare current collector. One effective measure to overcome this interface issue is the design of an artificial interlayer, which promotes a stable alkali metal plating/stripping process, uniform and dense alkali metal plating, and reversible alkali metal sources during charging-discharge cycles. Lee et al. introduced Ag–C nanocomposite layers into an anode-free solid-state battery, where Ag nanoparticles alloyed with Li during the initial charging stage.^[33] However, a significant portion of Ag migrated to the current collector side, assisting in the uniform and dendrite-free plating of Li metal. Apart from artificial interlayer construction, applying an appropriate pressure is another effective strategy to ensure close contact between the electrolyte and electrode during cycling. Zhu et al. proposed a conductive carbon-felt elastic layer that self-adjusts pressure on the anode side, ensuring consistent lithium-solid electrolyte contact.^[34] This layer simultaneously provides electronic conduction and relieves plating pressure, resulting in a dramatic increase in the first Coulombic efficiency from 58.4% to 83.7%, along with a more than tenfold improvement in cycling stability. Combining these two strategies is essential for resolving interface issues and achieving simultaneous operation of AFSSAMBs, ultimately paving the way for commercial implementation. It is worth noting that several challenges hinder the electrochemical performance of AFSSAMBs, beyond the unstable interlayer between the electrode and solid electrolyte, which we will discuss later in the “Challenges and Strategies for AFSSAMBs” section.

AFSSAMBs exhibit several significant advantages over conventional metal batteries:

- 1) Energy Density: The anode-free configurations, without the use of excess alkali metal at the anode side, deliver the maximizing power and energy density. Compared to conventional batteries, the absence of an anode allows for more active materials to be accommodated within the same volume, thereby maximizing utilization. In AFSSAMBs, although the application of SSE may reduce certain gravimetric specific energy because the SSE leads to the mass of the entire battery increasing filling the same volumetric capacity as the liquid electrolyte, the overall energy loss is outweighed by the gain effects stemming from the anode-free system design.^[19]
- 2) Safety: In contrast to conventional batteries with alkali metal present at the anode, AFSSAMBs have remarkably enhanced battery safety performance. On the one hand, the elimination of metal anode reduces the safety hazards associated with the chemical instability of alkali metal, such as battery explosion triggered by the reaction between alkali metal and moisture.^[35] On the other hand, SSE possessing superior thermal stability is introduced into the de-negative system, accordingly, AFSSAMBs overcome the stability problems that arise from the leakage of liquid electrolytes from the battery, thus preventing potential explosions.
- 3) Manufacture and Costs: In terms of preparation, an anode-free battery can greatly streamline the manufacturing process including tedious procedures associated with metal foil, extraction and purification of alkali metal, and eventual assembly with battery components. The simplified cell architecture, which demands far less preparation process, further slashes manufacturing costs and bolsters scalability for large-scale production. These cost reductions encompass not only the pure metal purchase and processing but also a diminished need for operational and preparatory environmental setups.^[19] However, the realization costs in AFSSAMB construction, involving guest structures and protective coatings, must be factored into a comprehensive value assessment.

In general, AFSSAMBs present a series of advantages in the realm of batteries, including but not limited to high energy density, enhanced safety, simplified manufacture, and cost-effectiveness. The innovative solid-state battery with a bare current collector on the anode side is a promising area of research, particularly for its potential for high energy capacity and reliability.

Challenges and Strategies for AFSSAMBs

Although AFSSAMBs offer several advantages, they still face critical challenges that require urgent attention. The key challenges affecting their performance are outlined below:

- 1) Unlimited Volume Expansion: Volume fluctuations during the charge-discharge cycles of AFSSAMBs can cause significant damage to the battery's internal structure, leading to interface degradation and electrolyte fractures.^[13] The stress in the initial charging process can induce minute lateral fractures on the surface of the electrolytes, and latterly, the

dendrites expand rapidly along these cracks. Notably, the original crack locations tend to develop numerous voids during the subsequent stripping process, further compromising the integrity and performance. Void formation and the intrinsic properties of solid-state electrolytes disrupt the initial contact between the electrolyte and the anode-side current collector. The loss of contact, in which the electrolyte is incapable of autonomously rectifying the voids and cracks due to the immobility characteristic of solid matter, significantly accelerates battery failure.^[36] The majority of alkali metal batteries utilizing solid-state electrolytes face the persistent challenge of infinite volume changes during cycling, ultimately resulting in battery failure within relatively short cycling periods. To address this challenge, strategies employed in alkali metal solid-state batteries can be adapted for application in AFSSAMBs. These strategies involve constructing interface structures and optimizing the design of the electrolyte and current collector, such as using 3D interior structures and applying mechanical pressure. However, it is crucial to tailor these strategies specifically to the unique characteristics of anode-free batteries during the design process. The considerable volume deformation observed in AFSSAMBs during the alkali metal plating and stripping processes on the anode side presents a substantial hurdle in transitioning from AFAMBs to AFSSAMBs, significantly impeding the improvement of CE. Therefore, innovative approaches are required to effectively manage and mitigate this volume deformation, ensuring the stability and performance of AFSSAMBs over extended cycling periods.

- 2) Low Reduction Potential of Alkali Metal: The high reduction alkali metal can induce an electrode-electrolyte passivation interface (SEI), and the stability of this interface profoundly influences cell performance.^[37,38] Ideally, electrochemical reactions between the anode metal and electrolyte form an electronically insulating SEI that promotes ion diffusion, reduces direct metal-electrolyte contact, and prevents electrolyte decomposition. In practice, the SEI with high electronic conductivity often forms. Due to significant volume changes and reactive interfacial reactions, this SEI is unstable, prone to cracking, and undergoes continuous reformation. Ultimately, issues stemming from the defective interlayer, such as uneven deposition, the formation of dendrites, and the irreversible consumption of alkali metals, critically impact the performance of anode-free batteries.^[15] Apart from the ideal stability in terms of structure and chemistry, two other crucial factors influencing the further performance of the interface are the conductive properties and composition of the SEI. The conductive properties necessitate that the SEI must effectively insulate electrons to prevent further reduction of the electrolyte, while simultaneously possessing high ion conductivity to ensure smooth shuttling and migration of lithium ions within the battery. The SEI primarily consists of tightly packed inorganic substances with a loose, porous outer layer made up of organic compounds.^[39,40] In comparison to conventional alkali metal batteries, AFSSAMBs require a more strategic design of the SEI modification at the interface between the

electrolyte and the bare current collector to achieve high cycle stability. While it may not always be feasible to ensure absolute stability in chemistry and structure over long-term cycling, we can enhance the conductive properties, alter the specific SEI composition, and achieve an optimal balance between the proportion of organic and inorganic compounds through various approaches such as electrolyte modification.^[41] These efforts will ultimately improve the overall performance and stability of AFSSAMBs.

3) Nonuniform Nucleation: In anode-free batteries, the deposition of alkali metal onto the bare current collector requires overcoming a nucleation barrier much higher than in traditional metal batteries.^[23] Consequently, the plating characteristics of lithium/sodium exhibit considerable non-uniformity during the charging process. This nonuniform nucleation promotes dendrite formation, and during subsequent cycles, the uneven deposition accelerates dendrite growth, degrading electrochemical performance and increasing the risk of short-circuiting.^[42] Additionally, the continuous formation of these dendrites is the primary cause of the irreversible depletion of limited alkali metal resources, resulting in a more rapid decline in CE, capacity reduction, and battery failure, as compared to traditional batteries that possess abundant alkali metal sources.^[43,44] The uniformity of alkali metal plating and stripping has a crucial impact on the cycle capacity, particularly when only a bare current collector is present on the anode side. Several factors contribute to the uniformity of alkali metal deposition, including the higher nucleation overpotential during the plating process onto the bare current collector at the anode side, the surface microstructures of SSEs, and the manipulation of protocols such as internal pressure and temperature, which can lead to the growth of numerous dendrites.^[45–47] To date, most research has focused on developing strategies to manipulate uniform nucleation and modify dendrite growth through the use of SSEs with minimal defects, smooth construction, current collectors employing host structures modifications, and soft artificial interphase layers between electrolytes and electrodes.^[13,28,48] It is essential to identify the origins of this phenomenon in different material systems, and further in-depth research is urgently needed to explore the latest modification techniques that can ensure uniform nucleation during the charging process for AFSSAMBs.

These challenges primarily originate from the irreversible depletion of the finite alkali metal reserves in plating/stripping processes in AFSSAMBs. To achieve an optimized utilization of these stocks, it is imperative to address the aforementioned limitation in a comprehensive manner, aiming to foster a favorable deposition pattern and a suitable interface, thereby enhancing cycling stability and prolonging the lifespan. The advantages, challenges, and related strategies are summarized in Figure 4. To this end, several promising strategies are envisioned, encompassing: 1) design of the solid-state electrolyte, 2) construction of current collectors, and 3) manipulation of optimal protocols. The corresponding details are discussed as follows:

- 1) Design of the Solid-State Electrolyte: The field of anode-free battery technology has garnered considerable attention for solid electrolytes that possess superior mechanical strength, non-flammability, and high modulus.^[49] Nevertheless, their practical applications are still hampered by limitations such as low ionic conductivity and inadequate interface compatibility. The future design of SSEs for anode-free batteries must embody several critical advantages to guarantee the cycling stability and service life of these batteries. These include achieving high ionic conductivity and minimizing interface impedance, which are essential for maintaining efficient battery operations. Additionally, the SSEs must exhibit superior interfacial contact with the electrodes, ensuring seamless integration and ion transfer. Furthermore, the formation of a stable SEI layer, resulting from its reaction with the alkali metal, is paramount. This layer acts as a protective barrier, further enhancing the battery's durability and performance.^[50] By incorporating these features into the design, SSEs for anode-free batteries can be optimized to meet the rigorous demands of modern energy storage systems. The pioneering study in 2000, which involved the assembly of an anode-less battery utilizing solid electrolyte (LiPON), gave birth to the lithium cobaltate|LiPON|Cu battery.^[30] More recently, Abin Kim et al. have reported on a Li₂CO₃-proof LLZO (AH-LLZO) solid electrolyte (Figure 5a).^[51] This SSE, when assembled into a lithium cell, displays exceptional air handleability in humid conditions and superior Li metal wettability even after prolonged exposure to the atmosphere, thereby achieving exceptional electrochemical performance. This approach stands fundamentally distinct from previous methodologies, as it effectively curbs the initial formation of Li₂CO₃, rather than eliminating it post-formation. The Li₂CO₃-proof feature of garnet-type SSEs facilitates their practical application by capitalizing on their exceptional Li metal wetting property. Consequently, a dense, ultra-thin layer of Li metal (approximately 3.43 μm) is effortlessly attained, serving as a seed layer to guarantee uniform deposition of Li metal. The introduction of the ultra-thin solid-state lithium metal battery exemplifies a novel concept aimed at achieving high energy density by minimizing the excessive consumption of Li. Furthermore, Ziyang Lu et al. have designed an innovative "liquid-in-solid" electrolyte by utilizing Na-containing zeolite molecular sieves (Figure 5b).^[27] Through ion exchange and confinement of aggregated liquid ether electrolytes within the nanopores and voids of zeolites, they have achieved remarkable cycling stability and high capacity retention in a 4.25 V-class anode-free Na battery. This electrolyte combines the unique attributes of both liquid and solid-state electrolytes, offering material and conceptual advancements for the creation of innovative electrolytes that fulfill the stringent requirements for developing practical anode-free batteries.
- 2) Construction of Current Collectors: The unique aspect of the exclusive fabrication of AFSSAMBs lies in the direct deposition of scarce lithium or sodium sources from the cathode on the anode-side current collector, a step of paramount

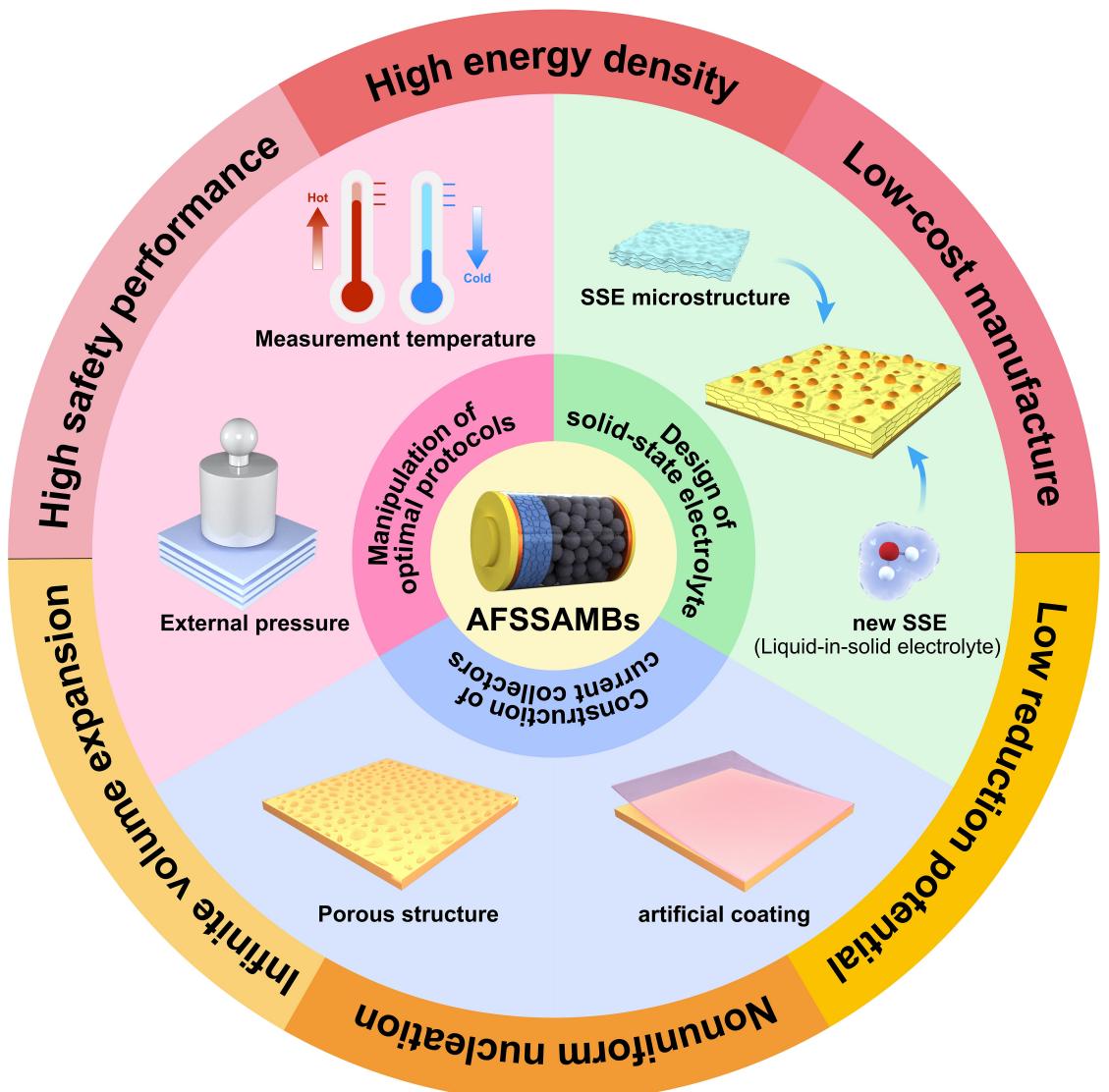


Figure 4. Schematic summary of advantages, challenges, and refined design strategies for AFSSAMBs.

significance.^[48] The material and surface structure of the current collector greatly influence initial nucleation, which in turn affects the growth and morphology of the deposited alkali metal. Furthermore, they have a significant impact on the formation and quality of the SEI, contributing to the development of a more robust and efficient SEI layer. Therefore, refining the anode-side current collector design, including the invention of innovative current collectors and the construction of artificial interlayers, is essential to enhance the performance of AFSSAMBs.^[52,53] Key objectives in designing current collectors for AFSSAMBs include reducing surface diffusion barriers and minimizing nucleation overpotential to promote uniform alkali metal deposition. An ideal current collector also exhibits exceptional electronic conductivity, remarkable chemical and electrochemical stability without any side reactions, and intimate contact with SSEs. Wen-Ze Huang et al. have developed a high-performance anode-free solid-state lithium battery

using a carbon-reinforced ionic-electronic composite current collector (Figure 5c).^[54] This design fosters a three-dimensional ionic-electronic conduction network, providing ample sites and scalable domains conducive to the nucleation and subsequent expansion of lithium metal. Furthermore, the interface architecture, a coating atop the current collector surface, exerts a pronounced influence on the efficiency of restricted alkali metal plating/stripping. Due to the excellent bending performance of 3D interconnected carbon paper, this structure is also suitable for flexible and wearable energy storage devices, providing new possibilities for future battery design. Grayson Deysher et al. have used a porous aluminum current collector to establish intimate solid-solid interfaces with the sodium borohydride solid electrolyte. This approach enables the realization of highly reversible sodium plating and stripping operations, achieving both high areal capacities and current densities that were previously unattainable using conventional aluminum

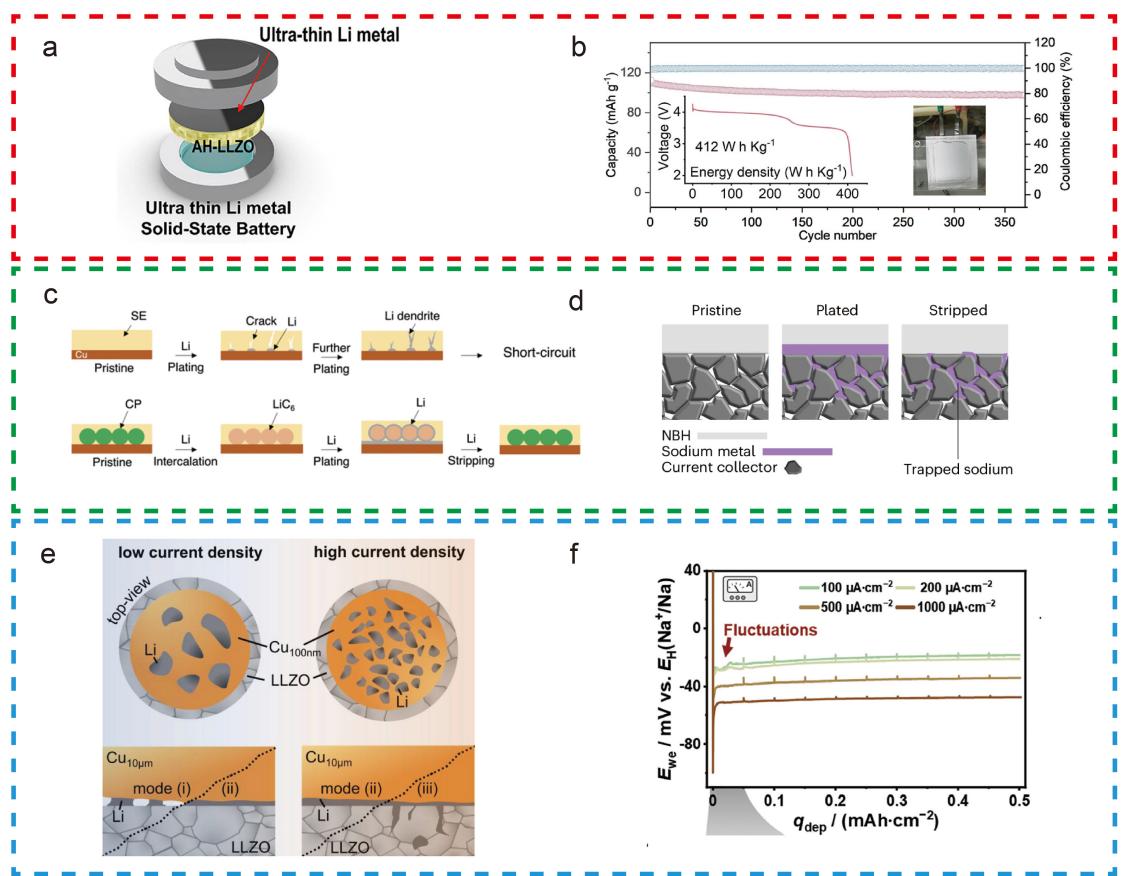


Figure 5. Design of the solid-state electrolyte. (a) Schematic diagram of an ultra-thin SSLMB. Reproduced with permission.^[51] Copyright 2024, American Chemical Society. (b) Cycling stability of high-voltage anode-free pouch cells using the Na-SSZE. Reproduced with permission.^[27] Copyright 2024, Wiley-VCH. Construction of current collectors. (c) Schematic diagrams of different current collectors for AFSSLBs. Reproduced with permission.^[54] Copyright 2023, Royal Society of Chemistry. (d) Schematic of Na trapping mechanism for porous current collectors. Reproduced with permission.^[22] Copyright 2024, Wiley-VCH. Manipulation of optimal protocols. (e) Schematic of the operando SEM setup used to characterize lithium plating in a Li_{id} | LLZO | Cu film cell stack. Reproduced with permission.^[59] Copyright 2023, Wiley-VCH. (f) Potential profile of cathodic deposition of sodium at a Cu|NZSP interface at various current densities. A pressure of 2 MPa was applied for measurements at different current densities. Reproduced with permission.^[21] Copyright 2024, Wiley-VCH.

foil (Figure 5d).^[22] The designed sodium anode-free solid-state battery full cell has demonstrated remarkable stability, maintaining stable cycling performance for several hundred cycles. This work elucidates the several critical factors that influence the electrochemical performance of AFSSAMBs designs, providing valuable insights to guide future advancements in the development of high-energy all-solid-state batteries.

- 3) Manipulation of Optimal Protocols: In addition to current collector and electrolyte design, testing protocols (e.g., charge and discharge current density, external pressure, cut-off voltage, test temperature, etc.) are crucial for optimizing AFSSAMB performance.^[55] These measuring conditions considerably influence the lithium/sodium deposition quality, the solid-state electrolyte stability, and the interfacial contact between electrodes and electrolytes.^[56] Recent studies highlight the importance of external pressure, which can deform solid components to improve internal contact, and test temperature, which affects ionic conductivity—both of which are key factors in the electrochemical performance of AFSSAMBs.^[57,58] These protocols affect lithium/sodium

deposition by preventing dendrite formation, reducing dendritic growth, and minimizing electrolyte reactions that consume active lithium/sodium and form SEI. Recently, setting appropriate charge/discharge current density, cut-off voltage, and employing an initiated formation strategy have emerged as crucial aspects for improving electrochemical performance. However, while measurement protocols may achieve favorable battery performance, identifying a suitable protocol necessitates substantial costs and time. Till Fuchs et al. have delved into the intricate interplay between current density and the current collector's role in shaping the lithium metal morphology during the initial charging cycle of lithium reservoir-free cells (Figure 5e).^[59] These research findings show a noteworthy enhancement in the lithium-particle density with an increase of current density at the Cu|Li_{1.25}Al_{0.25}La₃Zr₂O₁₂ interface. Furthermore, the utilization of thin current collectors ($d=100$ nm) facilitates the penetration of lithium whiskers, leading to highly heterogeneous interfaces. It meticulously demonstrates the importance of carefully selecting the current density and plating protocol in order to optimize the electrode system

for the growth of homogeneous lithium films, based on the presented findings. Till Ortmann et al. have conducted an exhaustive study on the combined influences of current density (j_{app}) and external pressure (p) on sodium deposition in Cu|NZSP|Na cells (Figure 5f).^[21] Their analysis underscores that higher current densities facilitate a more uniform distribution of sodium, whereas the influence of stack pressure remains relatively insignificant within the examined parameter range. This work concludes that "reservoir-free" cell concepts can be implemented for sodium solid-state batteries, potentially sparking further research endeavors in the field of sodium-based solid-state batteries.

Conclusion and Outlook

Adopting an anode-free configuration marks a critical step forward in the development of high-efficiency energy storage batteries. Within the class of batteries without additional alkali metal, AFSSAMBs stand out for their superior performance.^[6] For future practical deployment, the adoption of lithium/sodium metal mitigates limitations, offering heightened gravimetric and volumetric energy densities during cycling, streamlined battery manufacturing processes, cost reduction, and enhanced safety within a green environment.^[13] Furthermore, the superior properties of solid-state batteries, including non-flammability, impermeability, robust mechanical strength, and wide electrochemical window, when coupled with the anode-free architecture, culminate in achieving maximized energy density without compromising on safety.^[2] The AFSSAMB, which is composed of a unique prototype of anode current collector/solid-state electrolyte with separator/cathode/cathode current collector, has garnered increasing attention from researchers, as compared to traditional lithium/sodium metal batteries. As far as mainstream Li batteries are concerned, the anode-free Li metal pouch cells that have attained remarkable test performance have met acceptable safety standards.^[42] Notably, several battery start-ups have triumphantly integrated a ten-layer AFSSAMB into Li metal pouch cells showcasing exceptional performance, further underscoring the potential of this innovative technology.^[13] Meanwhile, we briefly outline several promising directions for future research on AFSSAMB. These include: 1) leveraging advanced energy materials to enhance the overall performance of batteries; 2) optimizing cell design to improve safety and streamline manufacturing processes; and 3) exploring the key factors affecting cycling performance and understanding failure mechanisms through advanced characterization techniques. While we have only provided a glimpse of these insightful viewpoints, there are still numerous factors that impact AFSSAMB and necessitate further exploration in the future. Furthermore, the development of AFSSBs is intricately linked with the advancement of SSEs. Many innovative and cutting-edge SSEs can be effectively combined with the anode-free strategy, resulting in higher volumetric and gravimetric energy densities, superior cycling performance, and a safer battery system.

In this concept, we introduced to the reader an overview of AFSSAMBs, including their intricate configuration and internal mechanisms compared to conventional metal batteries, the major challenges impeding the electrochemical performance, as well as the strategic advancements forged through the current advance of anode-free solid-state lithium/sodium batteries technology. Despite the remarkable progress achieved by researchers in this nascent field, the quest for AFSSAMBs with high CE and cycle stability remains a formidable challenge.

We aspire for this article to serve as a cornerstone, fostering a foundational understanding of anode-free alkali metal batteries with solid-state electrolytes among both nascent researchers and seasoned experts in the energy field.

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Conflict of Interests

The authors declare no conflict of interest.

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