EES Batteries

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Broader context statement

Bipolar all solid-state batteries (ASSBs) represent an emerging battery architecture attracting considerable interest due to their potential for high energy density, enhanced safety, and simplified packaging. By integrating a bipolar electrode architecture with solid-state technology, these batteries minimize the use of inactive materials, rendering a notable increase in volumetric energy density. The bipolar configuration simplifies the manufacturing process by reducing the number of components and assembly steps, consequently lowering production costs. This streamlined design also enhances thermal management, which contributes to improved cyclic life and overall stability of bipolar ASSBs. This review systematically examines bipolar ASSBs, which represent a paradigm shift from incremental materials improvements to a fundamental redesign at the cell and module level. This explores the optimization processes involved in their development, ranging from model cell design to the fabrication of Ah-level pouch cells, highlighting the direct correlation between process optimization and improvements in energy density. This contribution affords a detailed discussion of current research advancements in bipolar ASSBs, encompassing high ionic conductivity and solid electrolytes (SEs), stable electrode materials, and advances in interfacial engineering.

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From mold to Ah level pouch cell design: Bipolar all solid-state Li battery as emerging configuration with very high energy density

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Abstract

Bipolar all solid-state batteries (ASSBs) represent an innovative battery architecture that attract significant attention due to their high energy density, enhanced safety, and simplified packaging design. These batteries effectively reduce the use of inactive materials, thereby increasing volumetric energy density through the integration of bipolar electrode architecture with the advantages of solid-state technology. The employment of solid-state electrolytes (SEs) not only addresses the thermal runaway issues associated with routine liquid electrolytes but also expands the operational temperature range of the working batteries. This review systematically explores the optimization processes from model cell design to Ah-level pouch cells fabrication, emphasizing the direct correlation between process optimization and energy density enhancement. It also affords a detailed discussion on the current research advancements in bipolar ASSBs, including SEs with high ionic conductivity, stable electrodes, and interfacial engineering. Furthermore, it outlooks future perspectives on the application prospects in electrical vehicles, energy storage systems, and flexible wearable devices. The rapid development of artificial intelligence accelerates the optimization processes of bipolar ASSBs. As bipolar ASSBs achieve higher energy densities while maintaining safety and long-term cycling stability, they are poised to become a transformative technology in next-generation energy storage ecosystems.

Keywords: bipolar all solid-state batteries; high-energy-density batteries; pouch cells; solid electrolyte; lithium metal batteries.

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1. Introduction

The increasing global demand for efficient, safe, and environmentally friendly energy storage solutions has positioned bipolar all solid-state batteries (ASSBs) as a promising energy storage technology[1-8]. This innovative approach integrates the benefits of both bipolar batteries and ASSBs, offering significant potential for practical applications. ASSBs differ from traditional lithium-ion batteries (LIBs) primarily due to their use of solid-state electrolytes (SEs), which enhance battery safety and stability[9-16]. Unlike LIBs, which rely on liquid electrolytes and are associated with safety hazards, such as flammable electrolytes, thermal runaway, and short circuit risks caused by lithium dendrites, ASSBs utilize SEs to effectively prevent dendrite growth. This allows for the incorporation of lithium-metal anodes, resulting in very high energy density[17-21]. Consequently, bipolar ASSBs hold particular promise in applications such as flexible wearable devices[22], electric vehicles (EVs), aerospace, and large-scale energy storage, potentially becoming a core technology for future energy storage solutions. However, the practical applications of bipolar ASSBs is hindered by challenges related to poor ion conductivity, chemical stability, and interface compatibility with working electrode materials[23-29]. Furthermore, the complex and costly manufacturing process limits their large-scale production and wide application. Addressing these issues by reducing manufacturing costs and improving the scalability of production processes is essential for the future development of ASSBs.

The bipolar configuration battery, as depicted in **Figure 1**, represents a complementary innovation with significant potential when applied to ASSBs. Although this configuration has been utilized in routine battery designs, its application to ASSBs also unveils distinct advantages. In this setup, multiple cells are stacked in series, with each cell sharing a bipolar electrode. This electrode serves as the positive electrode for one cell and the negative electrode for the adjacent cell, effectively minimizing the request for complex internal connections commonly found in many battery packs. As a result, internal impedance is reduced, thereby enhancing both the energy and power density of ASSBs. This design is particularly advantageous for applications demanding high power output, such as EVs and large-scale energy storage systems[8, 30-36].

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Furthermore, the bipolar configuration streamlines the manufacturing process by decreasing the number of components and assembly steps, which subsequently reduces production costs. This simplification also enhances thermal management performance, thereby extending the cyclic life and stability of bipolar ASSBs.

The synergistic effect of bipolar configuration and ASSBs technology represents a emerging direction in electrochemical energy storage[37]. Unlike routine LIBs, which necessitate independent packaging before series or parallel connection due to the fluidity of liquid electrolytes, ASSBs can achieve bipolar stacking thanks to the non-flowability of SEs[38]. This capability not only enhance the high safety and stability inherent in ASSBs but also improves energy and power density through innovative bipolar configuration design. This is particularly advantageous in applications sensitive to volume and weight, such as EVs and aerospace, where bipolar configuration ASSBs can afford superior volumetric and mass energy density. Although scientific research on bipolar ASSBs is still in its early stages, current progress is promising[39]. Continuous advancements in SEs, including oxides[40-42], sulfides[43-45], polymers[46-49], and composite SEs[50, 51], alongside the optimization of bipolar electrode materials and manufacturing processes, are anticipated to overcome the limitations of current technologies[52]. These developments are expected to propel drive bipolar configuration ASSBs toward higher efficiency, safety, and economic viability. With ongoing research and technological innovation, this field is poised to achieve breakthrough progress and become a crucial component of the next-generation of electrochemical energy storage technology. Bipolar-configured ASSBs have garnered considerable attention in the energy storage sector due to their high energy density, enhanced safety, and simplified structural configuration.

In this contribution, the current research progress is summarized in three key areas: Firstly, it examines material design and performance optimization across oxide, sulfide, halide, polymer, and composite electrolytes. The analysis further delves into interfacial challenges, particularly strategies for improving ionic conductivity through advanced interface engineering. Building on these advancements, the integration of artificial intelligence (AI) has significantly accelerated electrolyte-electrode interface design and

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accelerated materials discovery through predictive modeling. Secondly, the work evaluates technological advantages such as scalable manufacturing potential and inherent safety features, while addressing critical challenges including interfacial degradation mechanisms and manufacturing complexity in bipolar configurations. Thirdly, potential applications are specifically analyzed for EVs, grid-scale energy storage systems, and next-generation portable electronics. The review concludes by outlining future directions focused on scalable fabrication methods, hybrid electrolyte architectures, and AI-driven closed-loop optimization systems for performance enhancement. Particularly emphasis is placed on the interdependencies between material innovation, manufacturing scalability, and application-specific performance requirements.

2. Development History of Bipolar Configuration Batteries

The concept of the bipolar configuration battery was firstly introduced in the 1920s, as illustrated in **Figure 2**[52-57]. This design aimed to reduce the internal connection resistance found in routine battery designs by integrating the cathode and anode materials directly onto a single bipolar electrode. The bipolar design effectively minimizes energy loss and enhances both power density and efficiency.

In the 1970s, lead-acid batteries with the bipolar configuration began to enter the market[58]. This bipolar configuration afforded a significant advantage over conventional lead-acid batteries by allowing for the compact arrangement of multiple electrodes, thereby reducing size and weight, increasing power density of a full lead-acid battery. Initially, these batteries found applications in various industrial settings, such as backup power systems and EVs. However, despite their design advantages, the widespread application of bipolar configuration lead-acid batteries was limited due to manufacturing complexity and high cost.

Throughout the 1980s, the innovation on the bipolar configuration lead-acid batteries focused on enhancing the battery reliability and optimizing the manufacturing process. Nevertheless, despite excelling in certain areas, the high cost and manufacturing challenges prevented these batteries from gaining widespread market adoption, allowing traditional unipolar batteries to maintain their dominance.

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With the rise of the electric and hybrid vehicle markets, the bipolar configuration of the batteries is revisited in the current century. The application of bipolar configuration design in nickel-metal hydride (NiMH) batteries began to attract strong attention. The bipolar configuration NiMH batteries are better suited to meet the high power and energy density of EVs[59, 60]. Particularly, these batteries demonstrate significant potential to increase power output while reducing size and weight in the field of hybrid vehicles. This design also affords valuable experience and technical reserve for the development of future battery technologies.

With the dominance of LIBs as the primary energy storage technology, there has been a renewed focus on the design of bipolar configuration with enhanced energy density and charging/discharging efficiency of LIBs. Additionally, it contributes to reducing internal resistance, extending battery life, and improving safety[61] (**Figure 3**). These improvements are particularly crucial for EVs and energy storage systems[62-64]. The selection of suitable materials, the optimization of manufacturing processes, and the exploration of modular design strategies are strongly considered recently.

The exploration of ASSBs is strongly concerned recently. However, the most current research is centered on mold batteries due to the absence of a mature preparation process for solid-state pouch cells. The advent of bipolar configuration batteries has made the realization of all-solid-state pouch cells more feasible, even achieving the Ah level capacities[37]. The simple structural design of bipolar configuration ASSBs offers several advantages, such as reduced cost, increased energy density, and improved energy efficiency. Despite these benefits, several challenges continue to hinder the advancement of bipolar ASSBs, as shown in **Figure 4a**. Firstly, the chemical instability of the electrode material can lead to the production of ionic insulation products at the interface due to electrolyte decomposition[65]. Secondly, the limited contact area between the electrode material and the electrolyte, coupled with significant volume changes during the charging and discharging processes, can result in contact loss, thereby reducing the effective transfer of Li^+ at the interface[66-68]. Thirdly, uneven current distribution at the interface between the lithium metal anode and the electrolyte, along with electronic conductivity grain boundaries in the solid electrolyte, can render

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premature reduction of Li^+ before they reach the cathode materials. This premature reduction leads to the formation of lithium dendrites at the interface and grain boundaries, which can interconnect and cause a short circuit[69]. Lastly, the difference in Li^+ chemical potentials between the electrode material and the electrolyte results in charge redistribution, creating regions of Li^+ depletion and enrichment[70-72]. Consequently, a space charge layer (SCL) forms at the interface, as depicted in Figure 4b, which poses an additional barrier to Li^+ transfer and increases the overall charge transfer resistance at the interface[73].

To effectively realize bipolar ASSBs, the design of current collectors presents significant challenges and meets several critical requirements[74-76]. Firstly, the collectors ensure efficient conductivity to facilitate the flow of current between the batteries without incurring noticeable ohmic losses. Secondly, they demonstrate chemical and electrochemical stability under operational conditions. Thirdly, it is essential for the collectors to maintain strong adhesion to working electrodes and resist potential battery shrinkage, while also exhibit high mechanical stability throughout long-term cycling. Additionally, overcharge tolerance is necessary, as variations in performance among the bipolar ASSBs result in a battery achieving a higher state of charge than other routine batterie. Furthermore, since the collector is directly connected to both cathodes and anodes, it remains stable across a wide voltage range and be compatible with both electrode types. Ultimately, the exploration of suitable collectors is crucial for advancing the industrialization of bipolar configuration ASSBs.

3. Research Progress on Bipolar ASSBs

The bipolar ASSBs commonly employ polymer-based, oxide-based, sulfide-based, or composite-based solid electrolytes. These electrolytes face significant challenges in batch preparation due to inherent limitations in ionic conductivity and a narrow electrochemical voltage window, which hinders fast charging and compatibility with high-voltage cathodes. Notably, the sulfide SEs exhibit ionic conductivity comparable to that of liquid electrolytes[67, 77, 78]. However, there is limited experimental investigation on sulfide-based bipolar ASSBs. A primary challenge is the development of reliable methods for preparing ultra-thin sulfide electrolyte films and electrodes that meet

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essential criteria, such as excellent film-forming properties, high mechanical strength, and high energy density targets[79-84]. This challenge leads to inconsistencies among stacked cells and poor electrochemical cycling performance in bipolar ASSBs. Nonetheless, bipolar ASSBs afford significant advantages by reducing the proportion of inactive materials and lowering both resistance and interface impedance, significantly surpassing the performance of routine battery configurations. These improvements contribute to enhanced energy density and electrochemical performance in bipolar ASSBs.

3.1. Emerging solid electrolyte for bipolar ASSBs

3.1.1. Polymer-based SEs

Polymer-based SEs are characterized by their excellent flexibility and high processability, rending them highly suitable for a wide range of applications in bipolar ASSBs. Current research efforts are primarily directed towards enhancing the voltage window, ionic conductivity, mechanical strength, and interfacial stability of these polymer electrolytes[32, 47, 85, 86]. The composite electrolytes with high ionic conductivity and robust mechanical strength are achieved by incorporating ion-conducting polymers such as poly-(ethylene glycol)-based polymers, along with lithium salts, plasticizers, and inorganic nanofillers like Al_2O_3[87-89], and SiO_2[90, 91]. These composite electrolytes exhibit excellent electrochemical performances in bipolar ASSBs.

The rational combination of supramolecular polymer electrolytes and polymer-ceramic composite electrolytes has been employed to significantly improve the thermal stability and electrochemical window of polymer-based SEs. The exploration of self-healing polymer SEs and supramolecular polymer SEs are also considered to enhance their durability and stability during the charging and discharging processes. As illustrated in **Figure 5a**, ultra-thin polymer electrolyte-based bipolar ASSBs were fabricated through the *in-situ* polymerization of vinyl ethylene carbonate (VEC) and poly-(ethylene glycol) diacrylate (PEGDA) supported by a polypropylene (PP) film. The non-fluidic properties of the electrolyte facilitated the creation of a high energy-density 24 V solid-state lithium-metal pouch cell, which demonstrated high flexibility and safety. Notably, no issue such as voltage drop was observed during folding and

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cutting, and the battery exhibited excellent cycling stability[32, 92].

The rational design of bipolar configurations aims to reduce series connections within working batteries and enhance energy density by sharing collectors. Specially, this structural compatibility leads to improved performance metrics such as increased energy density. However, the use of polymer-based interfaces between among electrodes often results in high interfacial impedance. To address this challenge, the introduction of conductive polymers on the electrode surface or the application of an interfacial layer with high ionic conductivity is proposed to compensate for interfacial Li^+ transport loss induced by bipolar stacking. Additionally, employing nanostructured electrodes can effectively increase the interfacial contact area, thereby improving the ionic conduction efficiency. Optimizing electrode-electrolyte combinations has significantly improved cycle stability and rate capability. Furthermore, the flexibility and malleability of polymer-based SEs allow batteries to adapt to various shapes and sizes, facilitating their use in a wide range of applications. This flexibility enhancement, combined with improved energy density, enables the development of advanced battery systems suitable for diverse and flexible applications.

3.1.2. Oxide-Based SEs

Oxide-based SEs such as $Li_7La_3Zr_2O_{12}$ (LLZO), have emerged as pivotal materials for bipolar ASSBs due to their high ionic conductivity and robust chemical stability. The ionic conductivity of LLZO oxide SEs has been further enhanced through doping with elements like Al, Ta, and Ga, as well as nanosizing, which also improves their stability at high temperatures and voltages[93, 94]. Despite these advancements, the fabrication of oxide-based SE membranes with high bulk density and low interfacial impedance remains a significant technical challenge. Current research primarily focuses on aligning bipolar electrodes with oxide-based SEs to address these issues. To mitigate interfacial incompatibility and reduce high interfacial impedance, various interfacial engineering techniques, such as interfacial coatings and modifiers, have been explored to enhance the stability between electrodes and electrolytes[95-97]. In addition, the rational design of nanostructured electrodes and porous electrolyte layers has improved ion conduction paths and reduced interfacial impedance, thereby significantly

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boosting the electrochemical performance of ASSBs. A notable achievement in this field is the successful preparation of a bipolar ASSB with an LMO cathode/LLZO/LTO anode configuration, as depicted in Figure 5b. In this configuration, the oxide-based SE interface was wetted with an ionic gel, resulting in excellent electrochemical performance and power density. This configuration meets the engineering requirements for cold-start conditions at 0℃, −10℃, and −18℃. Furthermore, the system demonstrated remarkable stability under extreme conditions, such as folding, cutting, and combustion, confirming the enhanced tolerance of bipolar ASSBs with the introduction of an ionic gel[98].

To enhance the electrochemical performance of ASSBs, the development and structural optimization of high-capacity electrodes are also considered. Notably, high-voltage Nichel-rich[99-101] and Li-rich Mn-based layered oxide cathodes[102], along with Si-based anode[103], have been extensively utilized in oxide-based bipolar ASSBs to significantly boost energy density. Concurrently, improvements in cycle stability and rate performance have been achieved by optimizing the interface structure and material formulation of both the electrode and electrolyte. The introduction of conductive networks within electrode materials is also investigated to enhance electronic and ionic conduction efficiencies, thereby further improving the electrochemical performance[104-106]. Despite the advantages of oxide-based SEs in bipolar ASSBs over other SEs, their commercial application is hindered by challenges such as densification, large-scale preparation of oxide-based SE sheets, interfacial impedance regulation, material coating, and the complexity of the production process[107-111]. The exploration of low-cost, high-performance oxide SEs, and optimizing cell structure design and fabrication processes are also considered to facilitate the large-scale application of oxide-based bipolar ASSBs.

3.1.3. Sulfide-Based SEs

Sulfide-based SEs are regarded as one of the most promising candidates for ASSBs, particularly due to the high ionic conductivity, which can reach up to 10^{-3} S cm^{-1}, comparable to that of liquid electrolytes[45, 112-114]. This characteristic is especially advantageous in the application of bipolar ASSBs. Unlike oxide-based SEs, sulfide SEs

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afford superior solid-state interfacial contacts, which significantly reduces interfacial impedance and facilitates rapid Li^+ migration between electrodes and SEs, thereby enhancing current conduction efficiency. Despite these advantages, interfacial instability remains a significant challenge for sulfide-based ASSBs, particularly in bipolar configurations where the extensive interface contact area between the electrode and SEs increases the likelihood of side reactions[79, 115]. To address this issue, an interfacial buffer modification layer, such as Li_3PO_4[116, 117] and $LiNbO_3$[118, 119], is applied to the electrode surface to improve interfacial stability, and effectively inhibit side reactions. Additionally, the application of a protective coating on both cathode and anode materials can prevent the growth of lithium dendrites and the oxidative decomposition of electrodes. Furthermore, the electrochemical stability of sulfide SEs can be enhanced by doping with inactive elements, such as introducing a small amount of selenium (Se)[89, 120].

In the encapsulation of bipolar ASSBs, achieving tighter hermeticity is crucial to prevent sulfide SEs from reacting with water and oxygen in the air, which adversely degrade their electrochemical performance. Zhu and co-workers have made significant advancements in the development of bipolar ASSBs by employing sulfide SEs[121, 122]. A key factor in their success is the application of an ethyl cellulose binder, which exhibits amphipathic properties, high binding capability, excellent compatibility with sulfide SEs, and remarkable thermal stability. These properties facilitate the creation of freestanding, robust, and thickness-controllable cathodes, SEs, and anode layers through the process of vacuum filtration. Consequently, the doubly stacked bipolar ASSBs achieve a high voltage of 8.2 V and a cell-level energy density of 204 Wh kg^{-1}, which exceeds the 189 Wh kg^{-1} energy density of the mono cell configuration. The design of bipolar ASSBs based on sulfide SEs is anticipated to play a significant role in wearable application, EVs, energy storage systems, and aerospace. Its high energy density, enhanced safety, and lightweight nature position it as a promising candidate for next-generation battery technology.

3.1.4. Composite SEs

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The design of composite SEs in bipolar ASSBs strategically integrates the benefits of composite SEs with a bipolar configuration to enhance electrochemical performance, structural stability, and energy density. Composite SEs are typically achieved by combining inorganic SEs, such as sulfides and oxides with organic polymers like PEO and PVDF, or other functional macromolecules[88, 110, 123-127]. This combination results in a composite electrolyte that exhibits both high ionic conductivity and robust mechanical properties. The enhancement of ionic conductivity and interfacial contact stability addresses the limitations of one single electrolyte and mitigates the high contact impedance issue at the solid-solid interfaces. The design of composite SEs leverages the high conductivity of inorganic SEs alongside the flexibility of organic electrolytes[128-131]. For instance, dispersing nanomaterials, such as nano-sulfide SEs like Li_3PS_4 or $Li_7P_3S_{11}$, into the polymer matrix, can create a continuous ion-conducting network[114, 132, 133]. This network significantly improves ionic conduction channels, thereby enhancing overall electrical conductivity and interfacial properties, with typical conductivities reaching 10^{-4} to 10^{-3} S cm^{-1}. As illustrated in Figure 5d, a 3-stack bipolar cell utilizing a flexible CSE-7 sheet (containing 7 wt% SCN) was designed and fabricated. This bipolar cell features a three-layer stacking structure of unit cells, comprising Cu/Li metal//CSE-7//NCM 424/Al connected in series. Upon assembly, the open circuit voltage (OCV) of the pouch-type bipolar cell was 9.67 V, indicating normal operation without short circuiting. The cell underwent 50 charging and discharging cycles, maintaining a capacity retention rate of 94%, and a coulombic efficiency of 100% after three cycles[134].

In the development of composite SEs for bipolar ASSBs, a stacked structure is employed, where multiple cell units are connected in series to enhance voltage output. The flexibility and malleability of composite SEs make them particularly suitable for integration with a bipolar design, resulting in a more compact and efficient cell structure[135-137]. Specifically, this structural compatibility not only improves energy density by allowing for an increased thickness of the cathode composite but also simplifies the manufacturing process due to the reduced requirements for airtightness

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and stability in encapsulation. Moreover, the flexibility of composite SEs compensates for interfacial Li^+ transport losses caused by bipolar stacking. Despite these advantages, the SEs compositing process requires further optimization to improve cost-efficiency in mass production. Enhancing production feasibility while reducing costs is essential for practical manufacture. Additionally, the compatibility and cycle life of these advanced energy materials warrant further investigation to ensure their long-term viability from the material standpoint.

3.2. Cell assembling technology

The stacking technology for ASSBs significantly enhances energy density and safety by optimizing the alignment of electrode and electrolyte layers (**Figure 6a**). By employing an advanced lamination process, this technology effectively reduces interfacial impedance and enhances ionic conduction efficiency. Consequently, these improvements render better electrochemical performance and increased cyclic stability. Given these advantages, stacking technology holds considerable potential for widespread application in EVs and renewable energy storage systems.

3.2.1. Cell stacking technology

The stacking technology plays a crucial role in determining both electrochemical performance and manufacturing efficiency of bipolar ASSBs. Several common stacking technologies are employed, each characterized by distinct features:

1) Monolithic laminated stacking: This traditional and widely used method involves sequentially stacking cathode materials, SEs, anode materials, which are then laminated to form a multilayer battery[138] (Figure 6b). The primary advantages of this approach include its simple structure, mature manufacturing process, and suitability for small-scale and experimental cell production[139, 140]. However, when scaled up for industrial production, challenges such as interlayer alignment accuracy and stacking uniformity can arise.

2) Continuous coil stacking: This technology creates a spiral structure by continuously coiling cathode, SE, and anode materials. This is widely used in cylindrical or pouch cell design. The benefits of coil stacking include enabling high energy density designs and a highly automated manufacturing process. Nonetheless,

this technique encounters issues related to stress concentration and fracture of the SEs during the coiling process for bipolar ASSBs.

3) Multi-layer co-press stacking: This method involves simultaneously pressing multiple layers of cathode, SE, and anode materials to from an integrated cell structure. It significantly reduces internal resistance by minimizing the interfaces between layers, thereby enhancing overall energy density and electrical conductivity. Multi-layer co-press stacking is suitable for large-scale production, improving the production efficiency, but it demands high standards for manufacturing equipment and process[141, 142].

4) Modular stacking: This approach involves modularizing multiple individually manufactured cells and assembling complete battery modules by connecting these modules in series or parallel. The primary advantage is its high flexibility, facilitating large-scale production and maintenance. Modularization allows for adjustable capacity and voltage according to application requirements. However, it may increase package volume and affect overall energy density[143, 144].

5) Laser-assisted laminated stacking: As an emerging technology, this method achieves precise alignment and connection of electrode and electrolyte layers through laser cutting and welding techniques. It enhances stacking precision, reduces parasitic resistance, and minimizes heat loss within the cells, making it suitable for manufacturing high-performance batteries. While laser-assisted stacking offers high automation and fast manufacturing speed, it requires significant equipment investment and process control[145, 146].

In conclusion, the performance of bipolar ASSBs can be impacted by the stacking techniques. Monolithic laminated stacking optimized for research & development and low-volume prototyping due to process simplicity, yet alignment accuracy limitations constrain industrial scalability. Multi-layer co-press stacking minimizes interfacial resistance, enhancing conductivity for large-scale production but demands advanced equipment. Increasing volume by Modular stacking, which offers flexibility and serviceability for grid storage/aviation. Precision and low heat loss for high-performance batteries can be provided by Laser-assisted laminated stacking, but require significant investment. The selection of an appropriate stacking method depends on specific application scenarios, manufacturing conditions, and performance requirements of bipolar ASSBs.

3.2.2. Coherent solution strategy

Ensuring the consistency of bipolar ASSBs from cell to module design is essential for optimizing performance, long-term cycling stability, and safety. The foundation lies in the quality and uniformity of the electrode materials. Selecting high-purity and uniformly distributed electrodes, SEs and coating processes is critical as the homogeneity and stability of these materials can minimize performance variations within individual cells. This, in turn enhances the overall performance consistency of the module[147]. Furthermore, optimizing material formulations to ensure uniform mixing and coating during the manufacturing process can further improve the consistency of bipolar ASSBs. The precision of the manufacturing process is also pivotal for cell consistency[148] with key processes including the thickness of the electrode material coatings, the lamination of SEs, and the specific lamination process for bipolar ASSBs[149].

Advanced manufacturing technologies, such as laser cutting and precision coating, are instrumental in ensuring uniformity in cell size, shape and active material distribution, thereby enhancing the consistency of the battery module[150]. Following cell production, rigorous capacity grading and consistency screening are essential steps to ensure module uniformity. Conducting multiple cycling charging and discharging tests, allows for the selection of cells with similar capacities, internal resistance and other key parameters for module assembly[35]. The data-driven optimization enables the module's overall performance and prevents excessive cell mismatch during use. Additionally, thermal management design within the module significantly impacts cell consistency. The incorporation of uniform heat distribution is essential to prevent localized overheating in bipolar ASSBs[151]. Improved heat dissipation material and structural design, enable cells to maintain consistent operating temperatures, minimizing performance variations and enhancing module consistency. Beyond physical manufacturing controls, real-time monitoring and analysis of production data are vital

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for promptly identifying and addressing consistency issues during manufacturing. The integration of intelligent manufacturing technologies and the optimization of process parameters through big data analysis can continuously improve cell consistency[152-154]. This proactive approach allows for the prediction and adjustment of potential consistency problems in the manufacturing process, thereby ensuring the reliability and efficiency of bipolar ASSBs. These ultidimensional approaches spanning materials, manufacturing, screening, thermal design, and data analytics significantly enhance the consistency of bipolar ASSBs from cell to module, ensuring their reliability and safety in application, which is critical for commercial deployment.

3.2.3. Cell to module design

In the design process of bipolar ASSBs, the capacity division strategy from the cell to the module is crucial for ensuring consistency and stability. Initially, after cell completion, a preliminary capacity division test is conducted. This test primarily aims to stabilize electrochemical performance through extended cycling, thereby conditioning the electrode materials and SEs within the cells[155]. During this process, key parameters such as capacity and internal resistance are meticulously recorded for subsequent screening. Following the initial capacity division, cells are categorized based on their capacity and internal resistance, grouping those with similar performance characteristics[156]. This categorization is particularly significant for bipolar ASSBs due to the unique current pathways in the series and parallel connection of different cells within a module, which directly determines the module's overall performance and lifespan. Poor consistency among cells can induce localized over-charging or over-discharging, thereby compromising the safety and efficiency of the module. To further ensure cell stability, a secondary capacity division test is typically conducted before module assembly. This step screens out cells that exhibit degraded performance after the initial division, verifying their reliability under long-term cycle testing and enhancing module consistency through extended cycling[157]. Once the module assembly is complete, an overall capacity balancing test is performed. This test assesses the consistency of the cells within the module and the module's overall performance, including temperature management, internal resistance, and total capacity[111, 158, 159].

Through this module-level test, any abnormal behavior of individual cells can be identified for replacement, ensuring the final product's high performance and safety. The detailed of all test data are recorded, which are integrated into the production process and material selection. The production process and material formulation can be optimized by analyzing these data to further enhance the consistency and reliability of bipolar ASSBs.

To meet the demand for high voltage and capacity, multiple bipolar ASSBs can be connected in series or parallel to form a battery pack. The design of such a battery pack requires careful consideration of modular design, current collector optimization, and safety protection. Modular design is crucial to facilitate the expansion and maintenance; therefore, bipolar ASSBs typically adopt a modular approach, allowing each module to operate independently or allow easy replacement. Besides structural design, optimizing the conductive components is also vital. The current collector, which serves as the conductive layer connecting the cell or modules, can be designed to ensure low impedance and high conductivity while minimizing weight[160-162]. This often involves the applications of surface-modified Cu-Al composites[52, 64]. Although ASSBs are inherently safer due to the absence of flammable liquid electrolytes, safety considerations (such as short-circuit and thermal runaway protection) remain essential in module design[163], as illustrated in **Figure 7**, which exhibits the thermal propagation pathways. An advanced battery management system can further enhance safety by monitoring temperature, voltage and current in real time to prevent over charging and discharging. The energy density can be further enhanced by optimizing the mass of the modules. Through the capacitance division strategy, the performance of bipolar ASSBs can be optimized from individual cells to entire modules. This optimization ensures high efficiency, safety and long-term cycling stability in practical applications.

4. The bipolar ASSBs

4.1. Materials innovation

Advanced energy materials are pivotal in determining the performance of bipolar ASSBs, necessitating further research to prioritize the exploration of superior SEs and electrodes. A primary focus of this research will be the discovery of SE materials with

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enhanced ionic conductivity and broader electrochemical windows. Composite SEs, which integrate inorganic materials with polymers, are specifically engineered to improve mechanical stability while maintaining excellent electrochemical performance. Moreover, optimizing the stability of inorganic SEs such as sulfides, halides, and oxides, is crucial to prevent decomposition in air or side reactions with electrode materials.

In terms of electrodes, future advancement aims to increase energy density by introducing novel high-capacity options, including Li-rich Mn-based cathode materials[164-166], Ni-rich cathode materials[167, 168], and Si-based or even lithium-metal anode[169-171]. Addressing the interfacial stability between electrode materials and SEs is a crucial challenge that demands immediate attention, particularly in terms of mitigating interfacial reactions and the growth of impedance. Furthermore, the microstructure and mechanical properties of SE separators play a crucial role in influencing both the cost and performance of bipolar ASSBs. To optimize these systems, it is essential to enhance the strength of thin SEs and thick cathodes while ensuring that Li^+ transport remains unimpeded.

4.2. Preparation process optimization

To advance the commercialization of bipolar ASSBs necessitates significant improvements in the preparation process are essential. Currently, the production of ASSBs is hindered by high costs and complex procedures. Consequently, the development of low-cost and high-efficiency preparation technologies, that emphasize simplified fabrication processes and mass production techniques should be strongly considered[172]. A promising development in this area is the emerging “dry battery electrode” technology, which offers significantly advantages over traditional wet coating methods as shown in **Figure 8**. These advantages include environmental friendliness, reduced costs, enhanced compatibility, higher production efficiency, and improved electrode performance. To further optimize the densification of SEs and the electrode-SE interface, techniques such as hot pressing and extrusion can be employed. These methods facilitate smoother ion transport pathways within bipolar ASSBs. Additionally, ensuring homogeneity and interfacial stability between the various material layers is crucial for future process improvements. Strategies such as integrated cathodes/SEs/anodes preparation, novel coating technologies, and multilayer co-extrusion are anticipated to enhance the precision of multilayer structure fabrication, ultimately optimizing the overall electrochemical performance. Furthermore, maintaining the optimal stacking pressure of bipolar ASSBs is necessary to ensure performance without compromising cost and energy density.

4.3. Device design optimization

Bipolar ASSBs demonstrate considerable potential for enhancing energy and power density in device design, however, they face several design challenges. A critical area of future research will be interface engineering and structural optimization. Structural optimization requires careful consideration of factors such as the number of layers, thickness, and material selection in bipolar ASSB design, which are crucial for further efficiency improvements. The incorporation of a conductive coating or functional layer between electrodes and SEs can effectively reduce interfacial impedance and improve cycling performance. Furthermore, thermal management is an independent challenge that must be addressed, as uneven heat dissipation can adversely affect cycling stability. Therefore, optimizing heat dissipation is vital to prevent localized overheating within the module, which is critical for commercial deployment.

Bipolar ASSBs hold significant promise for future development, particularly through advancements in materials innovation, process enhancement, and device design optimization. As depicted in **Figure 9**, these batteries are expected to become a crucial element of future energy storage technologies. Their potential applications span a wide range, including wearable devices, EVs, and energy storage systems[173-175]. Consequently, bipolar ASSBs are anticipated to play a pivotal role in these diverse fields, underscoring their importance in the evolution of energy storage solutions.

4.4. AI-driven innovation for bipolar ASSBs

Artificial Intelligence (AI) has emerged as a transformative force in advancing Bipolar ASSBs, overcoming the inefficiencies of traditional trial-and-error methodologies[176-178]. By integrating machine learning (ML) and deep learning (DL) algorithms, AI can accelerate the discovery of high-performance solid electrolytes through rapid analysis of multidimensional materials data, and enable precise predictions of critical properties such as ionic conductivity, electrochemical stability windows, and interfacial compatibility. Generative adversarial networks (GANs) and reinforcement learning further transcend conventional design paradigms by proposing metastable material phases and artificial crystal structures absent in natural or synthetic databases, effectively expanding the materials genome[179-181]. AI-powered multiscale simulations can elucidate degradation mechanisms under operational extremes, including thermal gradients and mechanical stress, while Monte Carlo-based interface engineering optimizes solid electrolyte interphases (SEI) with enhanced Li^+ transference and reduced interfacial resistance. By synergizing cross-domain knowledge from density functional theory, phase-field modeling, and ab initio molecular dynamics, AI can deliver solutions that simultaneously satisfy ionic transport, thermodynamic stability, and processability requirements. By driving data-driven material discovery and optimization, AI not only accelerates the research and development of bipolar ASSBs but also reduces costs, offering robust technical support for the commercialization of next-generation high-performance batteries[182]. In summary, as a cornerstone of ASSBs commercialization, AI established an innovation pipeline that combines computational precision with experimental validation, positioning itself as an indispensable tool for next-generation energy storage systems.

5. Conclusions and perspective

Bipolar ASSBs integrate the advantages of bipolar electrode architecture and solid-state chemistry, emerging as a transformative energy storage solution with broad applicability. For example, the safety can be enhanced by eliminating metallic interconnects between cells, thereby preventing cross-unit short circuits caused by dendrite penetration or mechanical failure. Furthermore, the efficient vertical (through-plane) current conduction is enabled along the shortest path, minimizing internal resistance and polarization losses. And the uniform current distribution can be promoted by the planar design, mitigating detrimental edge effects and improving electrochemical homogeneity during long-term cycling. By utilizing stacked bipolar layers that minimize inter-cell connections, this technology enhances energy density while reducing manufacturing complexity and material costs. The implementation of

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SEs significantly improves safety by suppressing lithium dendrite formation and thermal runaway risks, enabling deployment in safety-critical sectors such as EVs and aerospace systems. These safety and performance characteristics also position bipolar ASSBs as viable solutions for grid-scale energy storage and next-generation wearable technology.

Despite these advantages, three primary challenges impede their commercialization:

1) Limited ionic conductivity and unstable electrode-SEs interface at high-voltages.

2) The complex manufacturing processes requiring specialized equipment.

3) The material compatibility constraints between components. Addressing these limitations requires coordinated advancements in material engineering and production technology.

Recent progress in sulfide-based SEs with ionic conductivities exceeding 10 mS cm^{-1}, coupled with roll-to-roll manufacturing innovations, suggests pathways for overcoming these barriers. The technology's evolution will likely be driven by three parallel developments:

1) Synthesis of novel SE materials with enhanced electrochemical stability.

2) Optimization of bipolar electrode architectures through computational modeling.

3) Implementation of standardized manufacturing protocols for large-scale production.

As shown in **Figure 10**, prototype bipolar ASSBs already demonstrate 400 Wh kg^{-1} energy density with 80% capacity retention after 1000 cycles, meeting baseline requirements for automotive applications. In the transportation sector, this technology could enable EVs with 800 km ranges while reducing battery pack weight by 40% compared to conventional lithium-ion systems. For grid storage applications, the inherent safety of bipolar ASSBs permits higher energy density configurations without compromising system reliability. The eventual market adoption will depend on achieving cost parity with liquid electrolyte batteries, currently projected for 2028-2030 based on learning curve analyses. As research transitions from laboratory-scale to pilot production, bipolar ASSBs are emerging as a cornerstone technology for sustainable energy systems. Their unique combination of safety, energy density, and manufacturing scalability aligns with global decarbonization imperatives, particularly in transportation electrification and renewable energy integration. This technological trajectory positions bipolar ASSBs as a critical enabler for achieving net-zero emissions targets while meeting growing energy storage demands.

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Author contributions

Q. Z., W-J. K, C-Z. Z., and J-Q. H. conceived the project. W-J. K., C-Z. Z., L. S., J-L. L., Y-C. L., X-Y. H., P. X., J-K. H., J-Q. H., and Q. Z. wrote and edited the manuscript. All authors commented on the manuscript.

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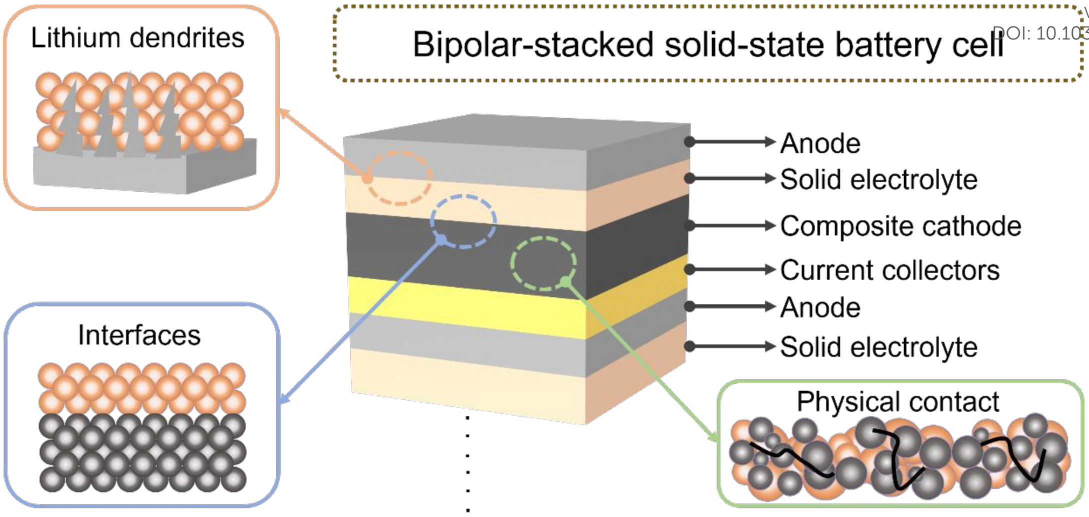

Figure 1. The schematic representation of a bipolar ASSBs. Insets are magnified sections that highlight the three main challenges facing solid-state batteries with metal anodes: inhomogeneous metal deposition, formation of blocking interface and contact loss on electrochemical cycling.

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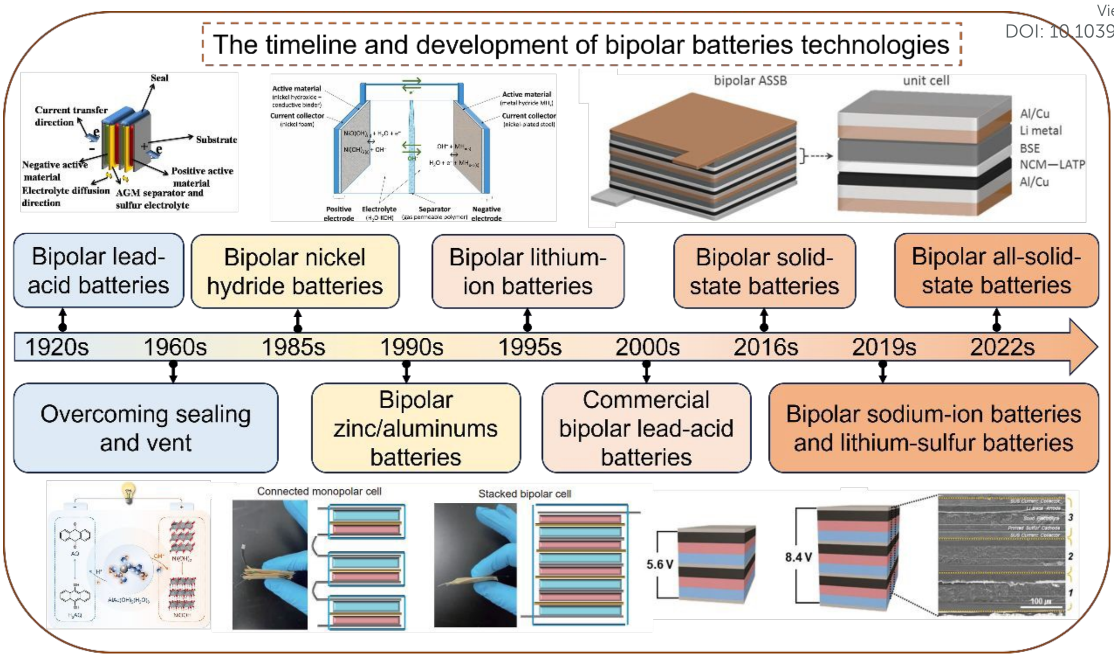

Figure 2. The timeline and development of emerging bipolar batteries technologies[52-57]. (1, Copyright 2017, Wiley-VCH; 2, Copyright 2022, Elsevier; 3, Copyright 2018, Wiley-VCH; 4, Copyright 2024 American Chemical Society; 5, Copyright 2022, Springer; 6, Copyright 2019, Wiley-VCH).

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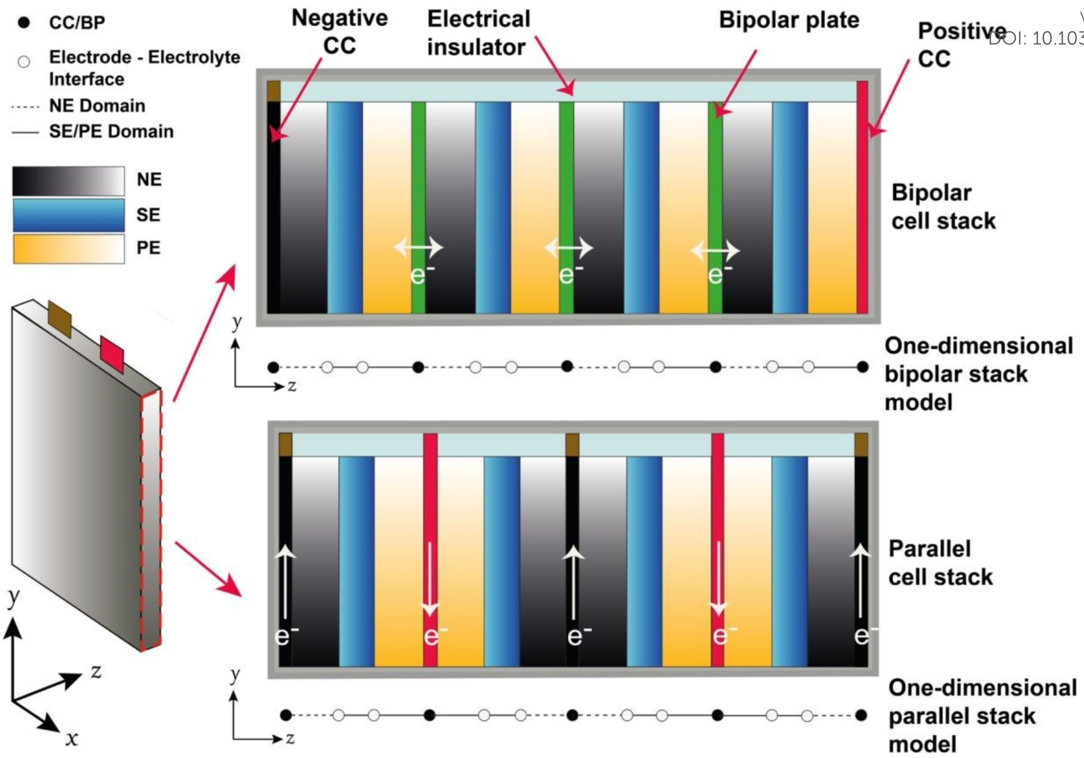

Figure 3. Configurations of the bipolar (top) and parallel stack (bottom) inside the pouch. In a bipolar stack, the electrical current flows from one unit cell to the adjacent unit cell through the BP, whereas in a parallel stack, the electrical current flows in-plane along the CC to the external tabs[59, 60]. Copyright 2020, The Electrochemical Society.

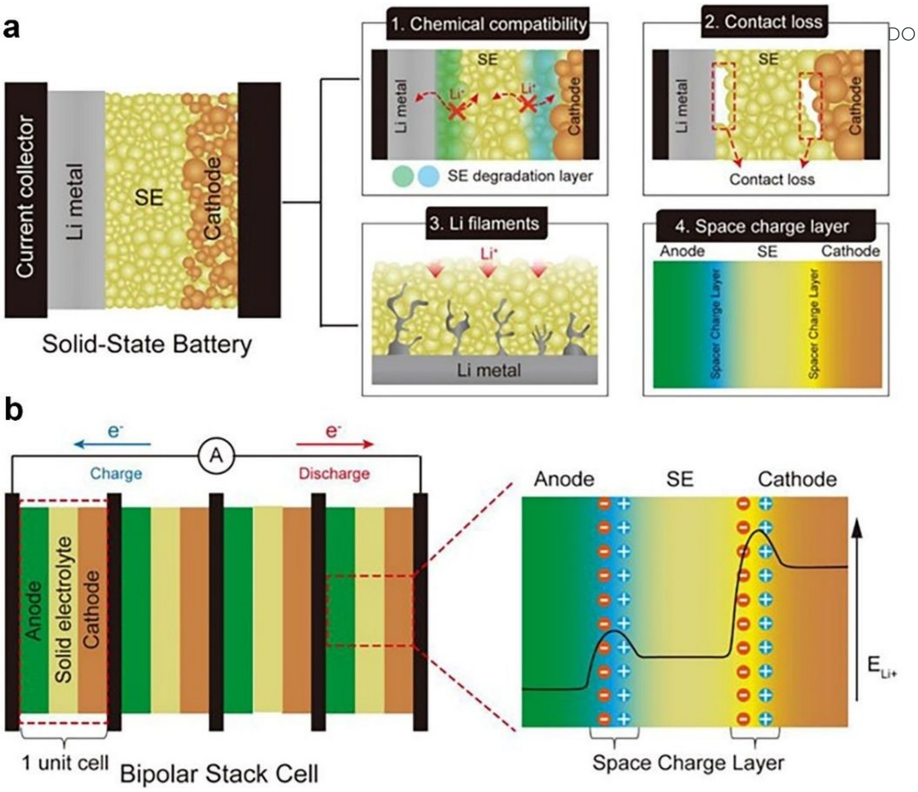

Figure 4. The schematic representation of solid-state battery and bipolar stack cell: (a) various issues between electrode/electrolyte interface, (b) space charge layers in a bipolar stack cell (black line indicates the unequal Li chemical potential of the electrode/electrolyte interface of the cell during charge)[73]. Copyright 2022, Springer.

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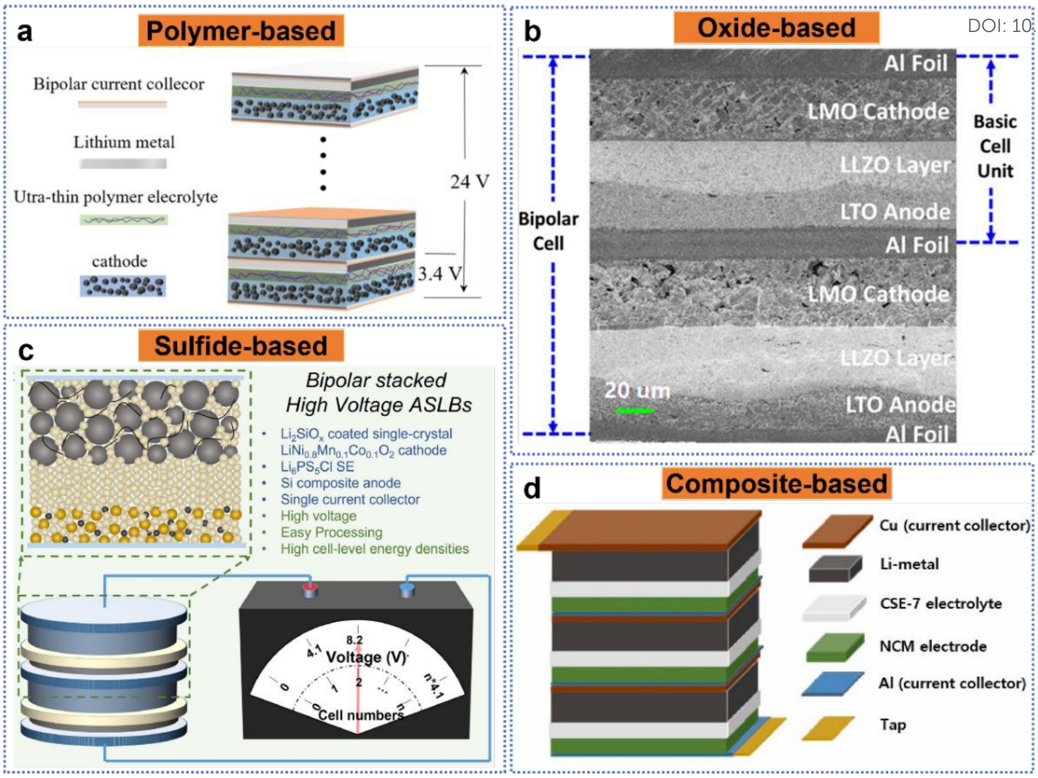

Figure 5. Application of bipolar ASSBs with different SEs: (a) demonstration of a 7-layer 24 V bipolar cell using an ultra-thin crosslinked carbonate ester electrolyte[92], Copyright 2022, The Electrochemical Society. (b) cross-sectional SEM image of the pouch-type LMO/LLZO-LTO bipolar solid-state battery interfacial wetted by the ionogel[98], Copyright 2022, American Chemical Society. (c) merits of the high voltage bipolar-stacked ASLBs and composition distribution in each layer[121], Copyright 2022, Elsevier. (d) schematic illustration: design and evaluation of 3-stack bipolar cell[134]. Copyright 2016, Elsevier.

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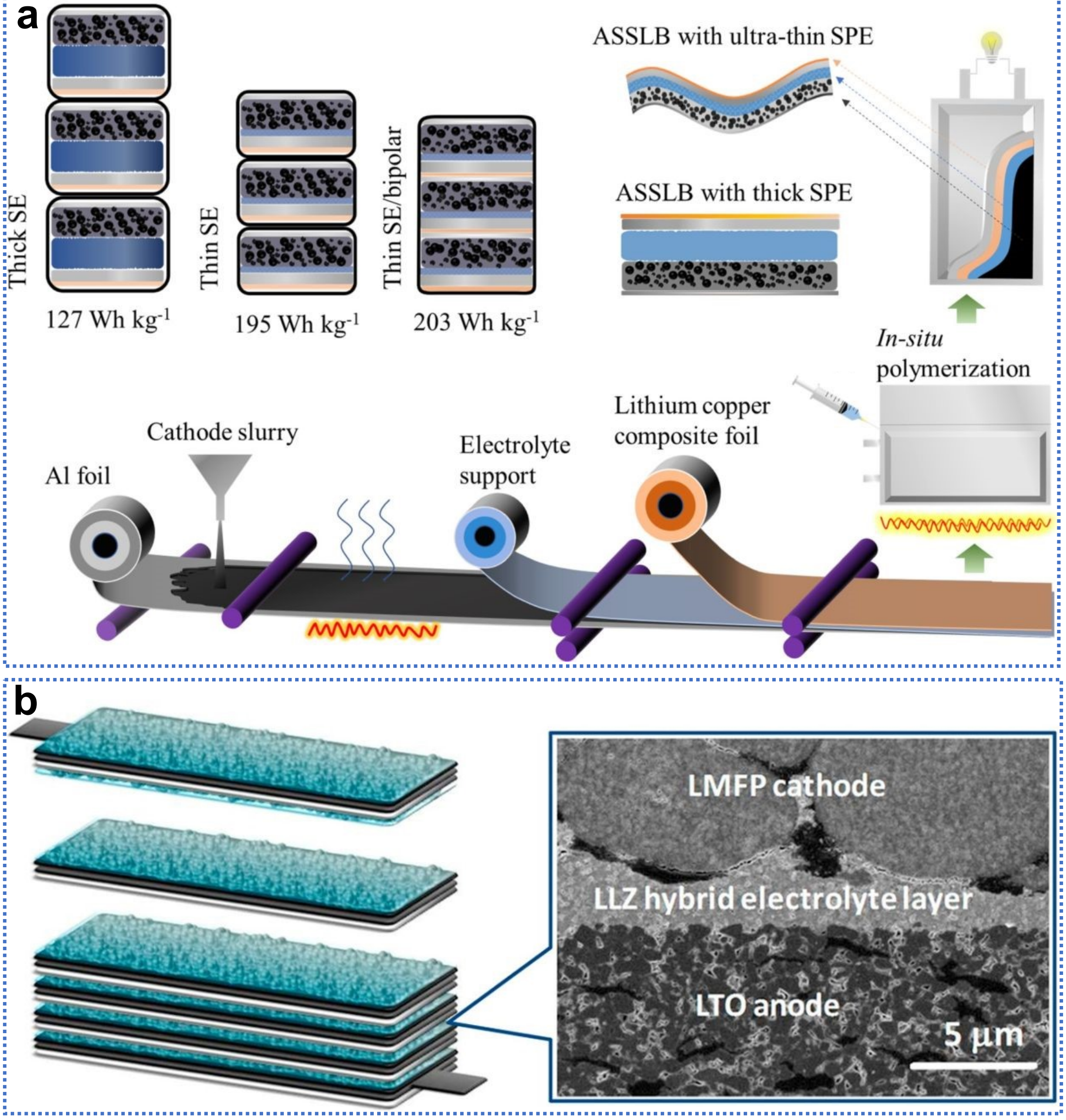

Figure 6. Schematics of the preparation process for large scale production of ASSLBs (a) the comparison and preparation of the cell-level energy density of ASSLBs with thick electrolytes, ultra-thin electrolytes, and bipolar setups[92], Copyright 2022, The Electrochemical Society. (b) schematic process for preparation of bipolar battery and the photograph of pouch-type bipolar battery (SEM image of the cross-section of the fabricated bipolar battery using LMFP cathode)[138]. Copyright 2016, Elsevier.

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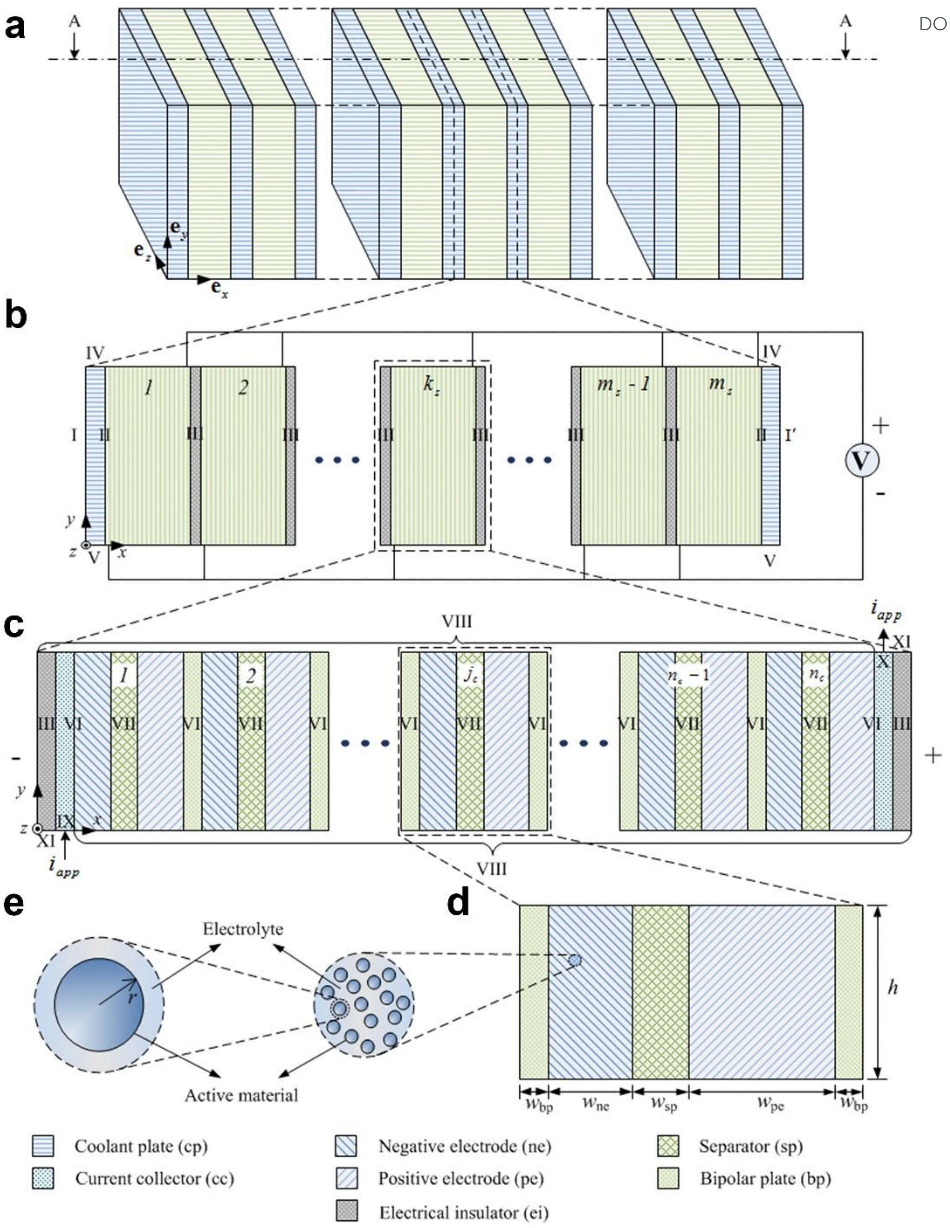

Figure 7. Schematic of the lithium-ion battery (a) a pack, (b) cross-section of a representative bipolar pack (named repeating module) with the roman numerals indicating the interfaces and boundaries of stacks and coolant plates, (c) cross-section of a stack with the roman numerals indicating the interfaces and boundaries of cells and various functional layers, (d) cross-section of a single cell, (e) agglomerate structure of active material in the electrodes[163]. Copyright 2015, Elsevier.

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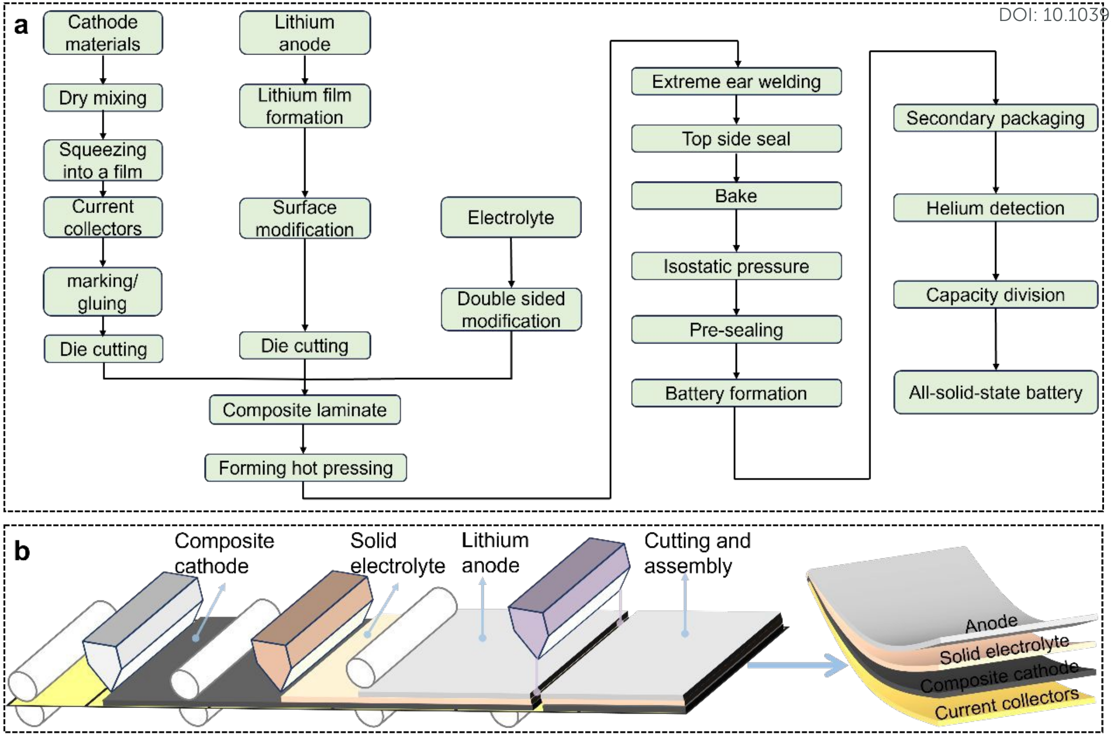

Figure 8. Preparation of bipolar ASSBs using dry electrode method: (a) Flow charts and (b) schematic diagram for preparing bipolar ASSBs by dry battery electrode technology

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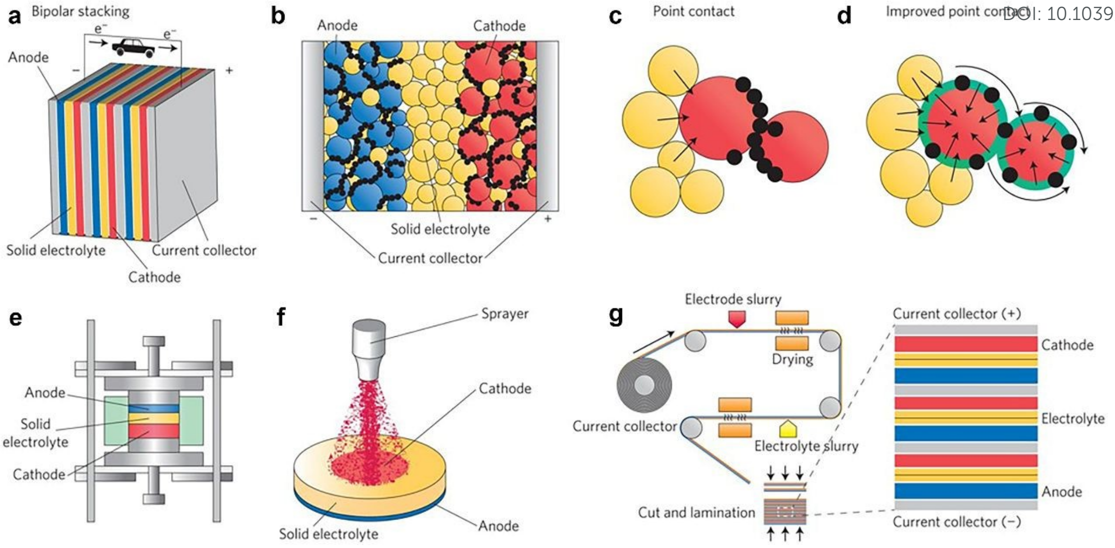

Figure 9. Configuration of solid-state batteries and fabrication processes for performance improvement, (a) in a bipolar configuration, the electrode materials are coated on the two sides of the current collector, reducing the weight and volume of the battery package, (b) a typical solid-state battery consists of a cathode, an anode and a solid electrolyte, (c) a zoomed-in image of the contact between the electrolyte(yellow spheres), which is limited in a typical solid-state battery, the black spheres represent carbon black and the black arrows indicate the Li^+ migration pathway, (d) by putting a mixed conducting network coating (green) on the surface of electrode materials, the electrolyte-electrode contact is enhanced, (e) a powered pressing process for fabricating solid-state batteries, (f) a pasting route analogous to that used in solid oxide fuel cell fabrication, (g) a wet coating process for fabricating solid-state process. The obtained electrodes are cut and laminated together to make the solid-state batteries[173]. Copyright 2016, Nature group.

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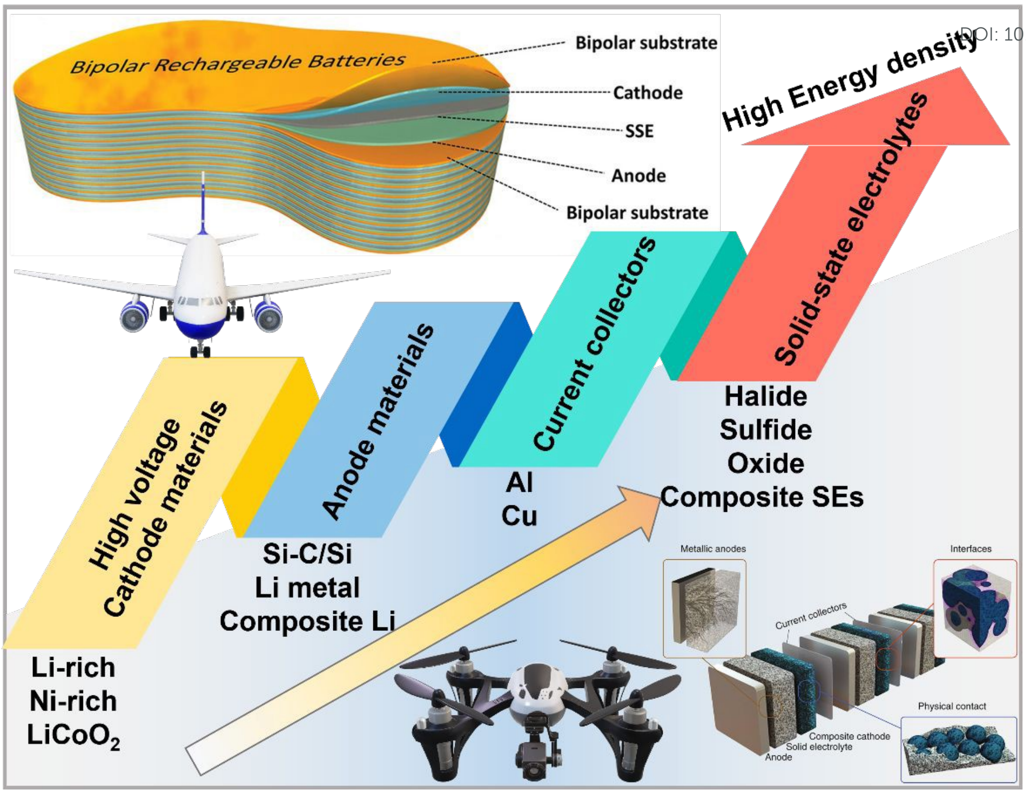

Figure 10. Prospects of Bipolar ASSBs with higher energy density[23, 58]. Copyright 2016, Nature group. Copyright 2020, Wiley-VCH.

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Data Availability Statement

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.