From Lithium-Metal toward Anode-Free Solid-State Batteries: Current Developments, Issues, and Challenges

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The development of rechargeable batteries with high-energy density is critical for future decarbonization of transportation. Anode-free Li-ion batteries, using a bare current collector at the anode side without any excess of Li, provide the highest volumetric energy density (>1500 Wh L⁻¹) among all possible cell configurations. Furthermore, elimination of the anode material coating reduces material consumption and greatly simplifies cell production, which in turn lowers costs. Although significant progress has been made recently by the application of modified current collectors, optimized cycling parameters and improved liquid electrolytes, insufficient efficiencies, and dendritic growth during lithium plating lead to poor cycle life of typically less than 100 cycles as well as safety issues. Alternatively, very recent studies have demonstrated anode-free solid-state batteries that combine the benefits of high energy anode-free cell configuration and solid-state systems with high safety, exceeding 1000 cycles. This review provides an overview of recent developments toward anode-free solid-state batteries and highlights the current issues and challenges in this nascent field. It is concluded that, although major challenges remain at the present, the lessons learned in the fields of liquid electrolytes and solid-state lithium metal batteries can accelerate the development of anode-free solid-state batteries of practical relevance.

1. Introduction

Rechargeable batteries with high energy density, long cycle life, and low cost are considered key enablers for sustainable consumer electronics, electric vehicles (EVs), and smart grid energy storage. Lithium-ion batteries (LIBs) have been emerged to one of the most widely used energy storage systems. Current commercially available LIBs consist of multiple galvanic cells, each composed of: cathode current collector (CC) | cathode material layer | separator | anode material layer | anode CC. The porous electrode layers and the separator are infiltrated with a liquid electrolyte. Typically, the anode and cathode materials base on intercalation chemistry. During charging, Li-ions are extracted from the cathode material (e.g., LiNi₁₀Co₁₀Mn₁₀O₂, LiNi₀₂Co₁₀Al₁₀O₂, or LiFePO₄) and intercalate into the anode material (e.g., graphite or Li₂Ti₅O₁₂). This process is reversed when discharging, providing electrical energy. Academia and industry have evaluated various approaches to improve energy density at the cell level and have made continuous progress, such as the development of high-capacity anode[5-7] and cathode[8] materials, novel electrolytes,[9] improvements in electrode design and composition,[10] and the optimization of cell architecture.[11,12] It was found that the development of high-capacity electrode materials has by far the greatest potential for optimization.[13] Li-metal anodes are usually considered the ultimate solution for high-energy batteries, for example, Li-metal batteries (LMB) and Li-metal solid-state batteries (LMSSB), as they provide the highest gravimetric (GED) and volumetric (VED) energy density.[14] However, from a theoretical point of view, so called anode-free cell concepts can provide even higher energy density.[15,16] Anode-free Li-metal batteries (AFLMB) are composed of: cathode CC | cathode material layer | separator | anode CC. During charging, Li-ions extracted from the cathode are electrodeposited at the anode CC. The Li-metal plated in-situ is dissolved again and intercalated into the cathode during discharging of the cell. The absence of a Li-ion insertion host at the anode side reduces the weight and the thickness of the cell, increasing both GED and VED significantly. Furthermore, the cost, energy, and technological requirements associated with anode production are saved, including slurry preparation, coating, and drying in dry room atmosphere.[16] However, several challenges prevent the practical application of AFLMB so far. Generally, the “mossy” growth of electrodeposited Li and reactivity toward liquid electrolytes lead to continuous electrolyte decomposition and the formation of “dead Li” under
repeated cycling and thus typically very low plating/stripping efficiency.\cite{7}

Figure 1 compares the GED and VED of the different types of battery cells (details on the computations are provided as Supporting Information). As a reference, we consider cells based on NMC811 cathodes with a thickness of 100 μm and a porosity of 25%. In this case, a conventional LIB with graphite-based anode (25% porosity, N/P = 1.1) exhibits a VED (GED) of 751 Wh L\(^{-1}\) (277 Wh kg\(^{-1}\)). Replacing the liquid electrolyte with an SSE does not change the VED, if the SSE occupies the same volume as the pore electrolyte and separator in the liquid electrolyte-based cell. In contrast, replacing the liquid electrolyte with a sulfide-based SSE reduces the GED to 266 Wh kg\(^{-1}\). The reduction in GED is due to the higher density of the SSE. Since the SSE occupies the same volume as the liquid electrolyte, the mass of the entire cell increases while the specific capacity remains the same, resulting in a decrease in GED. This effect is enlarged the higher the density of the SSE is and makes materials with high density (e.g., LLZO) unfavorable in such cell configurations. Using flat Li-metal (N/P = 1.1) instead of a porous graphite electrode increases both VED and GED significantly due to the higher ratio between the masses of the cathode material and the cell. However, it should be noted that laboratory scale LMSSB are commonly assembled with a large excess of Li, which dramatically lowers the practical energy density (Figure 1d,e). For example, increasing the amount of Li-excess from N/P = 1.1 to N/P = 11 reduces the VED (GED) dramatically from 1197 Wh L\(^{-1}\) (393 Wh kg\(^{-1}\)) to 437 Wh L\(^{-1}\) (297 Wh kg\(^{-1}\)) as recently also pointed out by Kravchyk et al.\cite{39} in their breakdown analysis of LMSSB with Li-garnet SSE. The anode-free configurations, with a bare Cu CC at the anode side, provide the highest nominal energy density in both cases, liquid and solid electrolyte systems. The VED (GED) of the AFSSB is calculated to 1514 Wh L\(^{-1}\) (408 Wh kg\(^{-1}\)), achieving the targets defined for a battery cell by the European SET-Plan Action 7 for 2030.\cite{47}

Owing to their superior energy density, AFSSB are particularly relevant for mobile electronic devices and transportation applications. Note that the computations of GED and VED were performed for the discharged state. Actually, the volume of cells with Li-metal anodes changes according to the thickness of the Li layer deposited on the anode side during charging. This slightly decreases the VED of the anode-free configurations and Li-metal based cells, however, without affecting the general trends in VED of the different cell concepts shown in Figure 1 (see Supporting Information for details).

The comparison of different cell concepts regarding nominal GED and VED in Figure 1 assumes similar utilization of active materials between liquid electrolyte and SSE-based cells. This assumption requires similar electrochemically stability windows of the liquid and solid electrolyte systems. Reducing the electrochemical stability window lowers the utilization of the active material according to its typical intercalation profile. Accordingly, both specific capacity and cell voltage are reduced, resulting in lower GED and VED. Thus, the ranking of GED and VED of different cell concepts in Figure 1 is only valid if sufficiently stable electrolytes are used, highlighting the crucial importance of the electrochemical stability window for the development of SSB and AFSSB, as discussed in more detail below.

2.1. Energy Density

In addition, at higher currents, the dendritic growth of Li can lead to penetration of the separator and short circuit of the cell, which represents a significant safety risk due to the flammability of the liquid electrolyte. Alternatively, the use of solid-state electrolytes (SSEs) is regarded a promising solution to realize practical anode-free batteries.\cite{15,18,19}

The SSEs are typically non-flammable, more stable against lithium metal, and less susceptible to dendrite formation. Inorganic SSEs for solid state batteries (SSB) are commonly based on oxides\cite{20,21} (e.g., garnet Li\(_{7}\)La\(_3\)Zr\(_2\)O\(_{12}\) (LLZO), perovskite Li\(_{3}\)(Li\(_{0.5}\)Ta\(_{0.5}\))O\(_3\) (LLTO), NASICON-type LiTi\(_4\)(PO\(_4\))\(_4\), and LISICON-type Li\(_{14}\)Zn(GeO\(_4\))\(_4\)), sulfides\cite{21,22} (e.g., Li\(_2\)S–P\(_2\)S\(_5\) and LGPS, Argyrodites), or on combination in hybrid concepts\cite{23} (e.g., garnet/sulfide). Note that the terms “sulfide” and “thiophosphate” are used analogously in the scientific battery community. From the chemical point of view, these materials contain tetrathiophosphate (PS\(_4\))\(_3\)– ions or condensed forms, for example, (P\(_2\)S\(_5\))\(_3\)–, etc. and are thus thiophosphates. A sulfide S\(_2\)– anion is rarely present, that is, for argyrodites. Nevertheless, for reasons of familiarity in the battery community, the term “sulfide” will be used in the following. Organic polymeric SSE consists of a polymer matrix\cite{24} (e.g., poly(ethylene oxide) (PEO), poly(vinylidene fluoride) (PVDF), polyacrylonitrile (PAN), and poly(methyl methacrylate) (PMMA)) and lithium salts (e.g., LiClO\(_4\), LiN(CF\(_3\)SO\(_2\))\(_2\), LiAsF\(_6\), and LiPF\(_6\)).

Very recent studies have demonstrated anode-free solid-state batteries (AFSSB) that combine the benefits of anode-free cell configurations providing high-energy and solid-state systems with high safety. This review provides an overview of recent developments toward AFSSB and highlights the current issues and challenges in this nascent field. First, general aspects are discussed including theoretical considerations regarding the benefits of higher energy density, reduced manufacturing costs and favorable recyclability. In order to establish a link between liquid and all solid-state systems, the knowledge gained in AFLMB technology is then briefly recapitulated. Importantly, key findings from AFLMB research are extracted and their applicability in AFSSB is evaluated. Afterwards, recent studies and developments on AFSSB are summarized and discussed from an application point of view. Finally, the main challenges, including the Coulombic efficiency during formation of the cell, interfacial issues, dendrite growth during progressive cycling and implications of the cell design for the practical energy density, are highlighted and promising research directions are proposed to address these challenges to enable widespread application of AFSSB. We hope that this review will help scientific research, academic and industrial communities to better understand this emerging technology and explore attractive development strategies.

2. General Aspects

To evaluate the advantages of AFSSB, considerations of energy density gain, manufacturing and cost reduction potential as well as recyclability compared to other types of Li-based batteries are presented in the following.
Besides the actual cell concept, the energy density also depends on the electrode and cell design. Both the VED (Figure 1b) and GED (Figure 1c) increase with increasing thickness of the cathode, due to the decreasing share of inactive materials in the cell, which however comes at the cost of fast charging limitations.\textsuperscript{[9,26,27]} The tradeoff between high energy and high power originates from transport limitations that scale with the electrode thickness.\textsuperscript{[10,28–30]} Cells intended for high energy applications have thick electrodes, whereas high power cells (or fast charging capability) are designed with thin electrode coatings to reduce transport limitations at high current densities. The anode-free cell concepts clearly exceed the VED of both conventional and Li-metal batteries (Figure 1b). Furthermore, the gain in VED with increasing cathode thickness is still pronounced even at very high thicknesses (e.g., 150 µm), whereas conventional and Li-metal batteries already strive toward a limiting value. The gain in GED is significant between anode-free and conventional cell concepts, but less pronounced compared to Li-metal-based cell concepts (Figure 1c). This is due to the high gravimetric capacity of Li-metal (3860 mAh g\textsuperscript{-1}) and corresponding low mass needed to provide relatively large excess of Li capacity in the cell (e.g., N/P = 1.1). The GED of LMB and AFSSB is almost identical, since the weight advantage due to the elimination of the anode material is compensated by the higher mass (density) of the SSE compared to the liquid electrolyte. However, conventional organic liquid electrolytes in rechargeable LIBs still pose safety risks.\textsuperscript{[17]} With the development of large size batteries for automotive applications, 

![Figure 1. a) Schematics of cell configurations, stack weight and volume distribution, and estimated energy density for conventional Li-ion batteries and solid-state batteries with intercalation type electrodes, Li-metal anode, and anode-free configuration. b) Volumetric (VED) and c) gravimetric (GED) energy density of the different cell concepts as a function of the cathode thickness. d) VED and e) GED of solid-state batteries as a function of Li-excess in terms of N/P-Ratio, where N/P = 0 corresponds to anode-free configuration (AFSSB).]
the risk of fire and explosion has become a serious problem. LMB suffer from instability between the liquid electrolytes and metallic lithium, and dendrite growth at high currents, making their large-scale commercialization extremely challenging. Despite the variety of protection strategies proposed, the use of metallic Li in cells with liquid electrolyte still seems very challenging, especially because of the safety issues associated with the presence of the flammable organic electrolyte. Replacing the flammable liquid with solid electrolytes is considered an attractive strategy to mitigate the safety risks that hinder the full commercialization of large-scale batteries.\[14\]

### 2.2. Manufacturing and Costs

With the cost of battery packs for electric vehicles steadily declining,\[32\] a great challenge for implementing solid-electrolyte based batteries will be to produce high quality cells at a cost similar to that of conventional LIB.\[13\] Therefore, highly automated, scalable production processes are required.\[34\] Robust processes and quality monitoring are necessary during production to ensure a low error rate and minimize the rejection rate.\[15\] However, compared to LIB, the solid-state battery is still in its infancy and most practical experience exists only at the laboratory level. Xu et al.\[36\] recently reviewed the state-of-the-art regarding scalability of LMSSB, pointing out the gaps between lab-level cells and practical large-format batteries. Wang et al.\[37\] provided a very recent perspectives article dealing with the transition of SSB from lab to market, especially highlighting the links between electro-chemo-mechanics and practical considerations. Huang et al.\[38\] summarized manufacturing scalability implications of materials choice in inorganic solid-state batteries. Besides critical issues regarding large scale production and costs of different types of SSE and the composite cathode, which are similar for SSB, LMSSB, and AFSSB, the scalability of anode manufacturing and cell assembly still remains challenging.\[16,39\] The high reactivity of Li with components of ambient air (oxygen, nitrogen, carbon dioxide, moisture)\[40\] requires demanding dry room conditions, which comes at high acquisition, operating and maintenance costs. Alternatively, the application of an additional protective layer is investigated to increase the oxidation stability during manufacturing.\[33,41\] which, however, means additional process steps and corresponding costs. Furthermore, the fabrication of sufficiently thin lithium foils with acceptable purity and microstructure over large areas is extremely difficult and costly.\[17,42,43\] Schmuch et al. showed that material and processing costs can easily lead to Li foil prices of 300–400 $ kg\(^{-1}\)\[41\]. Processing to films with advantageous thickness (\(<100\) µm) could even result in costs exceeding 1000 $ kg\(^{-1}\), depending on the processing technique and the targeted film thickness. As an alternative to mechanical manufacturing, Li films with an advantageous thickness might be produced more effectively by melting processes, vapor-based processes, or electrochemical deposition in scalable manner. An alternative to the use of pure lithium is the application of thin composite layers in which an additional material acts as a host for metallic Li.\[44,45\] Furthermore, a series of Li-alloys have demonstrated good potential in constructing a better interface between anode and electrolyte.\[46\] While the use of composite or alloying anodes reduces the achievable energy density, when compared with pure Li, this could be offset by an even more substantial improvement in manufacturability enabled by the cell design.\[38\] However, there are currently no models or practical experience that would allow a reliable comparison of costs on an industrial level. In any case, it is currently not clear whether the costs can compete with those of typical LIB materials (\(<100\) $ kg\(^{-1}\)), making large-scale establishment of Li metal-based cells challenging. Furthermore, the physical properties of Li metal lead to difficulties in manufacturing. The tensile strength of Li metal is low, leading to fragility in the conventional roll-to-roll process. The creep behavior of Li metal causes penetration into defects of the SSE, resulting in demanding requirements for the homogeneity of the SSE surface. Fabrication of Li-metal composite anodes by electrodeposition, melt infiltration, or roll-in processes is somewhat less demanding but still faces unresolved issues regarding reactivity of Li and maintaining of the designed function in large-scale processes.\[44\]

Many strategies to improve Li metal anodes have been successfully demonstrated at the laboratory level. The laboratory level strategies mainly focus on the optimization of the interface/interphase and electrode structure.\[17,47\] However, direct transfer of these strategies to practical batteries appears not promising in most cases.\[16\] The strategies at the lab-level help tremendously in solving the problem from the mechanism point of view. However, rational application techniques are also important to realize these solutions in scaled-up battery systems.

Anode-free concepts, where the lithium metal anode is generated in-situ, have significant process cost advantages, as active material-related anode manufacturing steps, for example, causing process costs of 12–18% in LIB production,\[48\] could be completely eliminated. In addition to the direct cost savings, this also makes production less error-prone, resulting in shorter downtimes and larger production capacity. Due to the absence of Li metal during assembly, the process conditions are much less demanding, dramatically reducing acquisition, operating and maintenance costs. At the same time, the absence of metallic Li significantly reduces safety risks during manufacturing, thus saving the costs associated with safety measures.

Besides process costs, AFSSB production obviously saves materials consumption and associated cost. Fluctuations in the price of metallic lithium create cost issues for Li-metal batteries.\[49\] In anode-free configuration, the minimum amount of Li required for operation is stored inside the cathode, which can be produced using lithium compounds such as Li_2CO_3 or LiOH, whereas metallic Li anodes require much higher purity (e.g., by energy-intensive electrolysis).\[50\] Based on the cost model of Schmuch et al.,\[41\] anode material costs amount to approximately 20% in the case of LIB, and 33–57% in the case of LMSSB (N/P = 3). These costs can be saved in anode-free configuration, allowing significant reduction of materials costs. Although the cost reduction by the transition from LMSSB to AFSSB cannot yet be fully quantified reliably, it is clear that there is enormous potential for savings. To reliably estimate these crucial characteristics, future cost and production models\[41,52\] should also take the anode-free configuration into account.
into account. However, it should be noted that, as described in detail below, guest structures and lithiophilic coatings are often applied to the CC to enable stable cycling in an anode-free configuration. This diminishes some of the principle advantages of AFSSB, which should be considered as part of a holistic evaluation.

2.3. Recyclability

In sense of a circular economy, recycling technologies for batteries are crucial.[52] While for long-established battery systems, such as lead-acid or NiCd/NiMH, a large proportion of cells is recycled, first strategies for scalable recycling processes are currently being developed for lithium-ion batteries.[53–56] Since lithium solid-state chemistry is currently still under development, recycling approaches have only recently been investigated and reported in the literature. Due to the significant differences in chemistry and structure of LMSSB compared with conventional LIB, there are unique aspects to consider for recycling, for example, the composite material characteristics of LMSSB requiring significant effort in development of dedicated separation processes. Azhari et al. recently provided a comprehensive perspective article on recycling strategies for solid-state batteries.[57] The authors present a promising approach that uses a combination of hydrometallurgy and direct recycling, exploiting the specific physical properties of the different SSE types to separate them and reduce safety risks. Schwich et al.[58] discussed the recycling of a oxide/phosphate based cell. They compared different cell concepts using LLZO (Li3La2Zr2O12) or LATP (Li1.5Al0.5Ti1.5(PO4)4) as SSE and LCO (LiCoO2) or NCM811 (LiNi0.8Mn0.1Co0.1O2) as cathode active materials. At the anode side, a very thin layer of Li (5 µm) has been considered. The authors suggest a pretreatment employing crushing, thermal treatment and sieving/sorting followed by hydrometallurgical steps. Tan et al.[59] describe a recycling process of a Li | Li2P2S5Cl | LiCoO2 | LMSSB. It is highlighted that the process is less complicated when compared to conventional LIB, mainly due to the intrinsic nonflammable nature of the SSE and therefore reduced fire hazards during disassembly. Nevertheless, the presence of metallic Li in the cells requires special precautions during disassembly and further processing due to its high reactivity, in particular in solution-based processes, where it may cause rapid exothermal reactions.[60,61] Furthermore, Li metal is very adhesive resulting in issues with mechanical separation methods, such as sieving, shredding, or crushing. In AFSSB, the amount of metallic Li depends on the state-of-charge of the battery. In the charged state, a thin Li layer is present at the anode side, which is ideally completely removed in the discharged state. Thus, recycling of discharged AFSSB would reduce the complexity and safety hazards of the recycling process dramatically. Another advantage of solid-state batteries is that they can potentially be recovered and regenerated after extraction from cells, as it is pointed out by Tan et al.[62] This would significantly reduce process cost and energy consumption, in case the materials would not have be resynthesized from the raw materials or precursors. Again, such a treatment would be simplified dramatically in the case of AFSSB.

3. Anode-Free Li-Metal Batteries with Liquid Electrolyte

Before summarizing recent developments in the nascent field of AFSSB, we briefly recapitulate the most important findings and promising trends in AFLMB research, with a special emphasis on improvement strategies that may also be useful for AFSSB. An anode-free battery might be interpreted as a Li metal battery with zero excess Li. In other words, it is an obligation to use cathode materials in lithiated state and their Li content limits the available Li inventory. In turn, this means, that AFLMB face not only the entirety of challenges related to Li metal batteries, but also additional specific issues. As known since Peled’s pioneering work in 1979, Li metal in liquid electrolytes is inevitably linked to the formation of a solid–electrolyte interphase (SEI).[63] Although acting beneficial by stabilizing the Li surface, this layer typically does not withstand repeated plating-stripping cycles, leading to a continuous reformation and irreversible consumption of Li.[64,65] Just as detrimental, Li tends to form uneven deposits, often dendrites, which not only represent a safety hazard, but are also a further source of irreversible Li consumption, since dendrites can be dissolved at their root, leading to detachment from the anode and the accumulation of “dead Li” within the electrolyte.[66]

These well-known problems of Li metal batteries are amplified in case of AFLMB. As Li is plated directly onto the anode CC, any irreversible consumption of Li directly translates into capacity reduction, as there is no reservoir for compensating these losses. Hence, the key remedy for AFLMB lies in providing a reversible plating/stripping of Li. Multiple strategies have been employed so far, all of which can be categorized as either i) CC modification, ii) electrolyte development, iii) adjustment of cycling protocol and external measures, or iv) synergetic approaches. These approaches were examined in detail in recent overview articles.[15,16,19,67,68] In light of the present review, we briefly recapitulate the major findings of AFLMB research to assess its potential for improving AFSSB.

3.1. Current Collector Modification

Early work on AFLMB involved the plating of Li on a bare Cu CC.[68] This originates from the fact that Cu is conventionally used as anode CC in LIB. Unfortunately, bare Cu challenges Li with a large nucleation overpotential, favoring local current maxima and an uneven growth of Li.[69] A recent study of Shen et al.[70] indicates that (110) oriented Cu-crystals induce lateral growth of Li and dendrite-free cycling for several hundreds of cycles. However, the adhesion of Li deposits on Cu has been reported to be poor, which can be circumvented by, for example, using Sn-plated Cu[71] or pre-plated Li on Cu.[72] A theoretical study indicates that replacement of Cu with alloys of Li results in lower nucleation overpotentials and improved specific energy owing to a reduced density of the CC.[73] A larger number of experimental studies deals with 3D CC architectures, mainly aiming at a spatial confinement of Li deposits, suppressing the growth of dendrites. Umh et al. fabricated a hierarchical pore structure by electrodeposition of Cu using a dynamic template of H2 bubbles.
The resulting macroporous structure showed a superior cycling behavior for 140 cycles (>600 h) with 95% Coulombic efficiency (CE), while the planar Cu CC survived for 100 cycles (>300 h) only, exhibiting an initial CE of 89%, which dropped to 48% after less than 60 cycles (Figure 2e). The results suggest that the higher electroactive area of the structured CC results in a better contact of the Li deposits, hence promoting a more even distribution of currents and less dendritic growth.

The majority of CC improvements is realized by various coating strategies. Among organic coatings, polyethylene oxide (PEO) has attracted considerable interest. Hwang’s group applied porous PEO layers onto the Cu CC by spin-coating, allowing Li plating and stripping at stable CE and low overpotential, as demonstrated in full-cells using LiFePO4 as cathode. Originating from the same lab, coatings of multilayer graphene (MLG), graphene oxide (GO), and Li7La2.75Ca0.25Zr1.75Nb0.25O12 were reported. The average CE reached 97% to 99%, which represents significant improvement, which however still not satisfies the demands for desired cycle life of several thousand cycles. While the aforementioned approaches are usually referred to as artificial SEIs or protective layers, recent works highlight lithiophilic layers, which do not only protect Li deposits but enhance nucleation and adhesion, as in case of Ag nanoparticles, or oxide layers, such as Al2O3 and SiOx. Recently, multifunctional coatings, such as Al2O3/Polyacrylonitrile (PAN) composite were reported, exploiting combined benefits of the inorganic and the organic component. While Al2O3 results in the formation of conductive Li-Al-O and SEI-forming Al-F species, the flexible nature of PAN provides mechanical stability and nitrogen content improves the affinity toward Li.

### 3.2. Liquid Electrolyte Modification

Using conventional solutions of ~1 M LiPF6 in organic carbonates leads to a poor performance of anode-free batteries, which is attributed to the formation of “dead Li.” One popular approach lies in increasing salt concentrations, as for example 2 M LiPF6 in EC:DEC (1:1 v/v) + 50% FEC. However, increasing viscosity acts detrimental, making the addition of FEC as a diluent necessary. While full-cells using NMC111 with conventional electrolyte in the control experiment only yielded an average CE of less than 90% and sank to less than 40% capacity retention after 15 cycles, AFLMB using the concentrated solution showed an average CE of 97.8%, leading to a capacity retention to 40% after 50 cycles. Exceeding established additives such as FEC, the exploration of new additive species remains an important topic. Sahalie et al. used KNO3 and proposed a synergetic effect of i) electrostatic shielding by K+ ions, preventing tip-growth of dendrites, and ii) SEI contribution of NO3−, leading to the formation of Li nitrates for a stable and conductive SEI. Therein, a clear trend of improved capacity retention at higher KNO3 amounts was shown, although the best obtained value of 41% after 33 cycles using 0.5 M KNO3 still falls short of requirements for practical batteries.

An increasing number of studies is focusing dual-salt or multi-salt electrolytes, as for example an LiDFOB/LiBF4 mixture in FEC:DEC (1:2 v/v), as proposed by Dahn’s group. In their groundbreaking study, it was clearly shown how the performance of the dual-salt electrolyte exceeded the single salt solutions, yielding 80% capacity retention after 90 cycles (Figure 4f). Obvious differences in the morphology of Li deposits between the dual-salt electrolyte and a conventional LiPF6 electrolyte were observed (Figure 2g–n). A strongly altered SEI could be
identified as the beneficial factor, while the capacity decay was attributed to a continuous salt consumption. Besides higher electrolyte content and molarity, the authors suggested to explore salt mixtures including non-consumable components. Hagos et al. sought to improve LiPF_{6}-based electrolytes by a modification of the solvent mixture, adding ethyl methyl carbonate (EMC) to solutions of FEC and tetrafluoroethyl tetrafluoropropyl ether (TTE), yielding to an average CE of 98.3% for 80 cycles in a Cu/NMC111 AFLMB.\[87\]

Besides carbonate-based electrolytes, ethereal solutions, usually involving LiTFSI and LiNO\textsubscript{3}, as successfully established for research on Li–S batteries, are under heavy investigation. Also here, dual-salt strategies proved to be useful, as shown for LiTFSI/LiFSI mixtures in DME (particularly 4.6 m LiFSI + 2.3 m LiTFSI) by Y. S. Meng’s group.\[88\] Compared to the LiFSI single salt electrolyte, the binary solution resulted in different interphase properties, suppressed LiFSI precipitation, widened oxidative stability and an improved uniform Li deposition. Full-cells using NMC622 exhibited an impressive capacity retention of 88% after 300 cycles. A comparative study between a mixture of 2 m LiFSI + 1 m LiTFSI and a 3 m LiTFSI electrolyte in DME/DOL from Hwang’s group showed, that the beneficial effect is not only a matter of total salt concentrations. Instead, the different electrolyte chemistry leads to a modified SEI, providing fast ion conduction and mechanical stability and paving the way to 98.9% CE over 100 cycles.\[89\]

### 3.3. Cycling Protocol Modifications

A potentially strongly underestimated strategy lies in modification of external parameters, that is, focusing on the adjustment of temperature, pressure, cut-off voltages, current densities, etc. rather than modifying the cell chemistry. Pioneering work has been reported by J. R. Dahn’s group.\[90\] Changing the lower cutoff voltage of anode-free NMC532/Cu cells from 3.6 to 1.25 V, resulted in a decay of the initial CE from 99.8% to 99.0%. The authors showed that the lower CE obtained when discharging to 1.25 V reflects the actual CE of the setup, while the cutoff at 3.6 V results in an incomplete lithiation of the NMC cathode, leaving unused Li at the anode, thus artificially inflating the initial CE. On the other hand, capacities of cells cycled to 1.25 V decayed at a more moderate rate and a longer cycle life was achieved. In both cases, high pressure of 8 bar served benefic ally. An independent study confirmed these results, however highlighting that the positive influence of pressure is intertwined with an appropriate electrolyte selection.\[91\]

Furthermore, it was discovered that an initial “hot formation” at 40 °C already significantly improves the stability of subsequent cycling at 20 °C.\[92\] The mechanism was attributed to the formation of CO\textsubscript{2} during hot formation, acting as an additive.

### 3.4. Synergistic Strategies

Tuning multiple parameters toward the right direction is of course more effective than changing just one variable and, in fact, many of the abovementioned studies already involved synergistic strategies, as for example the investigations of cycling protocols were carried out using optimized electrolytes. In fact, simple combinations like the highly-concentrated 4 m LiFSI-DME electrolyte with a fast discharge—slow charge protocol, as used in Qian’s seminal work, can lead to surprisingly good results.\[68\] Similarly, when 3 m LiFSI was studied in DOL/DME with an optimized protocol consisting of slow plating and high rate stripping, benefits in terms of stable SEI were clearly demonstrated.\[93\] Among the most impressive results obtained for AFLMB so far is the work from Dahn’s group, reporting on LiDFOB + LiBF\textsubscript{4} electrolytes which are subjected to external pressure.\[75\] Nevertheless, it is obvious, that a thorough understanding of the individual approaches is necessary to enable effective synergistic strategies.

### 3.5. Lessons Learned for AFSSB

Transferring the knowledge in AFLMB research to the emerging field of AFSSB will be of particular importance to accelerate the developments. An outstanding approach demonstrated in both liquid and solid-state batteries is the CC modification by Ag nanoparticles. In 2016, Cui’s group investigated a number of substrates regarding their Li nucleation behavior.\[69\] The commonly used Cu required an overpotential of almost 50 mV for Li nuclei to form, while other elements allowed Li nucleation at much lower overpotentials. Among them, Ag appeared particularly attractive, showing an overpotential of a few mV only, forming a lithiophilic Li–Ag alloy. Consequently, further work demonstrated the modification of a Cu CC by Ag nanoparticles, enabling a high CE for Li deposition and dissolution.\[80\]

Since then, multiple studies have exploited the beneficial influence of Ag.\[94–96\] In fact, the lithiophilicity of Ag nanoparticles was confirmed independently of the electrolyte composition, hence suggesting the application in AFSSB. Similarly, transferring further successful CC modification approaches such as carbon-based wetting agents (e.g., g-C\textsubscript{3}N\textsubscript{4}\[97\] Graphene\[98\]) or 3D structures (e.g., Au-modified carbon fibers,\[99\] graphene cages\[100\]) from liquid electrolyte batteries to AFSSB is regarded to be highly promising. Furthermore, the possibility of cycling protocol modifications for AFSSB is highlighted. In fact, external measures such as elevated pressure and temperature are a common requirement for the operation of most SSBs.\[62\]

It is particularly interesting, that also in liquid-electrolyte-based cells, high pressure can act beneficially toward forming uniform Li deposits, as observed by Dahn’s group.\[91\] They recommend application of pressures between 1200 and 2200 kPa to improve the morphology of deposited Li and increase the cycle life of anode-free cells. Similarly, the hot-formation process reported by Dahn’s group\[92\] allowed a significant prolongation of the cycle life and, although more elevated temperatures might be necessary for solid-state systems, the development of such procedures for AFSSB might be as well a winning strategy. Finally, the success by modifying cycling/formation protocol should be transferred to AFSSB. While specifying defaults for charge and discharge rates is not very user-friendly, other measures, such as lower and upper cutoff voltage adjustments may have a large impact.\[100\] Especially for full-cells, a careful consideration of these values is indispensable. For instance, decreasing the lower or upper cutoff voltage of an AFSSB might initially
increase the capacity, but at the same time, the potentials of the cathode and the anode might exceed their individual stability regions. Given the challenges that AFSSB impose on researchers, truly outstanding concepts will have to make use of synergistic approaches, such as modified CC in conjunction with external measures and optimized cycling protocols.

While the abovementioned approaches are likely to work comparably in AFSSB, the variety of electrolyte modifications established for liquid systems cannot be applied. The lack of possibility to combine different solvents, salts and additives could be seen as a disadvantage. However, in our opinion, it should rather be seen as an immense possibility, as many problems of Li metal in liquid electrolyte could be bypassed.

4. Anode-Free Solid-State Batteries

4.1. Thin Film AFSSB

Earliest reports on AFSSB deal with so called thin film batteries (TFB), characterized by dense layers of the anode, SSE, and cathode material stacked between two CCs. Due to the low Li-diffusivity in the active materials, these layers are kept very thin (<5 µm). Because of the unfavorable active/inactive material ratio (e.g., cathode material vs CC), the energy density of TFB is typically very low. Accordingly, possible applications include devices with low power consumption, such as sensors and microelectronic devices.[108] Thin film SSB are commonly prepared by: i) physical deposition methods, such as thermal evaporation, pulsed laser deposition and sputtering; ii) chemical deposition methods, such as chemical vapor deposition, atomic layer deposition, and sol-gel deposition. The current state of the art and trends in TFBs were recently reviewed.[102,103] A promising trend is the development of 3D-structured thin-film batteries, which have the potential to overcome the disadvantages of planar architectures in terms of energy density. Although impressive progress has already been made in this area, scalable production routes are also lacking here.

First investigations concerning thin film AFSSB were carried out by Neudecker et al.[104] They demonstrated an LCO/LiPON/Cu cell successively constructed by high-frequency magnetron sputtering. The authors emphasize the need for a protective layer over the anode CC, without which rapid degradation occurs. The Li-free thin-film batteries with textured LiCoO2 cathodes (3.2 µm thickness) and protected anode CC yield areal capacities of 200 and 130 µAh cm−2 at currents of 0.1 and 5 mA cm−2, respectively, as well as excellent cycling stability (80% utilization after 1000 cycles). While the provided energy density of these thin film AFSSB is insufficient for large scale applications, the studies of Neudecker, Bates and co-workers[104-106] impressively demonstrate that reversible cycling of Li is possible in anode-free configuration and significantly improved when compared to liquid electrolytes.

Following these insights, Lee et al.[107] proposed a reversed structural configuration of a thin film AFSSB to circumvent the need for a protective overlay at the anode side. The initial stack configuration SS | LiPON | Li1.3V2O5 | Cu has been fabricated on a stainless steel (SS) substrate by sequential thin-film deposition methods. A discharge capacity of 43 µAh cm−2 µm−1 with an excellent stability up to 770 cycles is achieved at a current density of 0.1 mA cm−2. Yamamoto et al.[108] recently took up these ideas and designed an inverted cell stack, which enables the use of crystalline cathode materials and much larger coating thickness via aerosol deposition on the amorphous LiPON film. The SS | Pt | LiPON | LiCoO2 | Au cell operated at 4 V, delivered a capacity of 110 mA h g−1 and showed stable cycling behavior without the need for a sealing material (Figure 3a–c).

These AFSSB studies and works on LMSSBs show that LiPON effectively prevents the penetration of Li from the anode to the cathode. Notably, Li et al. reported a thin film battery spinel cathode | LiPON | Li anode that can cycle 10 000 times with minimal degradation and no evidence of Li loss or shorting.[109] A prominent, but not yet fully accepted, hypothesis for the exceptional performance of LiPON is that the absence of grain boundaries favors Li growth parallel to the CC and inhibits Li growth in the cathode direction. To investigate this, Westover et al.[110] modified the Li-free design (Figure 3d), employing a single cathode and four separate Cu CCs. The application of a second LiPON layer creates a LiPON | LiPON interface between the Cu CCs and parallel to the LCO cathode (Figure 3e). This allowed to prove that Li is confined to this artificial LiPON grain boundary by in-situ optical investigations. Notably, Li expands approximately 2 mm between two copper fingers during cycling but did not penetrate the few µm through the LiPON film between anode and cathode (Figure 3f,g). This study especially highlights that the microstructure of the SSE is critical to the performance of AFSSB and that the proper design of grain boundaries is highly important to increase the long-term stability.

4.2. AFSSB with Composite Cathode

While thin film AFSSB are considered a fundamental scientific breakthrough, they are intrinsically limited in terms of GED and VED at the cell level due to the unfavorable active/inactive material ratio. In contrast, solid-state batteries with thick active material coatings (50–150 µm), where the cathode is a composite consisting of active material, SSE, and possible conductive additives, provide much higher theoretical energy density (cf. Figure 1). Very recently, first impressive reports on such AFSSB have appeared on the scientific stage. Chen et al.[111] systematically investigated the influence of Li excess on the cycling behavior of Li metal batteries comparatively between SSE and liquid electrolytes. A garnet-type Li6.4La3Zr1.4Ta0.6O12 (LLZTO) pellet, with an LLZTO–cathode interface layer of solid-state plastic crystal electrolyte (PCE) and an anode–LLZTO interface layer of an Au thin film was combined with LFP cathode and varying amounts of excess Li at the anode side. The succinonitrile (SN)-based PCE layer is conformally attached to the LLZTO surface to reduce the typically high LLZTO/cathode interface resistance. The sputtered Au layer promotes uniform Li deposition and prevents contact loss during lithium dissolution. Lithium metal batteries (N/P = 1) with this SSE setup show an initial CE of 96.8% and subsequent CE of 99%, much higher than for the liquid electrolyte counterpart.
initial CE = 79.4%, CE = 90%), which directly translates into more stable cycling performance of the SSE-based system. However, the reduction of the Li-excess also leads to a dramatic limitation of the cycle stability. While stable cycling (160 mAh g\(^{-1}\)) at room temperature is shown for N/P = 215, only 32, 67, 172, and 186 stable cycles are realized for N/P ratios of 1.1, 2.7, 5.3, and 5.9, respectively. In the anode-free configuration (N/P = 0), a low initial discharge capacity of 76 mAh g\(^{-1}\) followed by a rapid capacity decay during cycling is observed, which is due to the insufficient CE of the Li-plating/stripping process, necessitating a high Li-excess in this system. While this systematic study impressively illustrates the advantages of SSE compared to liquid electrolytes in Li-metal batteries, it also shows the crucial role of the initial CE for the functioning of an AFSSB. Wang et al.\(^{[18]}\) achieved great improvements in this area. Following in-depth studies of the nucleation of Li at the Cu|LLZO interface, the authors constructed different cell types by laminating a Cu CC (10 μm) to polished LLZO pellets followed by pressure assisted heat-treatment. In half-cell configuration, Cu | LLZO | Li, large amounts of Li (5 mAh cm\(^{-2}\)) corresponding to 25 μm cm\(^{-2}\) dense Li) can be cycled reversibly (CE > 99%). The superiority of these results compared to the anode-free configuration in ref. [111], is most probably caused by the improved bonding between Cu and LLZO as a result of polishing the SSE and pressure-assisted heat treatment. In full-cell configuration, using a state-of-the-art NCA electrode (3 mAh cm\(^{-2}\)) infiltrated by PEO-LiTFSI, 2.7 mAh cm\(^{-2}\) was plated upon formation and further used as Li-metal anode. Subsequent cycling at 60 °C at a C/10 rate, only yields 0.75 mAh cm\(^{-2}\) with however relatively stable capacity retention over 50 cycles. The authors attribute the inaccessible capacity to the non-optimized PEO-composite cathode, which is supported by the facts that: i) significantly higher capacity (2.4 mAh cm\(^{-2}\)) is attained at 80 °C and ii) the half-cell measurements show high CE and

Figure 3. a) Cross-sectional SEM image of a thin film AFSSB (Si/Pt/LiPON/LiCoO \(_2\)/Au) formed on an Si substrate and selected charge–discharge curves at 1st (black), 55th (red), and 89th (blue) cycle at 5 μA cm\(^{-2}\). c) Discharge capacity as a function of cycles (numbers refer to the discharge current densities in μA cm\(^{-2}\)). Reproduced under the terms of the Creative Commons CC BY license.\(^{[108]}\) Copyright 2019, Elsevier. Schematic illustrations of d) common thin film AFSSB and e) a modified stack that has an LiPON|LiPON interface extending from the Cu CC to form an artificial LiPON grain boundary. f) Operando optical observation of dendritic Li growth within the artificial LiPON grain boundary of the during g) cycling of the modified thin film AFSSB. Reproduced under the terms of the Creative Commons CC BY license.\(^{[110]}\) Copyright 2019, American Chemical Society.
excellent cycling stability for practically relevant areal capacities of >4 mAh cm\(^{-2}\). Accordingly, although the performance of the full cell is currently insufficient, the results obtained in this study can be considered as a crucial step toward practical AFSSB. In particular, the importance of tailoring the Cu/SSE interface design to enable reversible cycling is highlighted.

Another necessary step to realize practical AFSSB is the transition from laboratory cells to application-ready formats. Above all, the proportion of inactive materials must be significantly reduced, for example, solid electrolyte separator (SES) thickness, to achieve energy densities at the cell level that exceed conventional LIB. For this purpose, Zegeye et al.\textsuperscript{[112]} developed an AFSSB employing ultra-thin polymer composite SSES laminated on anode CC and cathode surfaces. The composite polymer electrolyte (CPE) with a total thickness of 15–20 µm was prepared from PEO, lithium bis (trifluoromethanesulphonyl) imide (LiTFSI) salt, and Li\(_{0.25}\)La\(_{2}\)Zr\(_{1.75}\)Ta\(_{0.25}\)O\(_{12}\) (LLZTO) using a spin-coating method. The LLZTO filler reduces crystallinity and thus enhances lithium-ion conductivity. The polarization of Li | LLZTO/PEO-CPE | Cu cells is lower and the stability higher (<15 mV, 98.7% after 100 cycles) than that of Li | PEO-CPE | Cu cells (>40 mV, failure after 60 cycles). The improved CE and stable cycling are attributed to the LLZTO filler, which distributes the lithium ions more evenly, resulting in a lower tendency for dendrite growth. Employing LLZTO/PEO-CPE SSE in AFSSB with NMC cathode delivered an average CE of 98.8% and initial areal capacity of 2.15 mAh cm\(^{-2}\). However, the capacity drops to 41% after 65 cycles at 0.1 C. The differences in cycling stability between Li half-cells and AFSSB with NMC cathode indicate that the origin of degradation is on the cathode side. Apart from the above studies employing garnet type or polymer electrolytes, in general, solution strategies to improve cell-level energy density and materials for lithium storage at the anode and cathode side, respectively.

5. AFSSB Key Challenges and Most Promising Solution Strategies

Although the above summarized pioneering studies demonstrate significant progress toward practically relevant AFSSB, some critical challenges remain. Challenges for the different types of solid electrolytes (sulfide, oxide and polymer) can be very different. A series of recent review articles covers the state-of-the-art, challenges and promising solution strategies of SSE in general, sulfide electrolytes, oxide electrolytes, and the recently discussed halide electrolytes. Furthermore, fundamental findings on dendrite growth in solid-state batteries and advanced characterization techniques have recently been reviewed. Albertus et al.\textsuperscript{[136]} precisely discussed recent advances and prominent obstacles to realize solid-state Li metal batteries, including gaps in material science, processing science and design engineering. Furthermore, recent advances and perspectives on the fabrication of thin SSE and corresponding cell designs were reviewed. Cao et al. summarized processing strategies to improve cell-level energy density.

The following sections briefly summarize the key challenges and highlight the most critical issues related to AFSSB development. This includes the insufficient CE during formation and cycling of the cell, interfacial issues, inhomogeneous
Figure 4. a) Schematic of an AFSSB with NMC cathode, SSE, and an Ag–C nanocomposite anode layer. b) Schematic of Li deposition and dissolution during cycling. c) Sketch of a 0.6 Ah pouch cell and the bi-cell structure. d) X-ray CT of the cell and e) schematic of the pressurization process during fabrication and operation (2 MPa) of the AFSSB. f,g) Voltage profiles for different discharge rates at 60 °C plotted against the cell capacity and the specific capacity of the cathode material. h) Voltage profiles for different temperatures (60 to −10 °C) at a discharge rate of 0.1 C. i) Cycling stability and the Coulombic efficiency of the Ag–C|SSE|NMC pouch cell plotted against cycle number (charge/discharge rate 0.5 C/0.5 C, voltage window 2.5–4.25 V, 60 °C). Reproduced with permission.[113] Copyright 2020, Springer Nature.
nucleation, and dendrite growth during progressive cycling. Furthermore, the transfer from laboratory-level model systems to practically relevant electrode and cell designs via scalable routes is still pending. Academia and industry are intensively addressing these challenges, continuously making progress to improve AFSSSB and realize practical application. This includes material and design developments based on mechanistic investigations using advanced in-situ and operando methods, as well as the development of innovative manufacturing technologies.

5.1. Coulombic Efficiency and Lithium Inventory Retention Rate

As an AFSSSB operates using zero excess of Li, any Li losses will be reflected inevitably by capacity decay. It is commonly assumed that the amount of Li loss by far exceeds losses of cathode active material. This is reflected by Equation (1), showing that the extractable capacity in the nth cycle \( Q_n \) is determined by the initial capacity and the CE of Li-plating/stripping directly.\[15\]

\[
Q_n = Q_{\text{initial}} \prod_{n=2}^{\infty} CE_n
\]

However, in the recent review by Manthiram’s group, it was pointed out, that this holds true only if Li losses occur in either charge or discharge since the CE does not reflect losses taking place constantly in both steps.\[15\] Figure 5a displays the capacity retention for different CE. Obviously, following a power law, sub-% improvements of the CE toward 100% dramatically enhance cycle life. This is impressively illustrated by comparing 90%, 99% and 99.9% CE: at 99.9%, the lifetime becomes 10-fold as high compared to 99% and even 100-fold the lifetime obtained at 90%. Once more, it becomes evident, that a CE far above 99% is needed for AFLMB to provide a satisfactory cycle life.

As pointed out by Nanda et al.,\[15\] CE might not always be the best suited parameter to characterize Li losses in an AFSSSB. Considering the case of similar Li losses during charge and discharge, a capacity decay can occur, which does not affect CE. Therefore, the authors introduced the lithium inventory retention rate (LIRR), given by Equation (2):

\[
LIRR = 100 \left( \frac{Q_n}{Q_{\text{initial}}} \right)^{1/2}
\]

Using the capacity retention at a given cycle, n, the rate of Li depletion is calculated “backward”, avoiding potentially incorrect conclusions based on analysis of the CE only. Similarly, an LIRR of well above 99% is needed to guarantee for an appreciable cycle life. Figure 5b displays how the LIRR convolutes with losses that might originate from the cathode, considering a first cycle Li inventory loss of 20% and a first cycle cathode loss of 40%. It becomes clear that, for cathode materials exhibiting a significant irreversible capacity within the first cycle, the loss of cathode inventory (i.e., an irreversible capacity of the cathode that remains plated on the anode) masks the Li inventory losses, potentially leading to false conclusions regarding the LIRR of the AFSSSB. It is highlighted, that AFSSSB should always be cycled until cell failure to allow the differentiation of various capacity fading regimes and to avoid an overestimation of the LIRR.

Given the fact that most anode-free systems reported so far exhibit a clearly reduced CE compared to conventional systems, it is particularly interesting over how many cycles the superiority in energy density can be maintained. Figure 6a displays the evolution of VED over cycling for several systems. Considering the case of an AFSSSB with an average CE of 99% (blue line): such a cell would completely lose its advantages over a state-of-the-art LIB (black line) after less than 100 cycles, ending up with an energy density around 600 Wh L\(^{-1}\), subsequently dropping to zero after less than 500 cycles. It becomes evident, that a CE of at least 99.9% is necessary to preserve a high energy density for close to 1000 cycles. Furthermore, we want to point out the peculiarities of LMSSB.

To maximize energy density, the N/P ratio of Li metal batteries should be kept as low as possible.\[111\] Such a battery with a CE of 99% and an N/P ratio of 1.1 (blue line) exhibits...
a fairly high energy density of 1200 Wh L\(^{-1}\) and an initial capacity decay that is controlled by capacity losses originating from the cathode. However, after the reservoir of 110% additional Li is consumed, a rapid decay takes place, ending up in a lower energy density than the LIB in less than 200 cycles (cf. Figure 6a). One might intuitively seek to improve this by increasing the amount of excess Li, for example an N/P ratio of 10. Indeed, this system shows a much better capacity retention, however the energy density is intrinsically limited to less than 500 Wh L\(^{-1}\) due to the large excess of Li, making it impossible for this system to compete with conventional LIBs (cf. Figure 6a). This important issue was recently pointed out by Tian et al.\(^{[106]}\) Most Li metal batteries are assembled with an excess of Li of at least factor 10 by using an Li foil of which only a small fraction is used for cycling. In this case, however, it is not correct to assume a capacity of 3860 mAh g\(^{-1}\) for the anode. Instead, since 90% of the Li metal anode remains as a reservoir, the specific capacity drops to around 350 mAh g\(^{-1}\), which is less than that of graphite. It becomes evident, that excess Li is no viable route to develop Li metal batteries that can be competitive with established LIBs.

As reported by Dahn’s group, it is extremely important to carefully evaluate the obtained CE.\(^{[90]}\) In their study, NMC532 || Cu cells exhibited a high CE of >99.8%, which was artificially inflated by an Li reservoir formed by the irreversible capacity of the cathode. As this reservoir was depleted, the CE of <99% revealed the true efficiency of Li plating and stripping. Dahn’s group had in fact much earlier discovered that Li plating on a graphite anode proceeded at a CE of 97–98%, since only a part of the deposited very reactive Li can be recovered.\(^{[140]}\) It is widely accepted that Li tends to deposit in an irregular manner for a wide range of substrates, forming whiskers, which are likely to be encapsulated by SEI and detached from the electrode, ending as dead Li.\(^{[141]}\) Recent work by Wang’s group indicates that this might even be an intrinsic problem, irrespective of the substrate, since a retarded surface transport of Li on top of the deposit has a decisive role.\(^{[142]}\) For SSE, Han et al. additionally identified contributions of electronic conductivity in the electrolyte as an origin for dendrite growth, since higher electronic conductivities will lower the potential in the bulk electrolyte, increasing the driving force for dendrite formation.\(^{[143]}\) In a very recent study, Davis et al.\(^{[144]}\) employed multi-modal operating analysis to provide a direct comparison of the differences in SEI formation and Li plating between different sulfide SSEs and a carbon-free configuration. For the argyrodite LPSCl, after the initial SEI formation, the interface stabilizes and Li metal deposition starts. In contrast, for LGPS, the interface does not stabilize and the SEI continues to grow. The authors conclude that the transition in the reaction pathways from SEI formation to Li plating determines the CE in AFSSB. To achieve high CEs close to 100%, synergistic efforts of the abovementioned approaches are required, that is, combined modifications of CC, lithiophilic coatings and protection layers, optimized electrolytes, and external measures. In particular, the recent review of Xu et al. recognizes interfacial modifications as the most important aspect, next to the fabrication of 3D host materials for Li.\(^{[145]}\)

5.2. Interfacial Issues

5.2.1. Interfacial Stability

Solid electrolytes in principle can cover a wide electrochemical window. Still, none of the electrolytes alone covers the whole range required for AFSSB operation. Especially SSE with highest ionic conductivity lack large stability ranges. Interfaces toward SSE can be classified into three groups:\(^{[120]}\) i) The most suitable one is a stable contact without thermodynamic driving force for any reaction. At the interface, either ii) a self-limiting passivation layer of electronically insulating phases or iii) a self-propagating mixed-conducting layer is formed. Thermodynamic stability ranges can be derived from first-principle calculations.\(^{[146–150]}\) Experimentally determined stability ranges reported in the literature need to be considered carefully. CV-based stability determination often overestimates reaction limits due to a limited...
(planar) electrode area. Careful studies on material composites of SSE and conductive agent with an increased reaction surface showed that the electrochemical windows are often much more limited and agree well with theoretical predictions.[148,151] Thus, the electrochemical reduction and oxidation potentials as well as decomposition products from theory are a valuable guide for the development of SSB cell concepts.

At the anode side, the electrochemical stability is limited by the reduction of cations. Due to the low redox potential of Li, the most stable compounds are binary, fully reduced Li-salts, for example, LiF, LiCl, Li2O, Li3S, Li3N, Li3P, etc. (Figure 7a).[146,149] Oxide-based SSE, including garnets (e.g., LLZO), perovskites (e.g., LITTO), NASICON (e.g., LATP), or LiPON, are not stable against metallic lithium (Figure 7a). LLZO exhibits the lowest predicted reduction potential of only 50 mV against Li/Li+ (Figure 7d).[148,149] LLZO is typically regarded kinetically stable due to a Li-intercalation overpotential stabilizing the Li|LLZO interface.[152] Thus, LLZO is considered to work with Li-metal on the anode side without SEI formation. NASICON and perovskites are less stable against Li-metal. Most prominent examples are LATP and LITLO. Both contain Ti4+ which is not stable against reduction forming mixed conducting phases.[153–155] LiPON was successfully used as SES in thin film SSB. Nevertheless, calculations predict a full reduction of P5+ and N5+ forming Li3P and LiPN2 as a stable SEI.[146,156] Both materials exhibit sufficient ionic conductivity. Sulfide electrolytes exhibit a relatively small electrochemical stability range (Figure 7a).[146,147,149] Typically, they are non-stable against reduction below 1.7 V, still many of them work with a Li-metal or LiIn-alloy anode. Regarding SEI-formation, sulfides can be divided into two groups. Metal free sulfides, that is, glassy or crystalline LPS (Li2S-P2S5-system, can be doped by BH4−, Oxide, halide, etc.,)[157–159] or argyrodites Li3PS4X (X = Cl, Br, I)[160,161] only contain non-metal main group elements as cations. At the Li/Li+ reduction potential they form electronically insulating Li salts, like Li3P, Li3S, LiX, which provide at least a poor ionic conductivity and thus work as a stable SEI.[162,163] On the other hand, metal-containing sulfides—that is, group fourteen M4+-cations in LGPS-type materials—form Zintl-like intermetallic phases upon decomposition (Figure 7c).[164] They are mixed conductors and thus the decomposition reaction propagates at the interface between intermetallic and SSE. Since this propagation is not self-limiting, intermetallic dendrites grow through the separator, facilitating a cell failure. To prevent the formation of these intermetallics, indium-anodes were introduced, working at the LiIn/Li+ potential (0.62 V vs Li/Li+). Typical examples of (semi-) metal-containing sulfides are LGPS-type materials (Li10M5P2S12, M = Ge,[165] Sn,[166] Li9.54Si1.74P1.44S11.7Cl0.3,[167] or Li7SiPS8[168]) or Thio-LISICON Li3.25Ge0.25P0.75S4.[169]

Figure 7. a) Electrochemical window (solid color bar) of potential solid electrolyte and materials for protective layers, for example. The dashed line indicates the oxidation potential for complete delithiation of the material. Reproduced under the terms of the Creative Commons CC BY license.[146] Copyright 2015, American Chemical Society. b) Thermodynamic electrochemical windows (calculated) of Li-M-X ternary fluorides, chlorides, bromides, iodides, oxides, and sulfides with the metal cation (M) in its highest common valence state. Reproduced with permission.[150] Copyright 2019, Wiley. c) Voltage profile and phase equilibria of c) LGPS and d) LLZO solid electrolyte during lithiation and delithiation based on first-principles calculations. Reproduced with permission.[148] Copyright 2016, Wiley.
Recently, halide SSE were reintroduced as Li-super ion conductors.\(^{[131]}\) Examples with the highest ionic conductivities (25 °C) so far are Li$_3$YBr$_3$ (1.7 mS cm$^{-1}$),\(^{[130]}\) Li$_2$YSb$_2$F$_7$ (1.1 mS cm$^{-1}$),\(^{[137]}\) or Li$_3$InCl$_6$ (2.04 mS cm$^{-1}$).\(^{[138]}\) They contain complex metal ions MX$_6$\(^{3-}\) which are non-stable against reduction (Figure 7b), although reduction potentials are relatively low, that is, 0.6 V versus Li/Li$^+$ for Li$_3$YX$_6$ (X = Cl, Br).\(^{[139]}\) Similar to the sulfides, the decomposition products are intermetallic phases that lead to a self-propagating instable SSE at the Li-metal anode. Another type of halide-based Li-ion conductors are Li$_2$OX-type antiperovskites (X = Cl, Br).\(^{[173]}\) Since all non-lithium ions are fully reduced, they are intrinsically stable against lithium.

At the cathode side, most SSE are prone to oxidation. The anionic matrix determines the oxidation stability (Figure 7b). Halides exhibit the highest oxidation potentials where fluorides and chlorides are stable above 4 V. Bromides and iodides are less stable with oxidation potentials at about 3 and 2.5 V respectively.\(^{[150]}\) Oxidation is predicted to propagate via different phases. LLZO exhibits a comparatively low oxidation potential of 2.91 V due to the formation of peroxides (Li$_2$O$_2$) (Figure 7d). LITO and LATP are electrochemically stable up to 3.71 and 4.31 V, respectively.\(^{[147]}\) Decomposition reaction includes oxygen evolution which is furthermore kinetically hindered. Sulfides are prone to oxidation already at low potentials in the range of 2.1–2.3 V (Figure 7a/c). The associated decomposition products contain binary sulfides (e.g., P$_2$S$_5$, GeS$_2$), poly sulfides and elemental sulfur,\(^{[146,147]}\) resembling the principle of a lithium–sulfur battery.

### 5.2.2. Interfacial Effects

Besides thermodynamic stability, further interfacial effects affect the performance of SSB, that is, transfer resistances at solid-solid hetero-interfaces, mechanochemical contact loss due to volume changes, and active material utilization due to insufficient percolation. These effects have only a limited impact on the lithium inventory, thus they will be mentioned briefly, and appropriate references will be given for further reading.

The charge transfer at the active material/SSE interface is studied extensively. Oxide and sulfide electrolytes suffer from different issues in principle. Manufacturing of ceramic, oxide-based electrodes needs a co-sintering step. Chemical reactivity at high temperature is a general problem that is addressed by a reduction of the sintering temperature and time or the selection of appropriate materials.\(^{[174–177]}\) Sulfide electrolytes suffer from high charge transfer resistances due to the formation of a space-charge layer at the sulfide (electrolyte) and oxide (active material) interface.\(^{[178]}\) The introduction of an ion conducting, but electronic insulating active material coating showed a beneficial effect on the Li-transport across the interface.\(^{[179,180]}\) Active material coatings for SSE are studied extensively. Recent overviews can be found elsewhere.\(^{[181–183]}\) Upon cycling, active materials can undergo severe volume changes. AFSSB in special exhibit an infinite volume expansion from virtually zero expansion in the discharge state up to a defined thickness during Li-plating. In composite electrodes the rigid assembly of solid materials need to cope with these changes.\(^{[184–187]}\) Expansion and subsequent contraction thus can lead to a contact loss toward the ion conductor.\(^{[188,189]}\) Recent studies indicate that a contact loss at the SSE might not be a limiting factor in solid-state batteries.\(^{[190]}\) Volume expansion can be compensated by blending of active materials.\(^{[184]}\) Lab scale cells typically are operated under an external pressure. Reliable pouch cell manufacturing is still in development, thus, the effect of pressure on cathode material’s volume changes as well as anodic lithium plating-stripping is still unclear. Recent studies based on sulfide electrolytes show that the initial densification of the cathode is a main factor.\(^{[191–193]}\) Furthermore, the available capacity of solid-state batteries can be significantly lower than the nominal capacity due to insufficient electronic and ionic percolation in the composite cathode. As a result, not all active material particles are either electronically or ionically connected and the cathode active material utilization is reduced compared to conventional cells. More details on the utilization level can be found elsewhere.\(^{[194–199]}\)

### 5.2.3. Implications for AFSSB

To consider the application of SSE in AFSSB, anodic and cathodic decomposition reactions need to be discussed and studied independently. Both reaction types have an opposite impact on the lithium inventory. Anodic reactions to form a stable SSE are a sink of Li-ions which are not available for further battery cycling. Cathode electrolyte interface (CEI) formation on the other hand can indirectly work as an additional Li-source. This is demonstrated well by a “one-material battery” based on LGPS (Figure 8a–e). By preparing composite electrodes from LGPS and carbon black (LGPS-C) a symmetrical LGPS-C | LGPS | LGPS-C was set up. The extent of electrochemical activity is underlined by an almost reversible cycling in the range of 1.5–3.5 V, reaching a capacity of 300 mAh g$^{-1}$. Cycling within the voltage window 0–2.0 V gave a first discharge capacity of even 1000 mAh g$^{-1}$ and partially reversible cycling at a specific capacity of 200 mAh g$^{-1}$.\(^{[190]}\) The redox activity of SSE is prominent for most sulfide-based materials. Solid-state batteries typically exhibit a low CE in the formation cycle, which is dominated by an overcharging at the cathode.\(^{[189,200–202]}\) The instability of most SSE at the charging potential lead to decomposition, which depends on the type of conductive carbon and the magnitude of areal contact to the SSE (Figure 8f–k).\(^{[200]}\) Although CEI formation provides an additional Li-source to an AFSSB, the irreversible effects are detrimental to cell performance and cycle life due to a growing overpotential at the cathode. Different, typically electron isolating and ion conducting, coatings are developed to increase the stability at the active material/SSE interface and at the conductive carbon/SSE interface.\(^{[202,203]}\)

While decomposition and passivation reactions within a composite cathode need to be reduced to a level that allows stable operation of an AFSSB, irreversible anodic reactions directly reduce the Li-inventory and need to be avoided. AFSSB thus need a stable or chemically inert anodic interface. As discussed above, most of the common SSE are thermodynamically not stable against Li-metal. Only LLZO is kinetically stabilized to directly work in an AFSSB. Other materials can be stabilized by anodic coatings, that is, an artificial SEI. Artificial SEI development derives from the background of Li-metal.
Thus, the primary focus lies on the stabilization of SSE forming mixed conductors in contact with Li-metal. A simple approach is the passivation of Li-metal by phosphates (Li$_3$PO$_4$ or LiH$_2$PO$_4$) by treatment with phosphoric acid. The surface treated anode allows stable Li-stripping-plating in symmetrical Li$|\text{LGPS}||\text{Li}$ cells. In another approach LiPON was used as a passivation layer on oxide-based electrolytes. Still, these artificial SEI are not stable against Li-metal but form a passivation layer containing Li$_2$O, Li$_3$P, LiH, or Li$_3$N. They thus also reduce the Li-inventory during charging as in a native SEI formation process. Regarding AFSSB, intrinsically stable artificial SEI layers are crucial. Another approach makes use of the inert behavior of Al$^{3+}$ against reduction. Li-aluminates or Al$_2$O$_3$ can provide a stable protection on LPS, LATP, or garnet-type compounds. Further inorganic layers that allow an anodic cycling without decomposition reactions are LiF or LiI as shown for sulfide electrolytes. Hexagonal BN was applied to LATP allowing for a stable Li-stripping-plating in symmetrical cells.

The instability of the inorganic SSE can be furthermore circumvented by organic materials. Polyethylene-oxide based polymers are already used in Li-LFP batteries commercially by, for example, Boloré/Blue Solutions. Thus, PEO-films were applied as an interlayer to protect LATP against reduction. The inorganic-organic hybrid material alucone (aluminum alkoxide) was deposited by MLD on the non-stable LSPS sulfide electrolyte. Deposited films allowed a stable Li-stripping-plating in symmetrical cells. Despite the different works on Li-plating, numerical values of the Li-inventory of solid-state batteries are still ill-defined. Since typical experimental setups rely on an anodic Li excess, Li-loss during initial SEI formation, reversibility, and CE at the anode side are hardly addressed yet. The reported CE thus commonly reflect cathodic irreversibility.

### 5.3. Dendrite Formation

#### 5.3.1. Mechanisms of Dendrite Formation

Multiple studies have shown the formation of Li dendrites in solid-state batteries. It is a well-known issue that Li dendrites can cause short circuits in the cell by growing through the SES and corresponding mechanisms of dendrite propagation in SSE have been studied intensively. According to theoretical computations, the SSE needs to have twice the shear modulus of Li to suppress dendrite growth, thus >8 GPa. Although this is achieved by inorganic SSE, for example LLZO, dendrite growth is still observed. Thus, mechanically hardness is not the only sufficient factor affecting dendrite growth. Instead, several individual parameters and mechanisms were investigated in the past decade and found to influence dendrite formation.

As a measure for the stability against dendrite formation, the critical current density (CCD) is commonly used. This is the highest current density before short circuiting occurs. CCD found in literature range between 0.15 mA cm$^{-2}$ or below and values as high as 1 mA cm$^{-2}$. Although correlations within one study can be drawn, based on, for example, the influence of doping elements or interface resistances, comparison between different works are hardly possible, since the CCD measurement are not standardized and very sensible to compositional changes.

![Figure 8. Comparison of schematic diagrams of a) solid-state battery with anode and cathode active materials and b) a “one-material battery” consisting of Li$_2$GeP$_2$S$_2$ solid electrolyte only. Charge/discharge curves (100 mA g(LGPS)$^{-1}$) of Li/LGPS half cells in the voltage range of c) 1.0–3.5 and d) 0.0–2.0 V. e) Cycling stability of LGPS cathode, LGPS anode, and LGPS/LGPS full cell. Reproduced with permission. Copyright 2015, Wiley. Initial charge–discharge curves (115 µA cm$^{-2}$) of SSBs (In/LGPS/c-LCO) f–j) with different types of conductive carbon in composite cathodes and k) without carbon additives. A magnified view of the initial region is shown on the right. While without carbon additions the plateau (3.3 V vs In/InLi) of the active material is directly reached, in the presence of carbon a sloping region is observed before approaching the plateau, indicating the occurrence of side reactions. Reproduced with permission. Copyright 2017, American Chemical Society.](image)
temperature and pressure during measurement and the interface resistances as well as sample properties like density, microstructure, and surface morphology. However, several studies found the positive influence of larger grain size,[218,220] increased cycling temperature,[219] and low interface resistance.[217] In post mortem analysis, the dendrites were found to propagate mainly along the grain boundaries,[221] by filling open porosity[222] or opening of cracks at the surface.[223]

Mechanistic studies were performed to understand the driving forces of dendrite growth. A complexity of parameters was found to be influential. In a recent work, Krauskopf et al. provided a thorough overview of the failure mechanisms due to dendrite growth.[224] The authors assigned dendrite formation to two main factors: i) current focusing at the interface and Li⁺ flux imbalance, leading to dendrite formation from the interface and ii) internal Li plating due to a sufficiently high electronic conductivity in the SSE. The electronic conductivity was used to explain differences in the dendrite formation tendency of electrolyte materials, for example, low CCD of LLZO compared to high CCD of LiPON.[143] While electronic conductivity is a material property and should be addressed independently for individual SSE, current focusing is a general issue in SSB. Inhomogeneous current density results in current hotspots and islands of Li nucleation at the interface. Since the self-diffusion of metallic Lithium is quite low, the deposited Li accumulates at these hotspots and acts as starting point for dendrites. Figure 9 gives an overview about the origins of current focusing on the Li/SSE interface. Incomplete interfacial contact, due to surface contamination layers or pore formation at the interface during plating/stripping, results in high current density at the contact spots and high interfacial resistance.[225] A clear correlation between high interfacial resistance and increased dendrite formation has been shown in a study with single crystal LLZO, excluding influences like grain size or porosity.[217] In addition to initial contacting issues, local contact loss can occur during Li plating/stripping if currents are higher than the Li-metal self-diffusivity. During stripping, voids can be formed, while the remaining contact points act as current hotspots during plating cycles.[226,227] A recent theoretical study of Seymour and Aguadero demonstrated that the segregation of alkali metal vacancies at the interface is closely related to the interfacial structure and adhesion.[228] Very recently, a straightforward strategy that addresses Li-SSE interface issues has been proposed by Liu et al.[229] They introduced α-MoO₃ nanobelts into molten metallic lithium, forming a Li-Mo composite, which improves wettability on garnet electrolytes. The application of external pressure can significantly improve Li-metal anode performance. Due to the external force a second deformation induced creep mechanism can transport lithium to the surface during stripping overcoming the diffusion limitation.[227,230,231] However, the mechno-chemical properties of solid electrolytes limit the application of pressure. Too high pressure facilitates an "extrusion" of Li through cracks and micropores.[230,232,233] Simulations suggest a preferred stack pressure of 20 MPa to maintain a sufficiently low contact interface resistance.[223] For LLZO a critical stack pressure of 2 MPa was determined to allow stable stripping and plating at current densities of 0.4 mA cm⁻².[231] On the other hand, the mechnochemical properties of the SSE reduce the applicable stack pressure, that is, to about 5 MPa in the case of sulfide electrolytes.[230] The importance of electro-chemo-mechanics for SSB development has recently been discussed in detail by Wang et al.[17] including the mechanical behaviors of the solid electrolytes, Li metal, cathode materials and interfaces.

Besides incomplete contacting, surface heterogeneities, like grain boundaries at the SSE surface, local compositional changes or defects, can lead to an inhomogeneous electric field and thus uneven Li deposition. Although found in experimental studies,[221] explanations for dendrite growth along grain boundaries has been discussed ambiguously and is still under investigation. Contrary to earlier works,[218] computational studies did not confirm faster Li ion conductivity along the grain boundaries compared to the LLZO bulk.[218] Instead, a different hypothesis was introduced, attributing the Li plating along grain boundaries to their soft nature compared to bulk properties.[143] This theory is supported by simulation works of Barai et al.,[236] showing that the current density at softer grain boundaries is significantly higher than in the bulk area, even if the grain boundary conductivity is several orders of magnitude smaller than the bulk conductivity. Thus, to prevent this self-perpetuating process, a thorough interfacial design and electrolyte surface engineering are crucial.

5.3.2. Implications for AFSSB

AFSSB generally face the same issues regarding dendrite formation as LMSSB. However, in AFSSB, the CC acts as base for Li plating. Thus, the nucleation and early growth behavior at the CC/SES interface plays a crucial role compared to LMSSB. The absence of lithium is accompanied by challenges, for example, a conformal contact to the SES to avoid current focusing in

Figure 9. Schematic illustration of the origin of inhomogeneous current distribution at the solid electrolyte/anode interface. Reproduced with permission.[228] Copyright 2020, American Chemical Society.
the case of current collectors which are much tougher than Li metal. On the other hand, the absence of lithium also provides additional degrees of freedom, for example by selecting or modifying the current collector, the nucleation and initial growth of the lithium can be positively influenced in order to minimize dendrite growth.

Early studies of the nucleation behavior of Li at a Cu CC attached to an LiPON-SES showed the formation of distinct Li islands beneath the Cu instead of layer-by-layer growth (cf. Figure 10a). This correlates with the well-studied nucleation behavior in liquid electrolyte systems, which are summarized in the following. Studies on the nucleation behavior of Li on Cu in liquid electrolyte also revealed the formation of distinct Li nuclei. An increasing overpotential at the Cu was found to increase the number of Li nuclei while decreasing their size (cf. Figure 10b). Although this leads to a higher covering of the CC with the first layer of lithium nuclei, a high number of small nuclei also lead to more porous deposits and inhomogeneous Li plating during prolonged cycling. In contrast, a single nuclei seed layer consisting of a high amount of small Li nuclei seemed to be beneficial for the following Li plating at lower current densities. Temperatures above room temperature, for example 40–60 °C, enhance the formation of larger Li nuclei with homogenous growth. The experimentally observed growth behavior is in good agreement with theoretical predictions by Ely et al. who correlated the overpotential with the formation of different size nuclei over a certain incubation time. An increasing overpotential favors the formation of nuclei above the critical size. Thus, with higher overpotentials, a larger number of stable nuclei are formed.

![Figure 10.](image-url)
The tendency of Li for whisker growth was also investigated thoroughly in liquid electrolyte systems. Crystallographic investigations revealed the tendency of Li to grow preferably along the $<111>$, $<110>$, and $<211>$ directions in a cubic body centered structure, forming single crystal nanowires in liquid electrolytes,[243] This preference of 1D growth of Li metal is in contrast to other materials used for batteries, for example Mg, which rather plates as homogenous layer on a CC surface. This difference could be attributed to two facts: i) the stronger Mg$-$Mg bond, compared to Li$-$Li bond, which explains the preference of Mg to form more complex structures instead of 1D whiskers,[244] and ii) the high diffusion coefficient enables Mg to smoothen the surface after nucleation.[245] Thus, strategies to overcome this intrinsic 1D growth behavior are of the utmost importance to achieve a homogenous plating at the SSE/CC interface to avoid Li loss and dendrite formation. Several strategies aiming for smooth Li plating are discussed in literature. Obviously, in contrast to liquid electrolytes, in AFSSB the Li nucleation is not only affected by the type of CC but also by the interface at the SSE. Only few studies exist, which deal with the plating behavior of Li at SSE surfaces. At the LiPON surface, Li plating in form of whiskers was reported.[238,246,247] Sagane et al. as well as Motoyama et al. reported the plating potential at the Cu/LiPON interface, which has a similar characteristic like the reported nucleation in liquid electrolytes.[238,246]

In contrast to liquid electrolyte systems, high current densities of 1 mAh cm$^{-2}$ were found to be beneficial for uniform Li distribution at the CC/SSE interface due to a more lateral growth, while lower current densities lead to growth of Li whiskers.[238] It was observed that the Li islands are formed by loosening the SSE/CC contact locally until the CC breaks and an Li whisker is formed.[237] The formation of the Li islands depends on the Young’s modulus of the CC. A material with higher Young’s modulus or a thicker CC layer leads to fewer Li nuclei and a more lateral growth of the Li islands. Thus, designing the CC can affect the Li plating behavior significantly. Although Cu is widely used as CC in contact with Li metal, in AFSSB other materials should be considered, since Cu shows a high nucleation overpotential. The nucleation overpotential is significantly lower for CC materials with a higher solubility of Li, like Au, Ag, Mg, or Zn, as shown for liquid[248] as well as for solid electrolytes[248] (cf. Figure 10c). These alloying metals could be used as layers between the SSE and the CC or as seeds for controlled nucleation. The beneficial effect of nucleation sites at a SSE was shown experimentally by Liu et al.[249]

Krauskopf et al. investigated Li nucleation at the LLZO/Cu CC interface, which exhibited also a whisker-like behavior (cf. Figure 10d).[250] The whiskers are preferably formed at surface defects, but can also occur at the whole surface.[251] It was shown that the whisker formation during plating can lead to Li loss in AFSSB due to low reversibility, outlining again the importance of controlled layer-by-layer Li plating. In contrast to Cu, an Au CC was shown to form an alloy with Li (Li$_x$Au) and only after the alloy is fully formed, nucleation of lithium starts beneath the alloy layer, with the energy barrier being significantly lower than in the Cu system.[250] Kim et al. showed that different alloying metals, namely Ag, Au, and Si, exhibit different energy barriers for Li nucleation, which correlates well with the Li plating and stripping behavior (best for Ag with the lowest overpotential) and in the same way with the coulombic efficiency of a half-cell as well as full-cells.[248] In another study Okita et al. showed the benefits of a Pt coating at the Cu CC on top of an LiPON SES.[252] Effects of the CC material on CCD of various SSEs have been poorly studied so far and should receive more attention in future studies.

These results clearly show the importance of the current collector on the Li plating behavior in AFSSB. To develop AFSSB with sufficiently high energy densities and reversible cycling, the influences of current collector morphology and chemical or electrochemical interactions need to be further investigated. In addition to CC modification, interlayers according to the findings in LMSSB can be considered for AFSSB. A thorough overview of applicable interlayers is given by Park et al.[253] Although the conditions in solid systems vary strongly from the liquid system, the studies to date reveal certain parallels between the two systems. Therefore, the transferability of the behavior in the liquid to the solid system should be further investigated and strategies from LMB and LMSSB research areas should be evaluated regarding their applicability in AFSSB.

Most promising suppression strategies for Li dendrite growth in LMSSB were recently reviewed by Cao et al.[254] Fabricating SES with high density, few defects, smooth and impurity-free surface, or very low electronic conductivity at the grain boundaries is considered to decrease the tendency to form dendrites. The introduction or in situ formation of soft artificial interphase layers between the CC and the SES could decrease the interfacial resistance due to conformal contact, leading to lower overpotentials and less dendritic Li deposition. Modification of the CC by employing host structures, lithiophilic coatings and inorganic interlayers could lead to more even Li deposition and higher reversibility as observed for AFLMB.[255] These approaches are partially similar or complementary to the strategies for increasing interface stability and enhancing CE. Consequently, it appears to be purposeful to develop holistic, synergistic strategies that master the individual challenges all at once.

### 5.4. Cell Design and Practical Energy Density

The energy density estimations regarding LMSSB and AFSSB in Figure 1 were made by replacing the liquid electrolyte in LMB and AFLMB, respectively. This includes thin SES, low volume fractions of SSE in the cathode, and limited Li resources or a bare CC on the anode side. Most literature reports on LMSSB and AFSSB are based on laboratory-scale studies, typically not using application-relevant dimensions or proportions of the inactive materials or introducing additional functional layers. This makes it difficult to estimate the actual achievable energy density and can result in performance parameters that are significantly behind those of conventional LIBs.[36] Randau et al. provided a comprehensive analysis, benchmarking the performance of solid-state lithium batteries.[255] Based on their literature survey and extensive analysis, the authors concluded that the differences in specific energy and specific power of available solid state batteries mostly originate from differences in layer thicknesses and internal resistance. They highlight that high specific energy and high specific power are difficult to achieve...
as long as thick SES are used. Figure 11a depicts the impact of the SES (Li₆PS₅Cl) thickness on the GED and VED of AFSSB. Both the GED and VED dramatically decrease with increasing thickness of the SES, pointing out the urgent need for thin SES (<20 µm for 401 Wh kg⁻¹ or 1460 Wh L⁻¹) and corresponding scalable fabrication methods. However, the latter dramatically depends on the type of SSE. Whereas sulfides can be prepared by slurry casting, and polymers can be fabricated at the large scale using tape casting or pouring technology, oxides must be sintered, complicating large scale continuous production.[36] Lee et al.[113] achieved a favorable SES (Li₆PS₅Cl) thickness of 30 µm by slurry casting and subsequent pressurization in a cell. Zegeye et al.[112] demonstrated a composite SES with a thickness of 15–20 µm prepared from LiTFSI in PEO and LLZTO using a spin-coating method. Schiffmann et al.[256] developed 25 µm thin SES based on LLTO by tape casting and subsequent sintering. Considering the GED, the implementation of oxidic SSE becomes even more challenging (Figure 11b). Due to the higher mass density, the energy density becomes more sensitive to the thickness of the SES. Thus, AFSSB employing oxidic SES must be designed carefully to outperform conventional LIB.

Similar to the thickness of the SES, the volume fraction of the SSE in the composite cathode affects the GED and VED of the AFSSB.[253] The energy density dramatically decreases with increasing SSE volume fraction in the composite cathode (Figure 11c). For example, when increasing the SSE volume fraction from 25% to 50%, the GED (VED) decreases from 408 Wh kg⁻¹ (1414 L⁻¹) to 313 Wh kg⁻¹ (1010 Wh L⁻¹). Thus, the SSE volume fraction in the composite cathode is a sensitive parameter that must be optimized carefully to make LMSSB and AFSSB competitive to established LIB. Model-based analyses show that SSE volume fractions of 20% are sufficient to provide ionic conductivity in the composite cathode that allows application-relevant charging rates.[194,195,199] However, there is a lack of suitable manufacturing processes capable to produce such composites in large formats with sufficiently low porosity.

Significant progress in AFLMB and AFSSB development has been achieved by implementing host structures, lithiophilic coatings or protective layers to facilitate homogenous Li plating and stripping and to increase the reversibility. However, these measures to some extent diminish the actual advantages of the anode-free configuration in terms of simplified production, material and cost savings as well as higher energy density. Figure 11d shows the results of a sensitivity analysis regarding the influence of the thickness and Ag volume fraction of an Ag–C composite layer on the anode CC on the GED of an AFSSB. As expected, the thicker the Ag–C composite layer and the higher the Ag loading, the lower the GED. For example, the GED (VED) is reduced from 408 to 352 Wh kg⁻¹ (1514 to 1278 Wh L⁻¹) compared to the bare CC when applying an Ag–C composite layer of 25 µm with 15 vol% of Ag. Lee et al.[113] used Ag–C nano-composite layers of 5–10 µm with approximately 8 vol% of Ag in AFSSB and achieved excellent CE, VED, and cycle life characteristics. Ultimately, the question must be asked as to what really makes an “anode-free” solid-state battery. Many promising approaches are based on the incorporation of lithiophilic coatings or CC with specific architectures to accommodate the deposited Li. In this context, it is unclear whether the principal advantages of AFSSB are still retained in practical cells, which should be considered carefully for future developments.
6. Conclusions and Perspectives

The anode-free configuration is a milestone in the development of solid-state batteries. AFSSB delivers the highest possible energy density by eliminating the anode active material and utilizing the maximum possible voltage output of the cathode. Due to the high specific volume of lithium, the gain in volumetric energy density can be particularly large compared to LMSSB with high N/P ratios. From a practical point of view, the elimination of free Li metal during cell manufacture and simplified cell assembly are significant advantages. Furthermore, AFSSB can reduce the cost per kWh by reducing materials consumption as well as energy demands during electrode production.

Figure 12 summarizes the promising design strategies for realizing high-performance and long-term stable AFSSB. Most of the knowledge gained from research on anode-free batteries employing liquid electrolytes can be transferred to the nascent field of AFSSB to accelerate the development process. In particular, synergistic approaches that combine the advantages of host structures, lithiophilic coatings, protective layers, pressurization, and specific formation protocols appear to be highly promising. However, some non-trivial challenges must be overcome before AFSSB can move to market. Initial CE and reversibility of Li-plating/stripping during cycling is extremely critical to the practical energy density and cycle life of AFSSB. While an AFSSB provides double the nominal volumetric energy density of an LIB, its practical success will be determined by the ability to reach an equal cycle life. Model based estimations indicate very high Coulombic efficiencies ≥ 99.9% to be required in AFSSB to achieve cycle life characteristics competitive to established Li-ion batteries. Only this will preserve the superiority against state-of-the-art LIBs in terms of energy density for approximately 1000 cycles. Modification of current collectors, including suitable host structures in combination with lithiophilic coatings, has been shown to be a viable option for increasing reversibility and should be further optimized to achieve CE close to 100%. Interfacial issues related to the thermodynamic stability of SSE need to be tackled by targeted interface engineering including protective coatings at the anode current collector and the cathode active material as well as by the development of novel SSE materials (i.e., oxidation stable halides).

Figure 12. Promising design strategies for realizing high-performance and long-term stable anode-free solid-state batteries.
The anode side current collector/solid electrolyte interface has significant influence on the Li nucleation behavior, which in turn affects Li growth characteristics. To avoid dendritic growth of Li through the solid-electrolyte separator and associated cell failure, targeted choice of materials and interface design is required. For example, comprehensive studies in liquid electrolytes show a significant dependency of Li plating mechanism on the type and surface states of current collector material. Such correlations should be further investigated for solid electrolytes, where only few studies exist. Furthermore, it has also not yet been investigated how unavoidable current density inhomogeneities in large-format cells affect Li deposition and whether homogeneous plating is possible at all in this case.

The practical energy density of AFSSB is sensitive to the cell design and the share of inactive materials. Model-based analyses show the necessity of using very thin solid-electrolyte separators and low volume fraction of the solid-electrolyte in the composite cathode to provide energy density competitive to established Li-ion batteries. Regarding gravimetric energy density, this issue becomes more the higher the density of the solid electrolyte used, that is, for oxidative SSE. While using host structures, lithiophilic coatings or protective layers on the anode current collector has been shown to improve the cycling stability of AFSSB, model-based analyses indicate that extensive use of these measures can dramatically reduce the energy density, outweighing the actual advantages of AFSSB. Therefore, these correlations should be considered carefully, otherwise the principle benefits of AFSSB will not hold for practical cells. To achieve this, scalable manufacturing processes must be developed that enable the production of components in the required geometric dimensions. The most promising approaches with prospects for continuous mass production are slurry-based casting processes for composite cathodes and SES. Regarding the anode side, many strategies for improving AFSSB have been successfully demonstrated at the laboratory level. However, a direct transfer to practical batteries seems very challenging in most cases. The laboratory-level strategies help tremendously in solving the problem from the mechanistic point of view. However, for commercial deployment, rational application techniques are important to realize these solutions in scaled battery systems. In the future, this aspect should also be given greater focus in developments at the laboratory level. With this review, we hope to further stimulate interest in AFSSB, as extensive research is still needed to explore the fundamental mechanisms through multiscale analysis, insightful performance development, and practical fabrication to realize market-ready AFSSB.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anode-free batteries, Li-metal, solid-state batteries, zero-excess

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