# All-Solid-State Batteries with Anodeless Electrodes: Research Trend and Future Perspective

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**All-solid-state batteries (ASSBs) are promising "beyond lithium-ion batteries" candidates owing to their high energy density and safety. Anodeless electrodes are critical components for enabling these attributes, offering a fundamentally distinct mechanism compared to conventional anode systems. This unique mechanism of anodeless electrodes has garnered significant scientific interest and has prompted extensive research. Based on recent advancements, this perspective provides comprehensive insights into anodeless electrode materials in ASSBs and outlines prospective research directions to address the remaining challenges and further ASSB performance optimization.**

## 1. Introduction

The electric vehicle (EV) industry, which began experiencing significant growth in the 2010s, has been rapidly expanding and is driven by the eco-friendly policies adopted by various countries. Despite the growing demand for sustainable power sources in EVs, lithium-ion batteries (LIBs) remain dominant. Despite the current market appeal of EVs, both consumers and developers are seeking advancements in driving range, safety, and charging times. To address these challenges, all-solid-state batteries (ASSBs) have emerged as a promising solution. ASSBs offer high energy densities and enhanced safety by substituting flammable organic electrolytes with solid electrolytes composed of polymers, oxides, or sulfides.[1] Research is actively ongoing in areas such as solid electrolyte materials, cathodes, anodes, and battery architectures to fully realize the potential of ASSBs.

Recently, the exploration of new approaches for anodes has intensified within the ASSB research field. For LIBs, graphite is the preferred anode material owing to its low reaction potential and high reversibility. However, its limited capacity constrains further enhancements in energy density, which represents a significant limitation.[2,3] As graphite is increasingly recognized as insufficient to exploit the high-energy-density advantages of ASSBs, alternatives such as lithium metal or alloy anodes have been examined.[4] However, these materials are also considered inadequate owing to mechanical and chemical challenges, failing to fully address the fundamental issues of both LIBs and ASSBs.

Accordingly, the concept of "anodeless" electrodes has emerged. For anodeless electrodes, lithium metal is deposited directly onto the current collector without a specific active material.[5–7] This concept is increasingly regarded as a promising anode application in ASSBs, and various relevant studies have been conducted. The anodeless design concept was initially explored in LIBs through the tuning of electrolytes and current collectors, which revealed stability issues owing to dendrite formation, low Coulombic efficiency, and electrolyte decomposition. One of the prominent reasons for this severe degradation stems from the structural features of anodeless electrodes, in which the mechanically vulnerable nature of LIBs fails to prevent the parasitic deposition of Li metal on the current collector. Recent advancements in ASSB technology have highlighted its ability to address these issues by leveraging structural robustness.[8] Notably, the integration of anodeless ASSBs (AL-ASSBs), which eliminate the need for a pre-formed anode, holds significant potential for reducing both battery complexity and production costs, thereby significantly stabilizing their electrochemical performance and enhancing their mechanical properties, owing to the inherent

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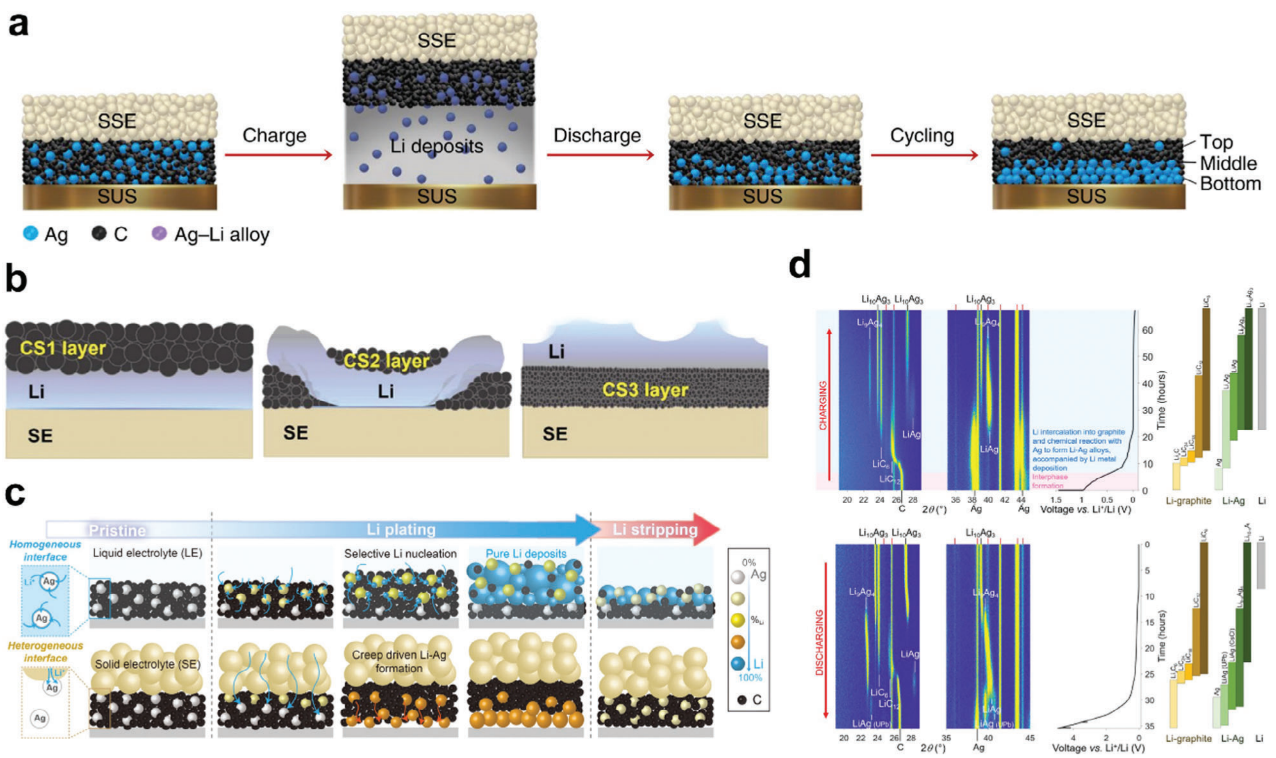

**Figure 1.** Comprehensive analysis of the lithium behavior and interfacial dynamics in AL-ASSBs. a) Illustration of the deposition and stripping behavior of lithium onto the current collector surface via the interlayer in the Ag/C system of AL-ASSBs.[9] Copyright 2020, Springer. b) Effect of nanoparticle size within the interlayer on the preferential sites for lithium deposition.[10] Copyright 2022, Royal Society of Chemistry. c) Comparison of the lithium-diffusion behavior influenced by the interlayer in LIBs and ASSBs, highlighting key differences in structural and interfacial dynamics.[11] Copyright 2024, Royal Society of Chemistry. d) Phase-transition behavior associated with structural changes in the Ag/C interlayer during the charge-discharge process of AL-ASSBs.[12] Copyright 2023, Cell Press.

stability of solid electrolytes. These attributes render battery systems safer and more durable than their commercial counterparts.

This perspective comprehensively reviews the latest research trends and advancements in anodeless materials and processes specifically for ASSBs. We categorize the characteristics of anodeless materials, review the history and operating mechanisms of each material, and discuss potential issues that may arise during commercialization. Particularly, we highlight the significance of Ag-based anodeless electrodes in addressing dendrite formation and enhancing the cycle life, drawing on recent achievements in interlayer-engineering strategies. Furthermore, we explore alternative metal systems (e.g., Mg and Zn) that offer cost-effective and scalable avenues for next-generation anodeless electrode designs. We also underscore the importance of fabrication innovations for achieving uniform large-area electrodes and accelerating commercialization. Based on this analysis, we propose a detailed discussion on the major challenges faced by researchers in this field along with prospective directions for future work. Thus, this perspective aims to contribute to the advancement of anodeless research and ultimate commercialization.

## 2. Development of Ag-Based Anodeless Electrodes for ASSBs

Silver has traditionally been used to enhance anode performance in LIBs; however, its role in ASSBs has become increasingly prominent with the study of silver/carbon composite-based anodeless systems (**Figure** 1a).[9] This represents a significant innovation that addresses major ASSB challenges, such as achieving high anode reversibility for long-term stability and introducing a stacked pouch-cell design that supports practical cyclability and energy density under low-pressure conditions (2 MPa). This system has endured over 1000 cycles, demonstrating substantial durability, achieving an energy density exceeding 900 Wh $L^{-1}$ and a Coulombic efficiency of 99.8%, thereby proving the feasibility of ASSBs for commercial applications. Previously, the absence of a physical barrier between the current collector and electrolyte made controlling the lithium-deposition morphology and efficiency challenging, leading to random formation and adverse reactions that reduced battery life. An Ag/C composite layer containing lithiophilic Ag and carbon black was used to achieve uniform lithium deposition and stripping and prevent Li-metal propagation through the electrolyte. Carbon black acts as the dominant material in the interlayer, effectively isolating lithium metal from the solid electrolyte and homogenizing the current density upon Li deposition. Advanced imaging results have confirmed the formation of a stable Ag-Li alloy, which enhanced dendrite suppression, the battery cycle life, and stability, thereby improving the prospects for AL-ASSB commercialization.

Research on the operating principles of Ag/C systems involves advanced analytical techniques and computational chemistry. These principles encompass the mechanism by which the

Ag/C composite layer facilitates lithium deposition on the anode current collector during lithiation and de-lithiation. The basic prerequisites for the preferential deposition site of lithium rely on the chemo-mechanical properties of the Ag/C interlayers. Park et al.[10] compared the deposition behavior of lithium metal in AL-ASSBs employing carbon materials of various sizes, as illustrated in Figure 1b. Their findings revealed that in protective layers, including the Ag/C, the particle size is key for determining the diffusion path of lithium ions within the interlayer as a mixed ionic-electronic conductor (MIEC), in which each nanoparticle interface functions as a driving force to facilitate coble creep in an anodeless system. In addition to pore size, when the adhesion between the solid electrolyte and Ag/C layer exceeds that of the current collector, lithium migrates toward the collector. Volumetric changes in Ag facilitate lithium-ion diffusion through the interlayer, which selectively controls the deposition sites and suppresses dendrite growth. Under these prerequisites, a reversible lithium current collector can be organized into three phases: initial charging, lithiation (electrodeposition), and de-lithiation (electro stripping).

### 2.1. Initial Charging

During the initial charging stage, lithium consumption occurs due to an irreversible reaction with carbon black, inducing additional lithium growth on the carbon surface that has reacted with lithium. At this stage, lithium consumption for MIEC formation appears as the irreversible capacity of the anodeless electrode. Through this interaction, the lithium-based MIEC formed on the carbon black surface facilitates lithium-ion transport and supports stable lithium deposition during subsequent lithium addition.

### 2.2. Lithiation

During lithiation, the alloying reaction between Ag and Li occurs at a defined potential when the pores of the Ag/C layer are fully densified by the lithium. Lee et al.[11] emphasized that ASSB systems form an MIEC structure within Ag/C composites during charging, distinguishing them from liquid systems (Figure 1c). They noted that Ag-Li alloys in ASSBs create a uniform phase gradient, enhancing lithium-metal diffusion and resulting in a more uniform lithium distribution that significantly improves battery performance.

### 2.3. De-Lithiation

In the de-lithiation phase, lithium migrates from the Li-Ag alloy, redistributing Ag back to the current collector and beneath the Ag/C buffer layers. Here, Ag acts as a seed for the lithiation/de-lithiation of lithium in subsequent cycles, supporting consistent lithium deposition and migration. Spencer–Jolly et al.[12] used in situ X-ray diffraction analyses to show that the Ag-Li alloy formed during these cycles plays a vital role in promoting uniform lithium deposition, evenly distributing the current density, and preventing dendrite formation (Figure 1d). Furthermore, they highlighted that Ag does not fully revert to metallic Ag post-discharge, indicating that the Ag-Li alloy maintains a stable current density across all voltage ranges, even after the cycle, enhancing the electrode stability.

Overall, these principles highlight the crucial function of Ag in enhancing the lifetime of ASSBs, leading to extensive research on Ag-based anodeless systems following the introduction of this novel anode concept.

## 3. Approaches for Foundational Experiments in Ag Optimization

Ag/C-based anodeless electrodes represent a significant advancement in the chemical suppression of side reactions. However, they face several challenges from an engineering and commercialization perspective.

Scaling up Ag/C-based anodeless electrodes poses significant dispersion and homogeneity challenges owing to the difference in the physical and chemical characteristics of the Ag and carbon black comprising the interlayer. The disparity in the chemical moieties and densities between metal and carbon nanoparticles complicates their dispersion, necessitating solutions to overcome this hurdle. Accordingly, Jung et al.[13] introduced a method for integrating silver directly onto the carbon surface, enhancing particle dispersion and preventing the aggregation of silver nanoparticles. In this study, Ag ions were first dissolved in a slurry solvent and then reduced to form nanoparticles on the carbon material during the coating and drying processes, as shown in **Figure 2**a. The resultant Ag/C composite particles exhibited superior dispersion compared to the simple blending of each nanoparticle and presented smaller particle sizes, significantly preventing a concentrated current density owing to Ag aggregation. Consequently, reduced nucleation overpotentials and enhanced AL-ASSB lifetimes were demonstrated. Notably, this composite contributed to the long cycle life of high-energy-density ASSBs, maintaining 91% of their capacity even after 500 cycles.

Recent studies have demonstrated that electrodes can be effectively fabricated using spraying techniques. The application of Ag/C and electrolyte layers via spraying has enabled the efficient formation of uniform large-area electrodes. Layer-by-layer spray coating produces high-density, uniform Ag/C layers that are ideal for ASSBs, enhancing their cycle life via overpotential reduction and dendrite formation suppression (Figure 2b).[14] Furthermore, according to Metzler et al.,[15] enhancing the dispersion of Ag by spray coating reduces the overpotential and suppresses dendrite formation within the Ag/C bilayer structure (Figure 2c). Notably, a structured bilayer localizes Ag closer to the surface of the current collector, increasing the uniformity of the lithium plating. This configuration minimizes the irreversible capacity loss of lithium metal and significantly enhances the cycle life and performance of the battery.

## 4. Beyond the Ag/C System: Potential of AL-ASSBs Through Alternative Materials

Although Ag/C systems are widely recognized for their excellent performance, the nature of Ag as a noble metal and its high cost have led many researchers to seek alternative materials. Ag, as

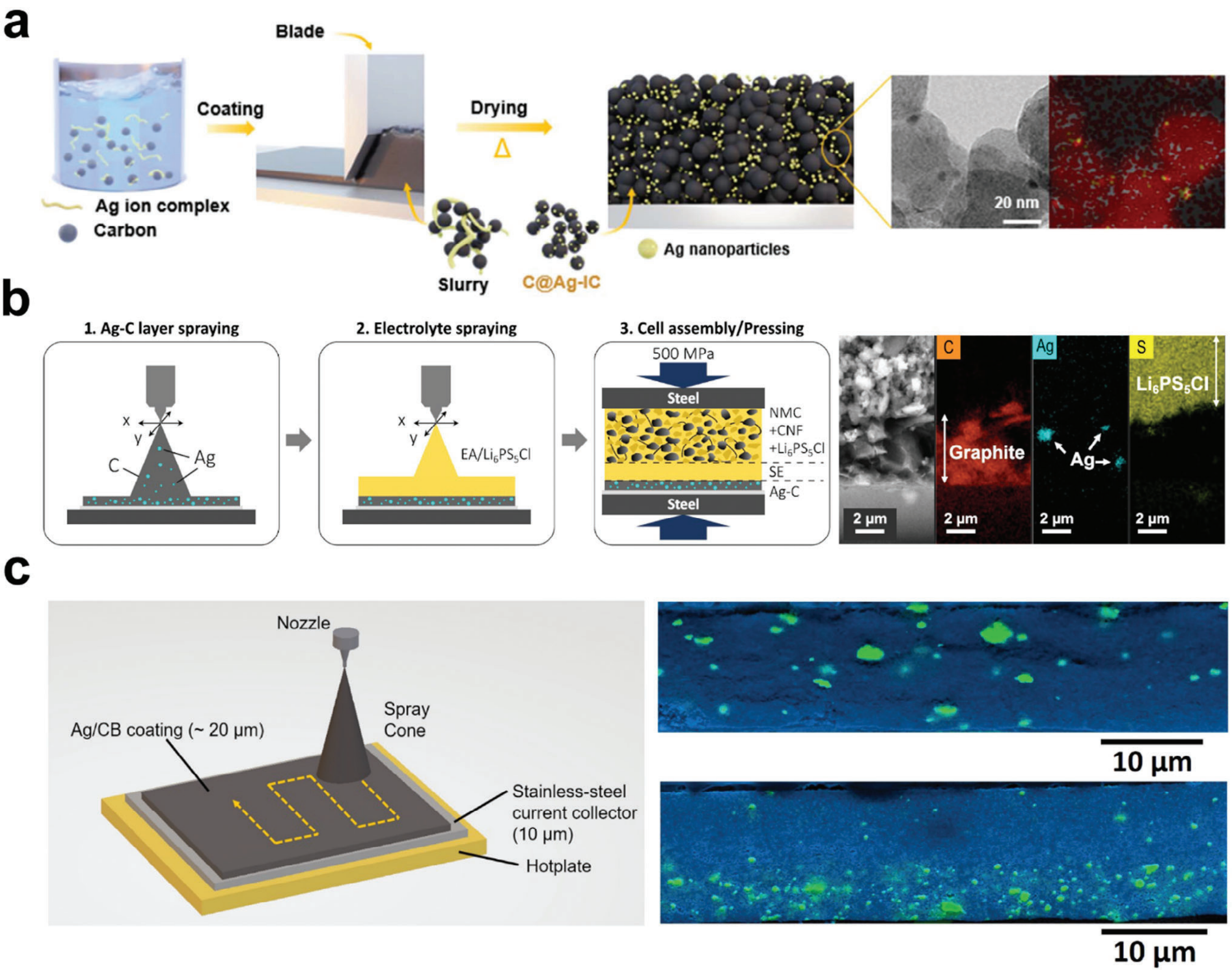

**Figure 2.** Advancements in the fabrication and characterization of AL-ASSBs. a) On-site synthesis method for the formation of Ag on carbon surfaces during electrode fabrication, ensuring enhanced dispersion within the composite material.[13] Copyright 2023, Royal Society of Chemistry. b) Feasibility of large-scale AL-ASSB manufacturing through a layer-by-layer spray-coating technique, highlighting its potential for scalable production.[14] Copyright 2024, Cell Press. c) Comparison of the dispersion characteristics of Ag/C layers fabricated using a pristine mixture and spray-coating method.[15] Copyright 2024, Cambridge University Press.

a raw material, is priced at \$31.1/oz (1.1 M \$/MT, based on data for November 2024). This price compared to other anodeless candidates such as Zn (3221 \$/MT) or Mg (2452 \$/MT) serves as the basis for this research strategy. When identifying substitutes for Ag, their performance and similarities in operational mechanisms must be considered. Ye et al.[16] investigated the formation of Li alloys and observed that the type of metal used to form intermetallic compounds and solid solutions alters the chemical potential within grains, thereby enhancing lithium-ion diffusion throughout the grains in solid solutions with active phase transition (**Figure 3a**). Notably, Ag and Li formed a solid solution across all compositions, leading to lithium deposition in alloy form rather than in metallic form, thereby significantly improving the reversibility and cyclic stability of the battery. They also proposed metals such as zinc, magnesium, gold, and aluminum as potential substitutes for Ag in Li-rich areas. Among these, Li-Ag alloys were found to have low energy barriers for phase transitions and minimal structural changes, maintaining high stability and reversibility during the lithium alloying and dealloying processes. These solid-solution alloys demonstrated exceptional performance, retaining 87% of their initial capacity after 250 cycles and exhibiting high Coulombic efficiency, thereby proving their effectiveness in extending the cycle life and dendrite formation suppression.

The wide range of solid-solution phases formed during lithiation, coupled with the resulting interfacial stabilization, has inspired innovative research into the Ag substitution with Mg. Jun et al.[17] used the properties of Mg particles to propose an anodeless system for ASSBs. Compared with Ag, Mg particles exhibited slower diffusion rates within the grains, leading to the formation of a lithium-concentration gradient (LCG) that ensures uniform lithium distribution around the particles. This arrangement allowed the Mg particles to "breathe,", i.e., expand and contract during lithium deposition and removal, facilitating

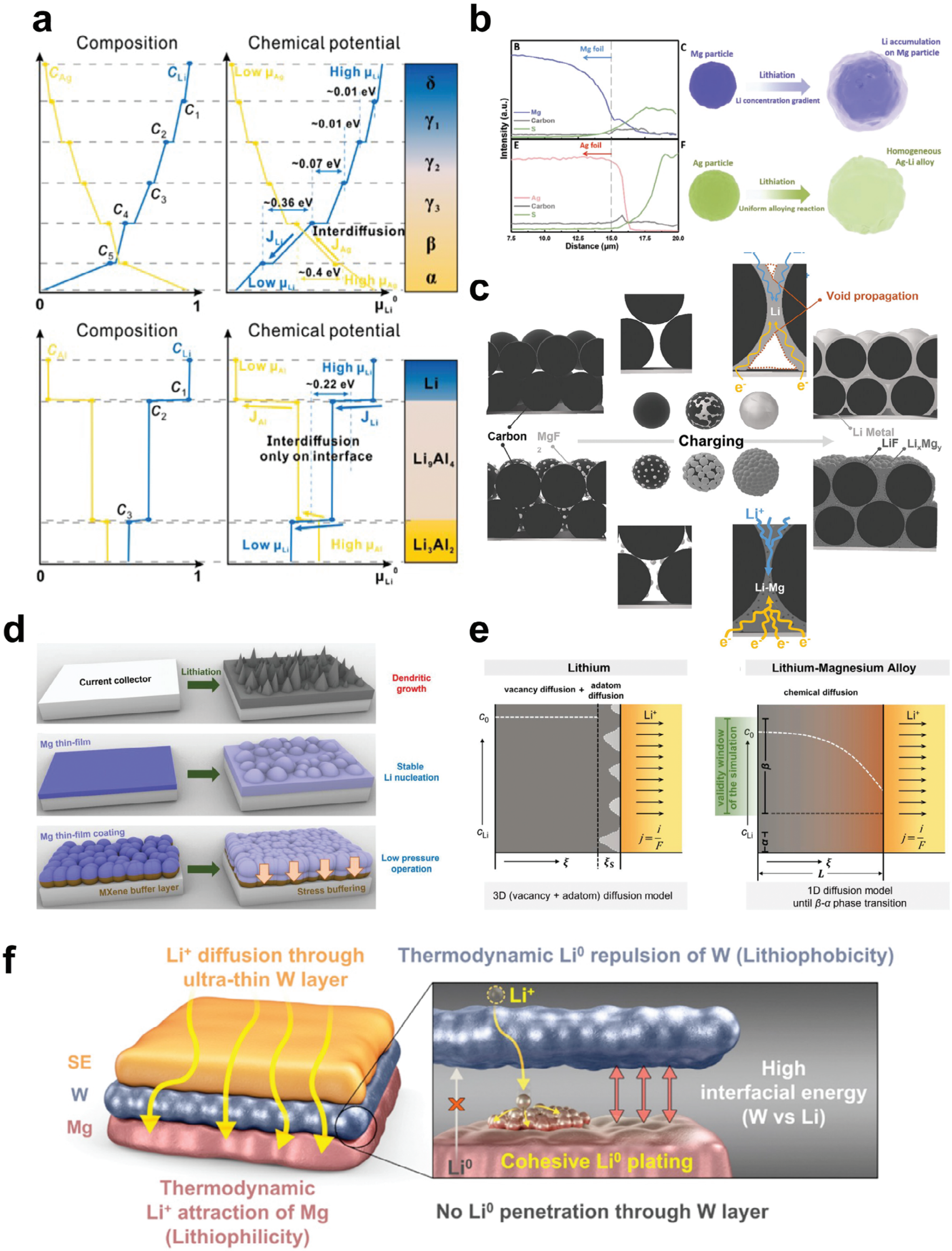

**Figure 3.** Illustration of the chemical, structural, and interfacial behaviors in advanced AL-ASSBs. a) Comparison of the chemical-potential trends between Ag-Li solid solutions exhibiting multiphase transitions and Al-Li intermetallic alloys with binary transitions.[16] Copyright 2023, American Chemical Society. b) Formation of LCGs driven by alloy kinetics in Ag and Mg, which form solid solutions.[17] Copyright 2024, Wiley-VCH. c) In situ conversion of $MgF_2$@C into Mg-Li alloy, facilitating lithium-ion diffusion and contributing to enhanced electrochemical performance.[18] Copyright 2024, Wiley-VCH. d) Low-pressure operation of AL-ASSBs utilizing MXene-Mg composites, which stabilize interfaces under operational stress.[19] Copyright 2023, Wiley-VCH. e) Computational analysis showcasing the ability of Mg-Li alloy to suppress void formation during lithium deposition due to its minimal morphological changes, ensuring interfacial stability.[20] Copyright 2019, Wiley-VCH. f) Summary of the effectiveness of a bilayer structure with contrasting lithiophilicity, enabling controlled lithium-ion diffusion pathways and suppressing dendrite formation.[25] Copyright 2024, Royal Society of Chemistry.

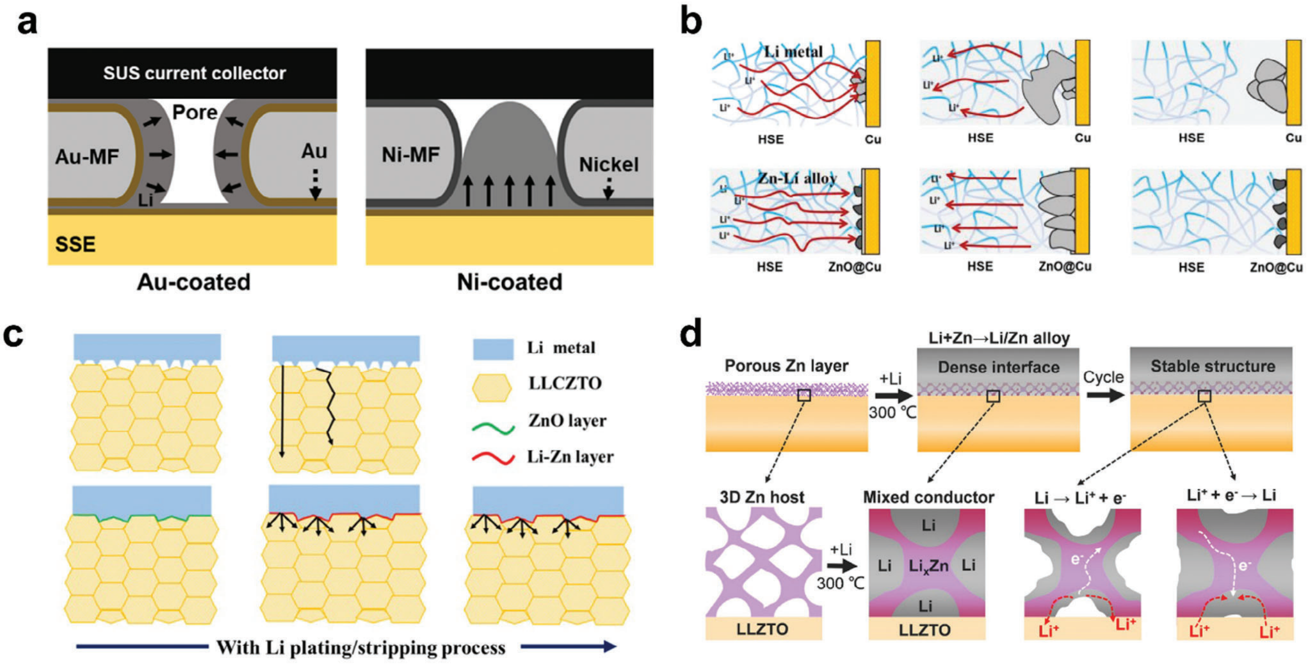

**Figure 4.** Design and analysis of lithium-deposition behavior and interfacial stability beyond the Ag/C system. a) Comparison of lithium-deposition behaviors on nanopore surfaces with varying metal species, demonstrating differences in lithium-diffusion rates and their impact on deposition patterns.[21] Copyright 2020, American Chemical Society. b) The role of thin-film ZnO-coated current collectors in providing nucleation sites, resulting in uniform lithium-metal deposition.[22] Copyright 2020, American Chemical Society. c) Dendrite-suppression effect and contact enhancement achieved through the in-situ decomposition of ZnO on solid electrolytes during lithium deposition.[23] Copyright 2020, American Chemical Society. d) Application of a stable 3D porous Zn matrix on the anode surface, offering improved structural stability and lithium-diffusion pathways.[24] Copyright 2021, Elsevier.

gradual and uniform lithium diffusion within the particles, as shown in Figure 3b. This unique LCG-based diffusion mechanism formed a solid solution around the Mg particles, enhancing the cycle life beyond that achieved with Ag nanoparticles alone. Electrochemical tests have shown that this system maintains over 99.9% Coulombic efficiency through 1000 cycles at 30 °C. Additionally, incorporating the sacrificial anode material $Li_3N$ in a cell configuration with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathodes enabled the retention of more than 80% of the capacity after 500 cycles, significantly contributing to the stable performance of the ASSBs.

Building upon this, Jeon et al.[18] integrated nanosized $MgF_2$ dots onto carbon surfaces and proposed a highly stable carbon substrate suitable for AL-ASSB design. Through sonochemical synthesis, $MgF_2$ was uniformly formed on the carbon substrate, transforming into Mg-Li alloy and LiF during cell operation (Figure 3c). This conversion suppressed dendritic growth and reduced the overpotential of lithium deposition, facilitating the formation of a uniform, dense lithium layer that promoted stable electrochemical reactions. Furthermore, the $MgF_2$/C electrode exhibited lower overpotentials and superior cyclic stability compared with conventional carbon electrodes, enhancing uniform lithium-ion diffusion and minimizing electrolyte-interface reactions. The experimental results demonstrated that ASSBs with $MgF_2$/C electrodes maintained 81.4% of their capacity after 200 cycles, showing a stable, uniform dispersion of the alloy metals in air without aggregation. This structure effectively prevented electrolyte interface degradation by inhibiting the growth of the lithium metal layer, thereby significantly enhancing the lifespan and performance of the batteries. Finally, they presented new possibilities for the design of interface-engineered anodeless electrodes for the practical application of ASSBs and suggested that the $MgF_2$/C composite is an effective anode material with high energy density and stability.

Oh et al.[19] demonstrated the potential of AL-ASSBs at low pressures (2 MPa) and ambient temperatures using MXene structures embedded with Mg as buffer layers to enhance their low-pressure application. In their study, the Mg layers improved the reversibility of lithium plating and stripping via low-energy alloying reactions with lithium. The MXene layers, characterized by their high ductility, effectively maintained stable electrolyte–electrode interfaces, even under low pressure (Figure 3d). Their experimental results showed that cells incorporating Mg-MXene bilayer electrodes retained 82.4% of their initial capacity under these conditions and exhibited a long cycle life. Further analyses, including electron microscopy and electrochemical-impedance spectroscopy, confirmed that the MXene layers mitigated mechanical stress during lithium deposition, thereby preventing an increase in interfacial resistance. Krauskopf et al.[20] conducted a theoretical analysis of the deposition and stripping rates of Li metal anodes and Mg-Li alloy anodes at the $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (LLZO) solid–electrolyte interface. They used an alloying-based computational chemistry model to show that Li metal requires a diffusion model that incorporates 3D structures, whereas Mg-Li alloys primarily involve lattice diffusion with minimal impact from structural changes (Figure 3e). The Mg-Li alloy also demonstrated excellent diffusion characteristics at low temperatures and pressures while maintaining stability at the LLZO

**Table 1.** Comparisons of electrochemical performances based on AL-ASSBs with Ag/C chemistry.

| Anodeless architecture | | | Electrolyte separator | Cathode | Capacity | Applied current | Temperature | Cycle life [capacity retention] | Cell type | Pressure [assembly] | Pressure (cycling) | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Anodeless Materials | Process | Contents | | | | | | | | | | |
| Ag/C composite | Pre-mixing | Ag:C = 25:75 | Li6PS5Cl | $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ | 6.8 mAh $cm^{-2}$ | 3.4 mA $cm^{-2}$ | 60 °C | 1000 cycles (99.8%) | Pouch cell | 490 MPa | 2 MPa | [7] |
| Ag/C composite | Ion complex | Ag:C = 5:95 | Li6PS5Cl | $LiNi_{0.7}Co_{0.1}Mn_{0.2}O_2$ | 6.2 mAh $cm^{-2}$ | 3.1 mA $cm^{-2}$ | 60 °C | 500 cycles (91.6%) | Pouch cell | 490 MPa | 4 MPa | [11] |
| Ag/C composite | Spray coating | Ag:C = 25:75 | Li6PS5Cl | $LiNi_{0.83}Mn_{0.06}Co_{0.11}O_2$ | 1.25 mAh $cm^{-2}$ | 0.75 mA $cm^{-2}$ | 80 °C | 800 cycles (63%) | Pellet cell | 500 MPa | 2.5 MPa | [12] |
| Ag/C composite | Spray coating (bilayer) | Ag:C = 25:75 | Li6PS5Cl | $LiNi_{0.83}Mn_{0.06}Co_{0.11}O_2$ | ≈2.4 mAh $cm^{-2}$ | 1 mA $cm^{-2}$ | 60 °C | 100 cycles (47%) | Pellet cell | 500 MPa | 4 MPa | [13] |

**Table 2.** Comparisons of electrochemical performance based on AL-ASSBs with Ag alternatives.

| Anodeless architecture | Electrolyte separator | Cathode | Capacity | Applied current | Temperature | Cycle life [capacity retention] | Cell typte | Pressure [assembly] | Pressure [cycling] | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|
| Mg powder | $Li_6PS_5Cl_{0.5}Br_{0.5}$ | $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ | 2.92 mAh $cm^{-2}$ | 0.5 mA $cm^{-2}$ | 30 °C | 500 cycles (80%) | Pellet cell | 380 MPa | 30 MPa | [15] |
| $MgF_2$@C composite | $Li_6PS_5Cl$ | $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ | 7 mAh $cm^{-2}$ | 3.5 mA $cm^{-2}$ | 60 °C | 300 cycles (61.32%) | Pouch cell | 490 MPa | 4 MPa | [16] |
| Mxene/Mg | $Li_6PS_5Cl$ | $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ | 2.64 mAh $cm^{-2}$ | 0.264 mA $cm^{-2}$ | 25 °C | 30 cycles (≈62%) | Pellet cell | 380 MPa | 2 MPa | [17] |
| W/Mg bilayer | $Li_6PS_5Cl$ | $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ | 3.7 mAh $cm^{-2}$ | 1.11 mA $cm^{-2}$ | 25 °C | 300 cycles (71.9%) | Pouch cell | 450 Mpa | 2 MPa | [19] |
| Au-coated membrane | $Li_3PS_4$ | Li metal (counter) | 0.1 mAh $cm^{-2}$ | 0.1 mA $cm^{-2}$ | RT | N/A | Coin cell | 405 Mpa | N/A | [20] |
| Prelithiated ZnO@Cu | PEO-based composite | $LiFePO_4$ | 0.5 mAh $cm^{-2}$ | 0.05 mA $cm^{-2}$ | 25 °C | 45 cycles (≈63%) | N/A | N/A | N/A | [21] |
| Sputtered ZnO | $Li_{6.55}La_{2.95}Ca_{0.05}Zr_{1.5}Ta_{0.5}O_{12}$ | Li metal (counter) | 0.2 mAh $cm^{-2}$ | 0.2 mA $cm^{-2}$ | 50 °C | N/A | Coin cell | N/A | N/A | [22] |
| Porous Zn | $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ | $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ | 0.75 mAh $cm^{-2}$ | 0.075 mA $cm^{-2}$ | 25 °C | 170 cycles (93%) | Coin cell | 50 Mpa | 30 MPa | [23] |

interface. Notably, Li-metal anode diffusion was significantly affected by temperature and pressure, with an increased diffusion efficiency observed under higher conditions.

Oh et al.[19] designed a bilayer structure composed of lithiophilic Mg and lithiophobic W nanoparticles for AL-ASSBs. They applied a Li-W/Mg bilayer nanostructure as a protective layer in an ASSB to suppress lithium-dendrite growth (Figure 3f). The lithiophobic W layer effectively inhibited dendrite formation across the protective layer, whereas the lithiophilic Mg layer enhanced the selectivity of the lithium deposition sites and homogenized the current density, enabling stable lithium plating and stripping. This bilayer structure demonstrated stable performance even under low stack pressure.

Studies employing other metal species such as Au and Zn have also been reported. Shinzo et al.[21] investigated the lithium deposition and stripping within a 3D framework using porous current collectors designed to suppress dendrite growth. They used a gold-coated 3D structure, in which Au formed an Au-Li alloy, effectively facilitating the homogeneous diffusion of lithium throughout the porous framework, as shown in **Figure** 4a. This system was proven effective for achieving uniform lithium growth, even for small pore sizes or high aperture ratios. Moreover, the framework acted as an MIEC, enabling stable lithium deposition/dissolution with a high Coulombic efficiency. By contrast, frameworks with only electronic conductivity tended to localize lithium deposition near the electrolyte surface, hindering uniform growth. Liu et al.[22] proposed using a ZnO thin-film coating to address the insufficient nucleation of seeds during lithium-metal deposition in an anodeless structure. During operation, the ZnO layer decomposed on the current collector, forming a Zn-Li alloy that served as an effective nucleation seed for lithium (Figure 4b). This alloy enhanced the LLZO wettability, thereby reducing the interfacial resistance and maintaining stability even at high current densities. Consequently, the alloy framework demonstrated excellent performance, exhibiting a high critical current density and low interfacial resistance. Zhang et al.[23] explored the impact of sputtering a ZnO layer onto a garnet-type solid electrolyte to suppress dendrite formation during lithium-metal deposition (Figure 4c). During the lithiation process, ZnO decomposed to form a Zn-Li alloy and $Li_2O$, promoting a uniform current-density distribution and reducing the interfacial resistance, thereby improving contact with the solid electrolyte. ASSBs using a pre-lithiated ZnO@Cu electrode exhibited high Coulombic efficiency and stable cycling. Zn-Li alloy formation aided the uniform growth of lithium metal and minimized contact losses at the interface. Wan et al.[24] employed a garnet-based solid electrolyte coated with a 3D porous Zn layer via sputtering (Figure 4d). This 3D structure enhanced the uniformity of lithium-ion conduction and increased conductivity, enabling consistent lithium deposition across the interface. This approach led to improved electrochemical performance under a high current density and demonstrated excellent characteristics for lithium stripping and plating.

## 5. Outlook

This perspective highlights significant advancements in the development of AL-ASSBs, emphasizing recent progress and emerging challenges. Although Ag/C-based AL-ASSBs exhibit remarkable potential and have been the focus of substantial research efforts aimed at practical applications, further research is required to address some crucial aspects that remain unresolved. Based on the findings of previous studies, this study aimed to provide insights into and propose strategic directions for the continued advancement of AL-ASSBs. We summarized the electrochemical performance based on various anodeless electrode materials covered in this perspective (**Tables** 1 and 2).

The introduction of Ag/C has emerged as one of the most successful approaches for hosting lithium in ASSBs. This system, which is distinguished by its excellent reversibility and low operational pressure, relies on nanoparticles composed of carbon and silver. However, the chemo-mechanical imbalance between carbon and silver presents significant challenges, particularly in achieving interlayer uniformity. Previous research indicates that this dispersion can lead to localized current densities, which ultimately compromise capacity retention during repeated cycles. The use of metal-supported composites or reduced metal nanoparticles during electrode fabrication has been identified as an effective strategy to address this issue. In terms of commercialization, not only the development of materials but also the ability to manufacture them in large quantities and fabricate large-area electrodes is crucial. Accordingly, the study of composites opens the possibility of securing large quantities of materials with uniform properties. Regarding large-area electrode production, advanced techniques, such as spray coating, offer significant potential for enhancing electrode formability and structural uniformity.

The exploration of alternatives to silver is essential, not only to address the high cost of silver but also to develop novel systems capable of achieving superior performance. A direct strategy for identifying silver substitutes involves the use of materials with similar operational mechanisms. Candidates capable of forming solid solutions with lithium metals, such as Mg, have shown considerable promise. Mg can be directly applied or incorporated as halide-based nanoparticles to enhance battery functionality. In addition to Mg, other materials such as Zn are viable options, offering opportunities to investigate diverse morphologies and innovative approaches for advanced battery applications.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

all-solid-state battery, anode-free, anodeless, magnesium alloy, silver/carbon

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