

Toward Sustainable All Solid-State Li–Metal Batteries: Perspectives on Battery Technology and Recycling Processes

Xiaoxue Wu, Guanjun Ji, Junxiong Wang, Guangmin Zhou,* and Zheng Liang*

Lithium (Li)-based batteries are gradually evolving from the liquid to the solid state in terms of safety and energy density, where all solid-state Li–metal batteries (ASSLMBs) are considered the most promising candidates. This is demonstrated by the Bluecar electric vehicle produced by the Bolloré Group, which is utilized in car-sharing services in several cities worldwide. Despite impressive progress in the development of ASSLMBs, their avenues for recycling them remain underexplored, and combined with the current explosion of spent Li-ion batteries, they should attract widespread interest from academia and industry. Here, the potential challenges of recycling ASSLMBs as compared to Li-ion batteries are analyzed and the current progress and prospects for recycling ASSLMBs are summarized and analyzed. Drawing on the lessons learned from Li-ion battery recycling, it is important to design sustainable recycling technologies before ASSLMBs gain widespread market adoption. A battery-recycling-oriented design is also highlighted for ASSLMBs to promote the recycling rate and maximize profitability. Finally, future research directions, challenges, and prospects are outlined to provide strategies for achieving sustainable development of ASSLMBs.

solvent with the anode, decomposition of the solid electrolyte interface (SEI) and cathode, and generation of flammable gases and oxygen, which may potentially lead to fires, explosions, and other safety issues.^[3,4] The root cause of the safety issues inherent to LIBs is the use of combustible liquid electrolytes, which have raised global concerns. These problems have been exacerbated in next-generation, high energy-density lithium-based batteries, such as Li–metal, Li–sulfur (Li–S), and Li–oxygen/air (Li–O₂/air) batteries.^[2,5] As a result, advances in safety and energy density are needed to keep pace with the rapidly growing market demand. Additionally, the development of high-energy-density and safe rechargeable Li-based batteries is crucial to decarbonize future transportation.

Replacing liquid electrolytes with solid-state electrolytes (SSEs) is considered a promising method for improving the safety and energy density of LIBs. For all solid-state Li-ion batteries (ASSLIBs), i.e., those

using SSEs and graphite anodes, the energy density will increase by more than 20% compared to LIBs when matched with high-voltage cathodes or high-capacity cathodes (cannot be matched with liquid electrolytes).^[6] However, given the practical limitations of the cathode/anode chemistry of LIBs, there is limited scope for improving their energy densities. Li–metal, as the ultimate anode, has attracted extensive research due to its high theoretical specific capacity (3860 mAh g⁻¹) and low electrochemical potential (-3.04 V vs standard hydrogen electrode).^[7] As an alternative to LIBs, all solid-state Li metal batteries (ASSLMBs) have received widespread attention from academia and industry owing to their safety and high energy density (>500 Wh kg⁻¹) (Figure 1).^[8,9] Given the limited resources, environmental sustainability, and urgent need for battery recycling once the current generation of electric vehicles is retired (the global LIBs recycling market is predicted to grow to \$23.72 billion by 2030), sustainable battery recycling technologies are important for future growth of this market.^[10]

Unfortunately, despite the impressive progress made in the application of LIBs, technologies for sustainable recycling of spent LIBs are not well established. Although the application of recycling technologies for LIBs such as pyrometallurgy and hydrometallurgy have been explored, none of these technologies are specifically designed for LIBs and suffer from low recovery rates, high energy consumption, and environmental

1. Introduction

Since the commercialization of lithium (Li)-ion batteries (LIBs) in the 1990s,^[1] their excellent properties, such as high energy density (approximately 250 Wh kg⁻¹), excellent cycle life, low self-discharge, and light weight, have greatly contributed to the proliferation and rapid progress of portable electronic devices and electric vehicles (EVs).^[2] However, when LIBs are overheated, their temperature rises exponentially, leading to thermal runaway, resulting in the melting of the separator, reaction of the organic

X. Wu, G. Ji, J. Wang, Z. Liang
 Frontiers Science Center for Transformative Molecules
 School of Chemistry and Chemical Engineering
 Shanghai Jiao Tong University
 Shanghai 200240, China
 E-mail: liangzheng06@sjtu.edu.cn
 X. Wu, G. Ji, J. Wang, G. Zhou
 Shenzhen Geim Graphene Center
 Tsinghua-Berkeley Shenzhen Institute & Tsinghua Shenzhen International Graduate School
 Tsinghua University
 Shenzhen 518055, China
 E-mail: guangminzhou@sz.tsinghua.edu.cn

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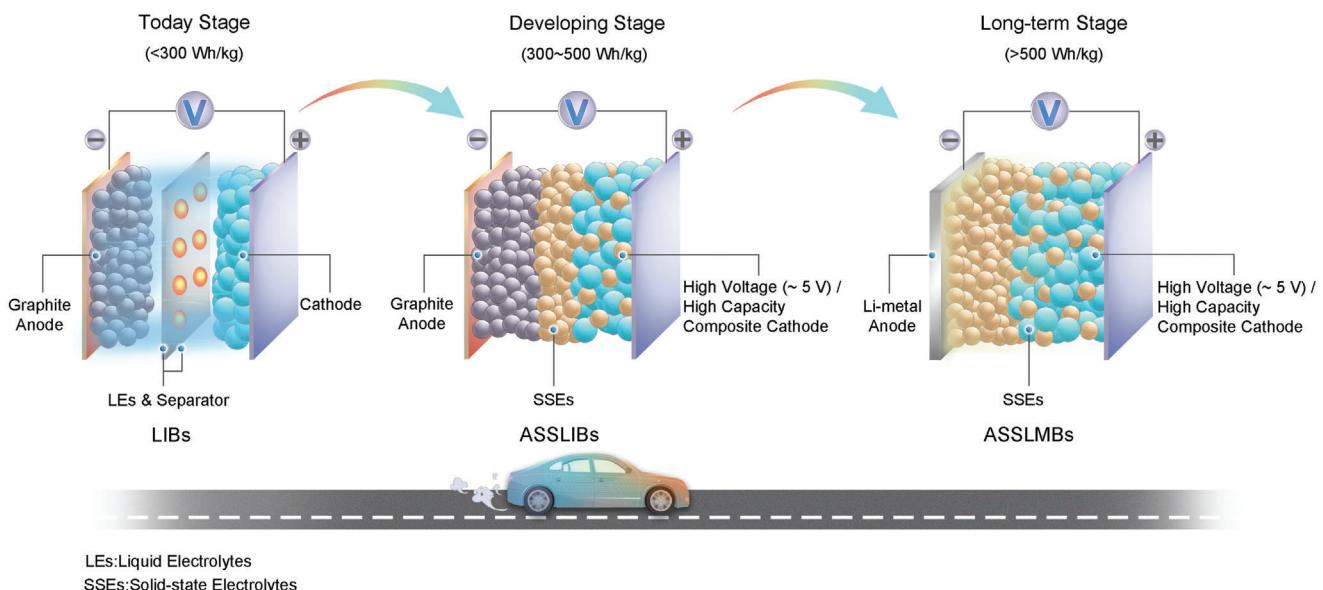


Figure 1. A brief schematic diagram of the development trend of Li-based batteries from LIBs to ASSLMBs.

unfriendliness.^[10–12] While simple and economical direct regeneration technologies (i.e., nondestructive recycling technology) have been demonstrated on a laboratory scale, several challenges remain, including gentle pretreatment processes to avoid chemical decomposition of materials, ensuring high purity of products, and industrialization of the technology.^[10–12] Compared to LIBs, the introduction of SSEs and Li metal anodes will introduce greater challenges to the recycling of ASSLMBs.^[13,14] Therefore, it is important to develop recycling-oriented battery designs and economic and sustainable recycling technologies for ASSLMBs before they are widely adopted in the market.

In this review, we begin with a brief summary of the developments in ASSLMBs technology. Four types of SSEs (i.e., oxide-, sulfide-, halide-, and polymer-based SSEs) are distinguished based on their typical chemical properties, moving from an understanding of their intrinsic properties to the rational design of SSEs for practical applications. However, the different types of SSEs applied to ASSLMBs face specific issues and challenges. A comparison of the structures and chemical components of ASSLMBs with those of LIBs reveals the challenges of ASSLMBs recycling with the introduction of SSEs and Li-metal anodes. We also discuss the feasibility of LIB recycling technologies such as pretreatment, pyrometallurgy, hydrometallurgy, and direct regeneration in ASSLMBs recycling as well as recent advances in recycling technologies for ASSLMBs. In particular, the importance of a battery-recycling-oriented design for ASSLMBs is highlighted. Finally, future research directions, remaining challenges, and perspectives on sustainable ASSLMBs recycling are highlighted.

2. Development and Progress of ASSLMBs

Currently, research into battery systems is primarily focused on safety, high energy density, low cost, and minimal environmental impact. Replacing conventional liquid electrolytes and graphite

anodes with solid-state electrolytes (SSEs) and Li metal, respectively, opens a new path for addressing safety issues and the growing energy density demand. The improved safety and energy density of ASSLMBs offer great possibilities for their application in various situations. However, the application of ASSLMBs is still in its infancy and they suffer from issues including poor interface contact, low ionic conductivity, and poor structural design of electrodes. Current lab-level ASSLMBs design and optimization is mainly based on solving the above problems but under precisely controlled internal and external conditions (such as temperature and pressure). Therefore, although some advanced methods have been validated in lab-level ASSLMBs, only a few successful experimental results are available on a practical scale, and there is a huge gap between lab- and scaled-up ASSLMBs. In the 2–4 section, we comprehensively examine the ASSLMB technology by covering four areas: recent advances, design, and manufacture, gaps in scale-up, and failure mechanisms. This will provide guidance for follow-up designs and research into sustainable ASSLMBs. In this section, we will focus on the development and progress of ASSLMBs, including SSEs, cathode, and anode.

2.1. SSEs

Replacing liquid electrolytes with SSEs can not only overcome the safety issues originating from the use of combustible organic solvents but also offer the possibility of achieving high energy density for Li-based batteries.^[15] The origin of SSEs can be traced back to the 1960s when $\text{Na}^+ \cdot \beta\text{-Al}_2\text{O}_3$ SSEs were introduced into sodium–sulfur (Na–S) batteries.^[16] With the discovery of polymer ionic conductors based on polyethylene oxide (PEO) in 1973, the scope of SSEs was no longer limited to inorganic conductors.^[17] Intensive studies have been conducted in both academia and industry to develop novel SSEs for high-performance ASSLMBs (Figure 2a). We believe that important breakthroughs will be

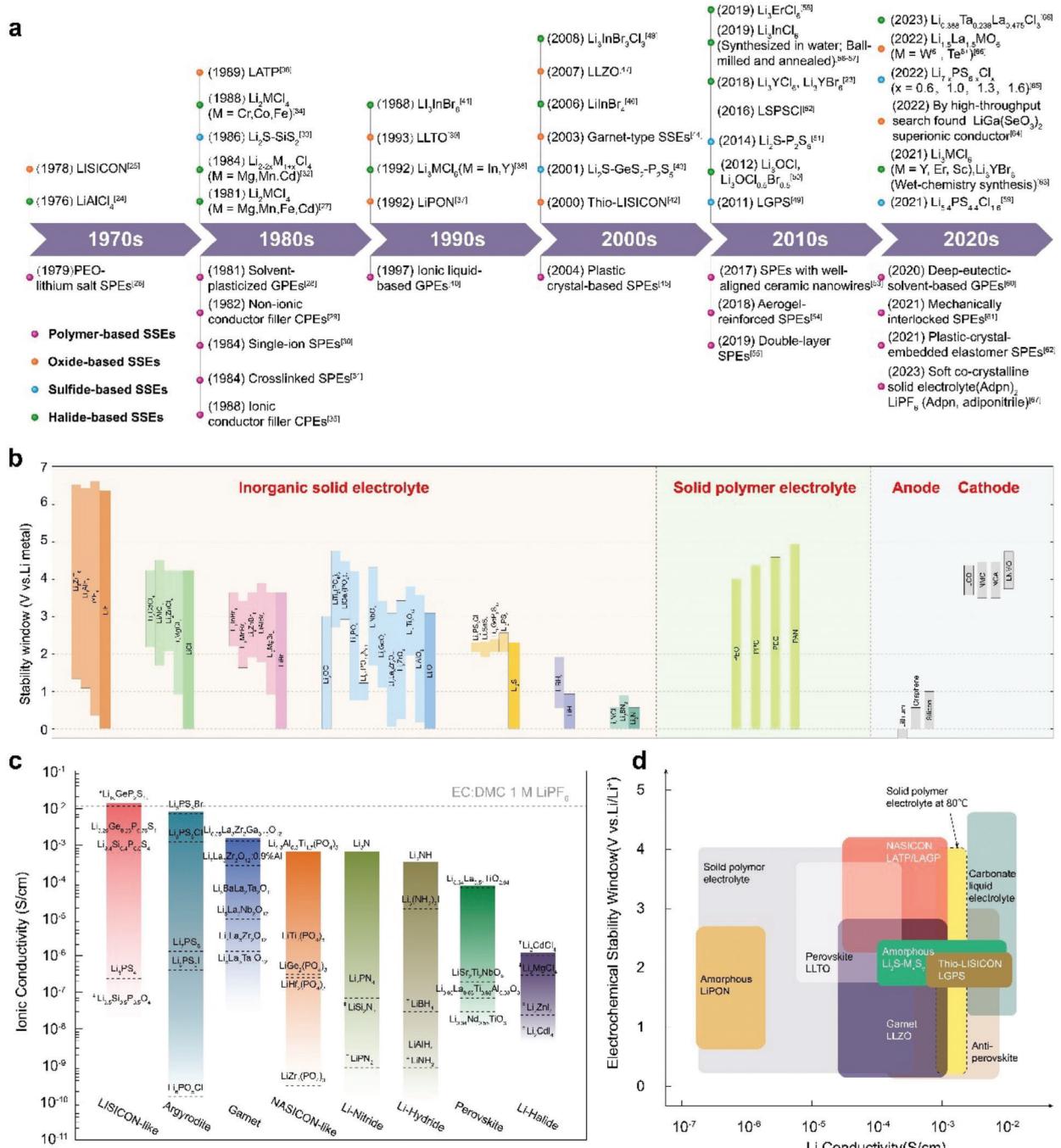


Figure 2. a) A brief chronology of typical SSEs for solid-state lithium-based batteries.^[23–68] b) Illustration of different types of SSEs stability windows versus anodes and cathodes operating potential. Adapted with permission.^[21] Copyright 2015, American Chemical Society. c) Illustration of the total ionic conductivity of inorganic SSEs at room temperature. Reproduced with permission.^[22] Copyright 2016, American Chemical Society. d) Comparison of electrochemical window and room temperature ionic conductivity (except that labeled with dashed line) of different types of SSEs. Reproduced with permission.^[18] Copyright 2020, American Chemical Society.

achieved in the near future. As a key component of ASSLMBs, an ideal SSE should simultaneously satisfy several vital criteria in terms of high ionic conductivity (i.e., similar to that of liquid electrolytes at room temperature), low electronic conductivity, excellent chemical/electrochemical stability, low interfacial resistance, and sufficient mechanical strength.^[18–20] Despite their promi-

nent advantages, challenges remain in the practical application of ASSLMBs (e.g., interfacial side reactions, low total ionic conductivity, high interfacial resistance, and poor air stability).^[18,19] For example, although many SSEs have a wide window of electrochemical stability, some have remained unstable to the lithium metal anode at low potentials and react with the cathode,

resulting in low interfacial charge transfer kinetics. The electrochemical stability windows of common SSEs compared to electrode materials are shown in Figure 2b,d.^[18,21] In addition, ionic conductivity, another important SSE parameter, can vary by several orders of magnitude even within the same structural family. The total room temperature ionic conductivities of well-known SSEs are presented in Figure 2c,d.^[18,22] Generally, SSEs for ASSLMBs can be divided into three major categories: oxide-, sulfide-, and polymer-based.^[9] In recent decades, halide-based SSEs have been less attractive due to their inferior ionic conductivity compared to oxide- or sulfide-based SSEs. However, a pioneering study in 2018 was able to achieve high room temperature ionic conductivity in halide-based SSEs, leading to renewed attention.^[23] This section will also address advances in the development of halide-based SSEs. Various types of SSEs, classified according to their components and chemical properties are introduced in this section.

2.1.1. Oxide-Based SSEs

Satisfactory ionic conductivity at room temperature (i.e., close to that of liquid electrolytes at room temperature) is a prerequisite for the use of SSEs in ASSLMBs, and oxide-based SSEs have met these requirements. In addition, oxide-based SSEs exhibit higher chemical and electrochemical stability than sulfide-based SSEs.^[69,70] However, because of the high mechanical rigidity of oxide-based SSEs, high-temperature sintering of the SSEs and composite cathodes is required to achieve close contact between the particles inside SSEs, and SSEs/cathodes.^[71,72] Generally, oxide-based SSEs for ASSLMBs can be divided into the following major categories: garnet (e.g., $\text{Li}_5\text{La}_3\text{Zr}_2\text{O}_{12}$), perovskite (e.g., $\text{Li}_{3.3}\text{La}_{0.56}\text{TiO}_3$), NASICON (e.g., $\text{LiTi}_2(\text{PO}_4)_3$), and LISICON-type (e.g., $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$) SSEs.^[19]

Garnet-type SSEs: Among all oxide-based SSEs, garnets are the most frequently utilized SSE type because of their high ionic conductivity, wider electrochemical window, and better SSE/Li-metal anode compatibility. In 2003, Thangadurai et al. first proposed a novel Li-ion oxide conductor, $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (where M is Nb or Ta), with a garnet-like structure and a room-temperature ionic conductivity of 10^{-6} S cm^{-1} .^[44] Subsequently, a novel cubic garnet-type structured $\text{Li}_{7-x}\text{La}_x\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12}$ (LLZTO, $0.4 \leq x \leq 0.6$) SSE was synthesized by element doping and structure optimization, and the ionic conductivity at room temperature reached 10^{-3} S cm^{-1} .^[73] High ionic conductivity is of high significance for garnets for their application in SSEs, which is affected by several factors such as lithium concentration, lithium coordination environment, and grain boundary resistance.^[18,69]

Perovskite-type SSEs: Li-based perovskites are another class of ionic conductors with the basic formula $\text{Li}_{3x}\text{La}_{2/3-x}\square_{1/3-2x}\text{TiO}_3$ ($0 < x < 0.16$, where \square is a vacancy) (LLTO), and structurally related materials all exhibit excellent bulk ionic conductivity at room temperature (up to 10^{-3} S cm^{-1}).^[39] However, due to the high grain boundary resistance, the overall conductivity of the assembled ASSLMBs is only 10^{-5} S cm^{-1} . Despite the high bulk grain ionic conductivity of perovskite-type SSEs, the limited grain-boundary ionic conductivity (potentially originating from charged grain-boundary cores and an insulating secondary phase at the grain-boundary phase) limits the overall performance of

the battery and may become the growth point of lithium deposition and lithium dendrites, restricting their application in ASSLMBs.^[2,74] Various strategies have been applied to improve the grain-boundary ionic conductivity of perovskite-type SSEs, such as employing an amorphous-silicate boundary layer, optimizing the proportion of Li in SSEs, and increasing sintering temperature.^[75–77] NASICON-type SSEs (i.e., sodium superionic conductors) are another large family of oxide-based SSEs with the formula $\text{Li}_{1+x}\text{A}_x\text{M}_{2-x}(\text{PO}_4)_3$ (where A is a trivalent cation, e.g., Al^{3+} , La^{3+} , and M is a tetravalent cation, e.g., Ti^{4+} , Ge^{4+}).^[18,78] Because of the prominent advantages of NASICONs, a series of novel derivatives have been designed and prepared; two representative compounds in this category (e.g., $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) and $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP)) have attracted significant research interest in recent years because of their high ionic conductivity at room temperature ($7 \times 10^{-4}\text{ S cm}^{-1}$), wide electrochemical window (6 V), and property of being air-stable.^[19,69,79]

LISICON-type oxide-based SSEs: LISICON-type SSEs (i.e., lithium superionic conductor) were discovered in 1978 when Hong et al. reported on a $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ Li-ion superionic conductor with a conductivity of 0.13 S cm^{-1} at $300\text{ }^\circ\text{C}$.^[25] Although LISICON-type SSEs have the advantages of thermal and water stability, their low ionic conductivity at room temperature and unstable contact with the Li metal and air limit their further development.^[80]

Currently, the development of oxide-based SSEs is still at the lab level, with research focusing on component and surface optimization. Because garnet-type SSEs are unstable in air, SSEs will react with water or CO_2 to form contamination layers (generating LiOH or Li_2CO_3) at the surface of the SSE, resulting in poor SSE/Li metal anode interfacial contact.^[81,82] Consequently, as garnet-type SSEs are synthesized or densified in air, the risk of surface contamination must be reduced to achieve a lower SSE/electrode interface impedance. Therefore, understanding the surface chemistry and stability of garnet-type SSEs is important for the development of ASSLMBs that employ garnet as a solid-state electrolyte. For perovskite-type SSEs, because Ti^{4+} undergoes reduction when in contact with Li metal, the LLTO interface also needs to be optimized to match the Li metal anode.^[83] NASICON-type SSEs are also unstable (i.e., Ti^{4+} and Ge^{4+} in LAT(G)P are reduced to Ti^{3+} and elemental Ge, respectively) when in contact with the Li metal anode, leading to continuous chemical-mechanical degradation and impedance growth.^[21,84] Clearly, direct-contact NASICON-type SSEs and Li-metal anodes result in unstable ASSLMBs; thus, further optimization of the SSE interface is required.

2.1.2. Sulfide-Based SSEs

$\text{Li}_2\text{S}-\text{SiS}_2$, as the earliest studied sulfide-based SSE, pushed the research of SSEs to another climax and has aroused great interest in the research of ASSLMBs.^[33] Over the past years, sulfide-based SSEs have attracted great attention because of their high ionic conductivity and advantages (e.g., solution processability, and they can be deformed under cold pressing) for battery manufacturing of sulfide-based SSEs compared with oxides.^[18,19,69] Generally, sulfide-based SSEs can be divided into two categories: binary and ternary systems. Binary systems consist of

Li_2S and P_2S_5 , such as Li_3PS_4 and $\text{Li}_7\text{P}_3\text{S}_{11}$; while ternary systems consist of Li_2S , P_2S_5 , and MS_2 (where M is Si, Ge, or Sn), such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and $\text{Li}_6\text{PS}_5\text{X}$ (where X is Cl, Br, or I).^[85] For sulfide-based SSEs with the same composition, the ionic conductivity of glass systems is at least one order of magnitude higher than that of crystalline systems because the reduction in crystallinity eliminates the grain boundary resistance. In 2001, LISICON-type sulfide-based SSEs were discovered in the $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ system and exhibited high ionic conductivity of $2.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C .^[43] In addition, heat treatment densification can further increase the ionic conductivity of sulfide-based SSEs; the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass system obtained an ionic conductivity ($1.7 \times 10^{-2} \text{ S cm}^{-1}$) close to that of the liquid electrolyte.^[51] Since these pioneering studies, sulfide-based SSEs have undergone rapid progress owing to their high ionic conductivity and densely packed electrolyte/electrode interfaces resulting from electrolyte plasticity.^[86]

Despite the excellent mechanical processability and high ionic conductivity of sulfide-based SSEs, their limited chemical and electrochemical stability remains a pressing issue.^[18,19,69] These issues include 1) stability between the composite cathode and SSEs: degradation at cathode/SSEs (e.g., facile oxidation of S^{2-} at approximately 2–2.5 V, leading to a decrease of lithium content and the formation elemental sulfur in SSEs;^[70,84,87] exchange of S^{2-} and O^{2-} , leading to the chemical mixing between cathode and SSEs and the formation of polyanions (e.g., PO_4^{3-} , SO_4^{2-}) and transition-metal sulfides (e.g., Co_9S_8 , Mn_2S_3)),^[21,70] and carbon (or current collector)/SSEs (i.e., accelerated decomposition of SSEs at carbon (or current collector)/SSEs interface, where SSEs and carbon/current collector provide Li-ions and electrons transport paths, respectively, leading to continued degradation of SSEs and ultimately decay of battery performance)^[88–90] interface, resulting growing interfacial resistance and capacity fade, especially at first-cycle; 2) stability between Li–metal anode and SSEs: P^{5+} and transition cations (e.g., Ge^{4+} , Sn^{4+}) in SSEs are reduced to lithium binary compounds (e.g., Li_3P , Li_2S), lithium alloys (e.g., Li–Ge), and metals (e.g., Ge).^[91–94] However, the formation of lithium alloys and metals at the SSE/Li–metal anode interface is detrimental and eventually results in the formation of electronically conducting metal chlorides and metal sulfides, driving the continued decomposition of SSEs.^[94,95] In contrast, many lithium binary compounds (e.g., LiI and LiCl) that exhibit ionic conductivity and electronically insulating properties are stable when in contact with Li metal anodes, contributing to the construction of a stable SSE/Li–metal anode interface and promoting stable battery cycling.^[21,95,96] Furthermore, the poor air stability of sulfide-based SSEs is their Achilles heel, which results in the generation of H_2S toxic gas in contact with water (i.e., hydrolysis reaction) and the increased processing cost from the dry inert atmosphere requirements, limiting their commercial application.^[97–99] Modification strategies, such as optimizing the composition of SSEs (e.g., phosphorous-free),^[100,101] substituting sulfur with oxygen (i.e., introducing oxides),^[102] can maintain high ionic conductivity and improve the air stability of sulfide-based SSEs. However, further clarification of the air stability of sulfide-based SSEs is important, and strategies for developing novel approaches to overcome the acute degradation of sulfides are urgently required.

2.1.3. Halide-Based SSEs

Since the 1930s, the ionic conduction behavior of halide-based SSEs (e.g., LiF, LiCl, LiBr, and LiI) has been evaluated; however, they were overlooked due to their low room temperature ionic conductivity ($<10^{-7} \text{ S cm}^{-1}$).^[103] Despite the extensive research on SSEs with lithium halide, including LiAlCl_4 , Li_2MnCl_4 , and Li_3InBr_6 , their inadequate ionic conductivity compared to oxide- or sulfide-based SSEs rendered them less attractive.^[24,27,104] In fact, it was not until 2018 that Asano et al. reported a groundbreaking study on high-energy ball milling and high-temperature annealing to synthesize halide-based Li_3YCl_6 and Li_3YBr_6 SSEs with high room temperature ionic conductivity ($>10^{-3} \text{ S cm}^{-1}$).^[23] Subsequently, halide-based SSEs have undergone rapid advancements due to their high ionic conductivity, which is similar to that of liquid electrolytes. Halide-based SSEs are generally formulated as Li_aMX_b (X = F, Cl, Br, I) based on the LiX matrix structure, with M (metal or non-metal) element doping and vacancy formation. Halide-based SSEs can be classified into four categories based on the M element type: 1) M is a group 3 element (e.g., Sc, Y, La–Lu); 2) M is a group 13 element (e.g., Al, Ga, In); 3) M is a divalent metal element (e.g., Ti, Mn, Fe, Cu, Zn, Mg); 4) M is a non-metal element (e.g., O, S, N).^[105]

Studies on halide-based SSEs with group 3 metal elements date back to 1984. However, despite early efforts, the resulting electrolytes did not garner significant attention until 2018.^[106,107] Following the synthesis of SSEs with high room temperature ionic conductivity ($>10^{-3} \text{ S cm}^{-1}$),^[23] several doping modification studies were performed, all demonstrating high room temperature ionic conductivity.^[23,108,109] Theoretical calculations suggested that certain electrolytes of this type could achieve a room temperature ionic conductivity $> 10^{-2} \text{ S cm}^{-1}$.^[110]

Halide-based SSEs with group 13 metal elements, developed in the 1970s are further categorized into the Li-Al-X , Li-Ga-X , and Li-In-X (X = F, Cl, Br, I) systems.^[24,111] Among these, the Li-In-X system, particularly the Li-In-Br system, has received considerable attention. In 1998, Yasumasa et al. reported that the Li_3InBr_6 ionic conductor exhibits superb room temperature ionic conductivity ($10^{-3} \text{ S cm}^{-1}$).^[41] Li_3InBr_6 and its substituted derivatives only exhibit high room temperature ionic conductivity during their high-temperature phase.^[48,112,113] Another Li-In-Br system (LiInBr_4) exhibits similar properties and requires conversion to a high-temperature superionic phase to possess high ionic conductivity ($10^{-3} \text{ S cm}^{-1}$ at 27°C).^[46] However, the poor thermal stability of the Li-In-Br system manifests the transformation of the high-temperature phase structure to the low-temperature phase structure during the cooling process, leading to a sharp decrease in ionic conductivity. This has severely limited the development of this SSE type and has led a gradual decrease in research interest. Meanwhile, Li_3InCl_6 , has demonstrated significant progress in recent years. Sun et al. were the first to synthesize SSEs with room temperature ionic conductivity of $10^{-3} \text{ S cm}^{-1}$ and develop a facile and scalable water-mediated synthesis route.^[56,57]

Divalent metal element-based halide SSEs have generally been divided into four categories: olivine, spinel, distorted, and Suzuki structures.^[34,114–116] However, the room temperature ionic conductivity of this type of SSE is not typically ($<10^{-4} \text{ S cm}^{-1}$).

Halide-based SSEs with non-metal elements are categorized as ternary lithium–nitrogen–halogen ($\text{Li}-\text{N}-\text{X}$, $\text{X} = \text{Cl}$, Br , and I . e.g., Li_6NBr_3 , $\text{Li}_9\text{N}_2\text{Cl}_3$)^[117,118] or lithium anti-perovskite electrolytes (e.g., Li_3OX , Li_2OHX).^[50,119,120] A novel SSE based on lithium-rich anti-perovskites (Li_3OCl , $\text{Li}_3\text{OCl}_{0.5}\text{Br}_{0.5}$) has been presented by Zhao et al. as having high room temperature ionic conductivity ($>10^{-3} \text{ S cm}^{-1}$).^[50] Subsequently, Jena et al. explored a set of lithium-rich antiperovskites and found that Li_3SBF_4 ($10^{-2} \text{ S cm}^{-1}$ at room temperature) and $\text{Li}_3\text{S}(\text{BF}_4)_{0.5}\text{Cl}_{0.5}$ ($>10^{-1} \text{ S cm}^{-1}$ at room temperature) have the potential for ideal SSEs.^[121] To date, several halide-based SSEs with room temperature ionic conductivity $>10^{-3} \text{ S cm}^{-1}$ have been developed, with some predicted to achieve ultrahigh ionic conductivity levels.

However, halide-based SSEs must meet several requirements for practical application, including appropriate ionic conductivity, structural stability, air stability, electrochemical window, and compatibility with electrode materials. Compared to oxide- and sulfide-based SSEs, some halide-based SSEs experience changes in ionic conductivity due to structural transformation, resulting in unstable battery operation. Specifically, Li_3InBr_6 and LiInBr_4 exhibit high ionic conductivity when transformed into a high-temperature phase during heating.^[46,122] However, cooling destroys their structure, reducing their ionic conductivity by several orders of magnitude. Thermal instability is a significant issue for halide-based SSEs for lithium batteries. Although halide-based SSEs are generally stable under dry air conditions, exposure to humidity can decrease their ionic conductivity. This is due to most metal halides being humidity-sensitive; halide-based SSEs are a combination of lithium and other metal halides.^[15] However, recent studies have shown that Li_3InCl_6 , synthesized via a water-mediated synthesis route, is stable to air and humidity and exhibits high ionic conductivity during the conversion between Li_3InCl_6 and $\text{Li}_3\text{InCl}_6 \cdot 2 \text{ H}_2\text{O}$.^[56] However, to reduce the impact of humidity during electrolyte synthesis, storage, and fabrication, additional studies are warranted to assess other halide-based SSEs with hydrated forms. The electrochemical window of halide-based SSEs highly depends on their composition, where fluoride-based SSEs exhibit higher oxidation stability (up to 6 V vs Li/Li⁺) than other halide-based SSEs.^[21,110] Based on experimental and theoretical results, most halide-based SSEs exhibit good chemical stability with oxide-based cathode materials. However, acceptable room temperature ionic conductivity has not been achieved for fluoride-based SSEs. Although chloride-based SSEs show promise, effective strategies are needed to address the issue caused by the low negative electrochemical potential of lithium metal. That is, to avoid the issue of reduced SSEs containing high-valence state metal elements when in contact with bare lithium.^[23,56] Understanding compatibility with electrode materials is essential to developing effective strategies capable of addressing the challenges associated with SSEs and anode materials.

2.1.4. Polymer-Based SSEs

Polymer electrolytes date back to 1973 when Wright et al. found that alkali metal salts can be dissolved in polyethylene oxide (PEO) to form polymer ion conductors.^[17] Compared to inorganic SSEs, solid polymer electrolytes (SPEs) have prominent ad-

vantages such as low cost, low interfacial resistance, low mass density, flexibility, and compatibility with large-scale manufacturing processes.^[9] Owing to these advantages, SPEs as potential solid electrolytes for high-energy-density batteries have attracted significant research attention and have been the subject of intensive study. Generally, polymer electrolytes can be divided into two major categories: solid-state polymer electrolytes and gel polymer electrolytes.^[20] Among these, gel polymer electrolytes are not discussed in detail here since they are not solid-state electrolytes. All solid-state polymer electrolytes generally consist of polymer matrices and Li salts, and sometimes incorporate inorganic fillers without the addition of liquid plasticizers. PEO, polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVDF), and poly(methyl methacrylate) (PMMA) have been used as polymer matrices for polymer-based SSEs.^[123–126] The ion transport mechanisms in SPEs involve the dissociation of ions from counterions by coordination with the electron-donor groups in the polymer backbone, transport of ions facilitated by the segmental motion of the polymer chains, and temporary re-association with counterions.^[20,127] The ionic conductivity of SPEs is determined by both the mobility and concentration of free charge carriers.^[127] Polymer matrices for SPEs should simultaneously meet the requirements of cation solvation (i.e., the ability to dissociate lithium salts and enable cations to hop from one coordinating site to another), high dielectric constant (i.e., favoring salt dissociation), high polymer backbone flexibility (i.e., favoring cation transport), and sufficient mechanical strength.^[20]

PEO-based SPEs: Among all polymer matrices, PEO and its derivatives have been the most intensely studied and applied because of the excellent solubility of Li salts and their stable contact with Li metal. Since PEO chains exist in a crystalline state below 65 °C, PEO-based SSEs present low ionic conductivity ($<10^{-5} \text{ S cm}^{-1}$) at room temperature, limiting their potential applications.^[20] Consequently, various strategies, such as polymer structural modification (e.g., grafting, copolymerization, and crosslinking), optimization of Li salts, and introduction of inorganic fillers (e.g., ceramic fillers, MOFs, and oligomer-tethered nanoparticles), have been applied to improve the ionic conductivity of PEO-based SSEs.^[9,20] Other polymer-based SPEs: Beyond the PEO matrix, significant efforts have been made to develop other polymer-based SPEs such as polysiloxane-, polyester-, and succinonitrile-based SPEs. Polysiloxanes, a member of the silicone family, exhibit high ionic conductivity because the flexibility of the Si–O–Si bonds leads to a low glass transition temperature.^[128,129] But polysiloxanes are not suitable for practical applications because of their poor mechanical strength. Polyesters with low glass transition temperatures and high dielectric constants have also been applied as SPE matrices.^[130,131] However, their low ionic conductivity and reactivity with Li metal anodes are obstacles to their application. Succinonitrile-based SPEs, which are typical molecular plastic crystals, exhibit high solubility in lithium salts because of their high polarity, which benefits their application as SPEs.^[20,45] However, the poor mechanical strength and compatibility of such solid electrolytes with Li metal anodes limit their application. These issues hinder their application in ASSLMBs. Sustained efforts should be made to improve ionic conductivity, enhance mechanical strength, and reduce reactivity with Li metal anodes to boost these SPEs rapid development.

Table 1. Summary of stability issues of different SSEs. The stability information of SSEs is based on ref. [18, 105].

SSEs type	Stability in air	Thermal stability	Mechanical properties	Stability with Li–metal	Electrochemical stability (at high potential)
Oxide-based SSEs Garnet (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) Perovskite (e.g., $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$) NASICON (e.g., $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$)	H^+/Li^+ exchange forming contamination layer (i.e., LiOH or Li_2CO_3)	Good stability superior over other SSEs	Excellent mechanical strength (Young's modulus > 50 GPa), extreme brittleness, poor fracture toughness	Stability for Garnet; Reduction from Ti^{4+} , Ge^{4+} to Ti^{3+} , Ge^{3+} for Perovskite and NASICON	Interfacial behaviors such as forming Li_2O_2 , La_2O_3 , $\text{Li}_6\text{Zr}_2\text{O}_7$ for Garnet; TiO_2 , O_2 , $\text{La}_2\text{Ti}_2\text{O}_7$ for Perovskite; $\text{Ge}_5\text{O}(\text{PO}_4)_6$, $\text{Li}_4\text{P}_2\text{O}_7$, AlPO_4 , $\text{Ti}_5\text{P}_4\text{O}_{20}$, TiP_2O_7 , O_2 for NASICON
Sulfide-based SSEs (e.g., $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$)	H_2S generation	Sufficient for battery operation, but further optimizations are needed	Poor mechanical strength (Young's modulus ≈ 9 GPa), better ductility, low fracture toughness	Reduction from P^{5+} , Ge^{4+} , Sn^{4+} to lithium compounds (e.g., Li_3P), lithium alloys (e.g., Li-Ge) or metal (e.g., Ge)	Interfacial behaviors such as forming element sulfur, sulfur-contain species, LiCl
Halide-based SSEs (e.g., Li_3InCl_6 , Li_3InBr_6)	Stable under dry air conditions; Exposure to humidity decrease their ionic conductivity	Thermal instability result in structural transformation	High deformability and flexibility with electrodes	The reduction of SSEs containing high valence metal elements when in contact with bare lithium	Oxidation stability is anion dependent; Oxidation potentials of fluoride-, chloride-, and brominated-based are 6 V, 4 V, and 3.2 V (vs Li/Li^+), respectively
Polymer-based SSEs (e.g., PEO-LiTFSI)	Water absorption	Poor stability toward practical application	Poor mechanical strength (Young's modulus < 5 GPa), better fracture toughness	Forming passive layer (i.e., lithium alkoxide species, LiF)	Forming ester species

Regarding SSEs, the challenge of lithium deposition within them is also a crucial issue. Suppressing lithium dendrite growth is an important motivator for the development of SSEs due to their high mechanical strength, particularly in inorganic SSEs. However, lithium dendrites are extensively observed in SSEs at interface, grain boundaries, voids, and soft areas. These dendrites grow and propagate during cycling more severely than batteries with liquid electrolytes. Due to the inherently different chemical and physical properties of polymer- and inorganic-based SSEs, the mechanisms of dendrite growth in SSEs differ. That is, in polymer-based SSEs, the soft nature provides flexibility and processability while also making it easier for dendrites to penetrate, causing short circuits and battery failure.^[132–134] In contrast, lithium dendrites form in inorganic-based SSEs due to discontinuous interface contact, grain boundaries, voids, and electronic conductivity, all of which accelerate their formation.^[135–137] In particular, the softening elastic property and low ionic conductivity of grain boundaries, as well as the partial electronic conductivity of SSEs represent the preferred sites for lithium dendrite growth.^[22, 138, 139] Such uncontrollable dendrite growth in SSEs during cycling leads to rapid capacity degradation and safety hazards. To suppress dendrite growth in SSEs various strategies are widely applied. For polymer-based SSEs, various

fillers, a 3D structure lithium metal anode, an artificial interface layer, and a single-ion transport polymer have been introduced. For inorganic-based SSEs, strategies to reduce the number of defects have included the formation of a smooth and impurity-free surface, applying an artificial interface layer, single-crystal SSEs, doping special elements, and increasing the density.^[132, 137] Indeed, numerous studies have sought to understand the mechanisms underlying dendrite growth in SSEs and develop suppression strategies to attain dendrite-free ASSLMBs.

This section presents a historical retrospective and the future perspectives of SSEs for ASSLMBs. The stability issues of SSEs in practical applications are also summarized. Based on the above discussions, we compared and clarified in detail the stability (i.e., stability in air, thermal stability, mechanical properties, stability with Li metal, and electrochemical stability) of the four types of SSEs, as shown in **Table 1**. The stability issues of SSEs and their associated interfaces will determine the practical development of ASSLMBs. Among these different type of SSEs, oxide-, sulfide-, and polymer-based SSEs will be highlighted in this review. Although halide-based SSEs have made significant progress in room temperature ionic conductivity after nearly two years of development, they are still in their early stage. Therefore, halide-based SSEs will not be covered in detail in this review.

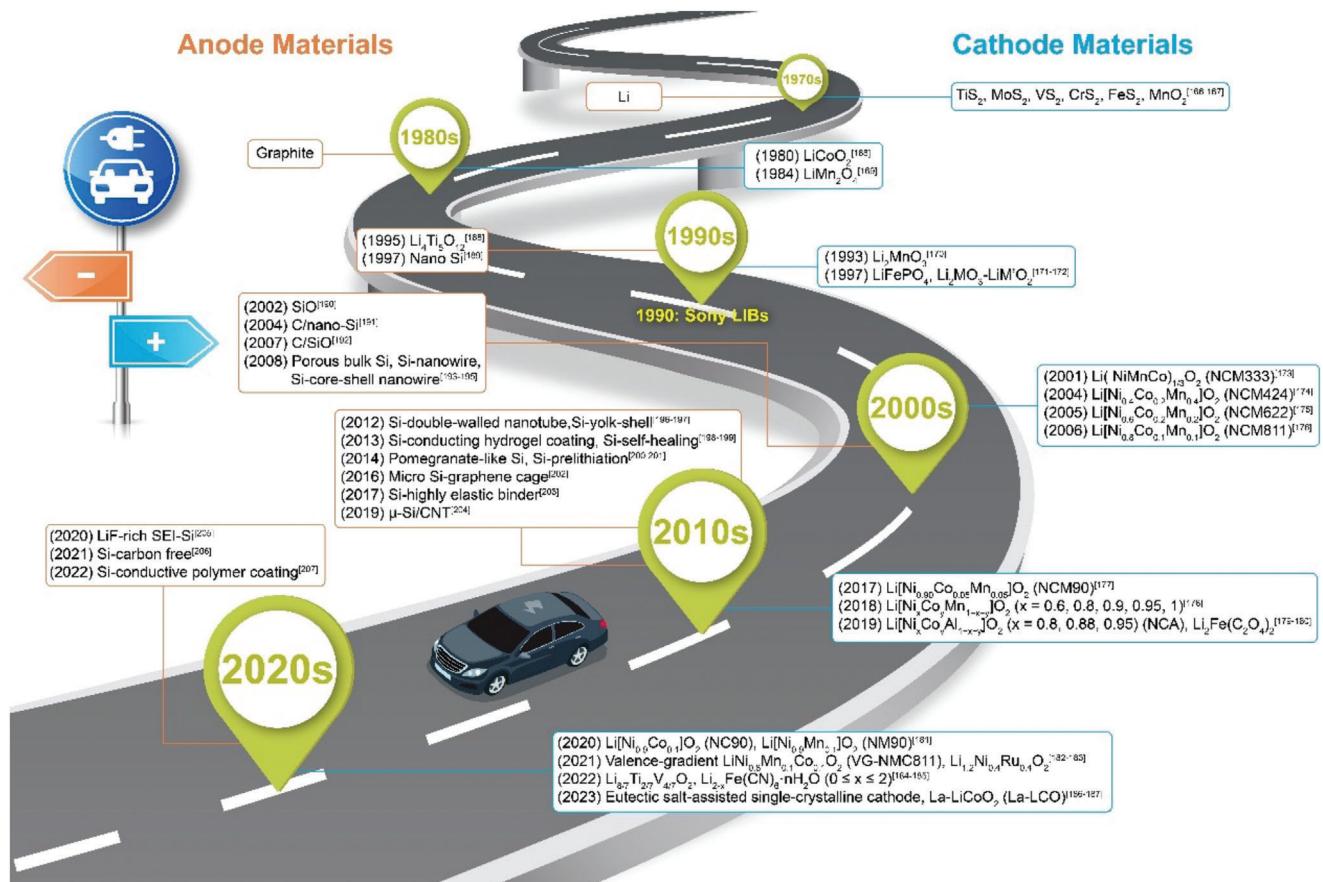


Figure 3. Timeline for the development of cathode and anode materials.^[166-207]

2.2. Cathode (Positive Electrode)

As a key component of Li-based batteries, cathodes constitute a significant portion of the energy density and cost of batteries; therefore, cathode recycling has attracted great interest. Figure 3 depicts the timeline of electrode materials from 1972 to 2023. Currently, commercial LIB cathode materials largely fall into three categories: layered (e.g., LiCoO_2 (LCO)), polyanion (e.g., LiFePO_4 (LFP)), and spinel (e.g., LiMn_2O_4 (LMO)) structure-intercalation cathodes.^[140] For ASSLMBs, Li metal anode can couple with the above-mentioned intercalation cathodes (e.g., LCO, LFP, and LMO) or high-capacity cathodes (e.g., sulfur (S), oxygen/air (O_2/air)).^[141-143] However, owing to the complex battery chemistry of Li-S and Li- O_2/air batteries, their development is still in its infancy. In contrast, because intercalation cathodes inherit the same cathode materials as LIBs, ASSLMBs based on intercalation cathodes are easier to integrate into current LIB manufacturing processes. Therefore, the application of intercalated cathodes with simple battery chemistry in ASSLMBs is of great interest to academia and industry. This has been demonstrated in the Bluecar electric vehicle produced by the Bolloré group and is currently being utilized in car-sharing services in several cities worldwide, where Li/PEO-based SSEs/LFP batteries were used to provide efficient and safe power sources. The expanding market of the Bluecar electric vehicle has amply demonstrated the technological feasibility of ASSLMBs.

ability of ASSLMBs. However, these intercalation cathodes cannot satisfy the increasing demand for high energy densities. High-voltage (e.g., $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and LiCoMnO_4) and high-capacity (e.g., $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and $\text{LiNi}_{0.88}\text{Co}_{0.09}\text{Mn}_{0.03}\text{O}_2$) cathode materials have also been explored as potential alternatives to conventional intercalation cathodes for increasing the energy density of ASSLMBs.^[144-147] A higher energy density can be attained for NCM ($\text{LiNi}_{1-y-z}\text{Co}_y\text{Mn}_z\text{O}_2$) by increasing the proportion of nickel (i.e., higher lithium extraction can be achieved because of the $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couples); however, the simultaneous high reactivity of Ni^{4+} leads to low thermal stability and increases safety risks.^[8,148] The cost of cathodes is another critical parameter for large-scale applications of ASSLMBs. Owing to the relatively high cost of cobalt, the future direction of cathode development has tended toward low-cobalt-content or cobalt-free cathodes.^[149] Considering the sustainability, cost-effectiveness, and environmental issues inherent to ASSLMBs, battery design, and recycling are crucial.

Research on replacing conventional liquid electrolytes with SSEs for integration into LMBs is growing rapidly, and many challenges (e.g., poor contact, element interdiffusion, electro/chemical instability, and stress-strain at the interface) remain for their practical application in electrode-electrolyte interfacial engineering.^[8,150] Among these, poor contact and electro/chemical instability between the cathode and SSEs from spontaneously emerging or accompanying charging/discharging

are the key issues of cathodes in ASSLMBs. Consequently, various modification strategies have been widely applied to ameliorate the issues listed above, including cathode design (i.e., compositional and morphological characteristics of the cathode, such as particle size, composition, and single crystal),^[151–153] SSE design (i.e., architecture and manufacturing, such as multilayer structure, in situ-polymerization, and porous framework)^[123,154,155] and SSE/cathode interface design (i.e., artificial interphase, such as polymer, oxide, and reactive metal).^[156–158] However, integrating these strategies into ASSLMBs to achieve desired properties remains a challenging task. In addition, a space charge layer at the SSE/cathode interface is another reason for the high interfacial resistance and rapid capacity degradation of ASSLMBs. The presence of a space charge layer, i.e., an electrochemical double layer at the SSE/electrode interface, typically leads to local charge carrier depletion or enrichment due to the difference in electrochemical potential, thus, impeding the transport of lithium-ions during charging and discharging and leading to poor lithium-ion transport across the interface.^[159–161] To mitigate the formation of this layer, modification strategies are applied, including modification of the SSE/cathode interface design and cathode particle surface.^[162,163] The theoretical calculations have confirmed the existence of the space charge layer, which arises from the different chemical potentials between SSEs and cathodes.^[161,164,165,166] However, directly observing lithium ions at the space charge layer at the atomic scale remains challenging. Hence, a comprehensive understanding of the effect caused by the space charge layer on lithium-ion transport at the SSE/electrode interface is lacking and requires experimental verification.

2.3. Anode (Negative Electrode)

As an indispensable component of Li-based batteries, the development of anodes will significantly contribute to the improvement of battery energy density. Various classes of anode materials (Figure 3) such as intercalation-type (e.g., graphite), alloy-type (e.g., Si, Sn, and In), and Li-metal anodes have been explored for use in solid-state batteries.^[2,208,209] Graphite, as one of the earliest developed anodes, has been widely used in commercial LIBs due to its safety and environmentally friendly properties. Based on the fact that the development of solid-state batteries is in its initial stages, graphite, as a highly reliable and reproducible anode material, has been used for solid-state battery process development.^[210,211] However, the low capacity of graphite (372 mAh g^{-1}) limits its further application; therefore, there is an urgent need to develop novel, high-capacity anode materials.^[212] Among high-energy alloy-type anode materials, silicon (Si)-based anode materials exhibit a higher theoretical capacity (3590 mAh g^{-1} , lithiated phase $\text{Li}_{15}\text{Si}_4$) than other alloy anodes, which is approximately 10 times that of graphite anodes.^[208,213] Furthermore, Si-based material is considered a promising anode for ASSLMBs because of its advantages such as high abundant resources, low cost, friendliness to the environment, and low work potential (0.4 V vs Li/Li⁺).^[214,215] Although Si-based anodes in solid-state batteries have received increasing attention, knowledge of their fundamental properties and application in battery technology are still in the initial stages.^[214,216] To

achieve solid-state batteries with high energy densities, it is necessary to overcome obstacles such as low silicon loading in the anode, low initial coulombic efficiency, poor electrical conductivity, mechanical degradation, and rapid capacity decay.^[208,217] Additionally, the exploration of Si-based anodes in solid-state batteries has been mostly used for sulfide-based SSEs, while chemical/electrochemical stability between Si-based anodes and sulfide-based SSEs, ionic/electronic transport in silicon-based anodes as well as its chemistry and mechanics remain unclear, making it worth exploring in the future.

However, despite the impressive properties of these anode materials, Li-metal anodes remain the ultimate anode for Li-based batteries.^[218] Furthermore, Li-metal anodes are indispensable for nonlithium oxide cathode materials (e.g., sulfur and oxygen/air cathodes), all of which are regarded as next-generation batteries because of their high energy densities (e.g., Li–sulfur, 2600 Wh kg^{-1} ; Li–oxygen/air, 3505 Wh kg^{-1}).^[218,219] Therefore, from the perspective of industrial applications, solid-state batteries using Li-metal as the anode material can theoretically meet the requirements of safety, excellent electrochemical stability, and high energy density. However, formidable challenges, such as the poor stability and compatibility of SSEs/Li–metal anodes (caused by the ultralow electrochemical potential of Li–metal anodes), poor interfacial lithium-ion transport (caused by the point contacts between SSEs/Li–metal anodes), and mechanical instability (caused by the complex stress effects during cycling), need to be overcome before ASSLMBs can become a viable technology.^[18,220] Consequently, various modification strategies have been applied to improve the performance of SSEs/Li–metal anode interfaces, including artificial SEI layers (e.g., ALD@Al₂O₃, Zn@Li₂O, amorphous Ge film),^[221–223] 3D anode designs (e.g., 3D Li–rGO composite anodes and lithium silicide–Li composite anodes).^[224,225] Considering that large-scale production of ASSLMBs requires both simple and rapid SSE/Li–metal anode surface treatment methods. Furthermore, to achieve the rapid industrialization of ASSLMBs, it is important to make the manufacturing process of ASSLMBs compatible with commercial LIBs.^[220,226] However, because of the differences between the composition and structure of ASSLMBs and LIBs, the cutting and stacking processes need to be optimized to solve issues encountered during assembly, such as deformation and high adhesion of soft Li–metal anodes, and the fragility of hard inorganic SSEs.^[227] To accelerate the transition from LIBs to ASSLMBs, it is necessary to design novel SSE/Li–metal anode surface layers and Li–metal anodes with safety assurance, excellent cyclability, and unique application benefits.

3. Evaluation in ASSLMBs Manufactory Technology

3.1. Design and Manufacture of ASSLMBs

The conventional battery manufacturing process consists of electrode, cell, and battery system manufacturing (Figure 4a). Lab-level experiments (e.g., material design and mechanism exploration) are essential for the proof of practical applications, whereas the battery configurations of practical batteries (e.g., cylindrical, prismatic, and pouch) are fundamentally different from the lab-level stages (e.g., coin, mold, and small pouch cell).

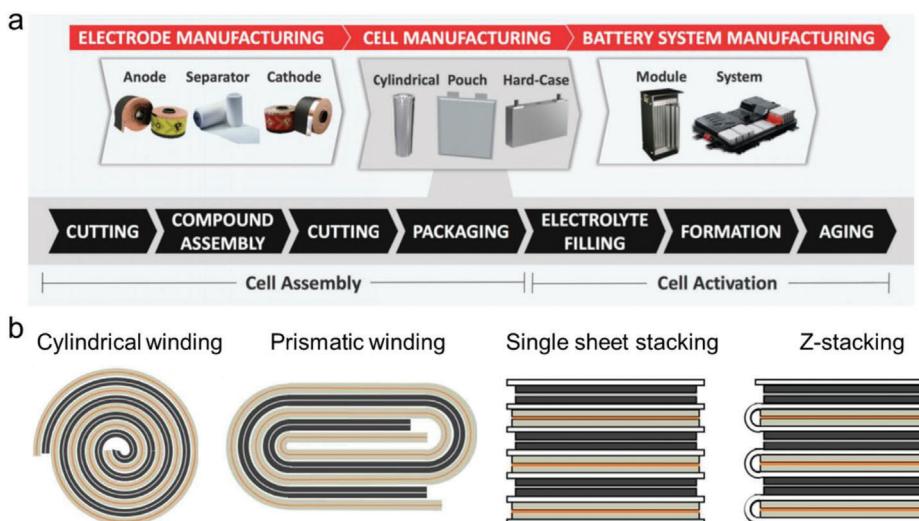


Figure 4. a) Manufacturing process of a conventional battery. Reproduced with permission.^[232] Copyright 2017, Elsevier. b) Schematic of typical shape of Li-metal batteries manufacturing processes. Reproduced under the terms of the Creative Commons CC BY license.^[228] Copyright 2020, The Authors, published by IOP Publishing.

These battery formats have specific advantages and drawbacks when used in ASSLMBs.

Cylindrical cells consist of a hard case (to protect the cell core from an external strike), winding electrodes (round winding), separators, and pressure valves, corresponding to the cylindrical winding (Figure 4b), which have been applied in battery modules for Tesla's electric vehicles (e.g., 2170, 4680 cylindrical cells). They have the advantages of production line maturity, high yield rate, production efficiency, and good product consistency.^[228,229] However, their sophisticated battery management system (BMS) and the fact that it is only suitable for SSEs with high polymer content (due to the strip electrodes and SSEs assembled by round winding), making their use in ASSLMBs very limiting. Prismatic cells consist of hard cases, winding electrodes (flat winding), separators, and pressure valves, corresponding to prismatic winding (Figure 4b), where aluminum-cased batteries can offer high safety and can be tightly stacked to achieve a higher volumetric energy density compared to cylindrical cells owing to high space utilization; however, they are also only suitable for SSEs with good flexibility (owing to strip electrodes and SSEs assembled by flat winding).^[228–230] Pouch cells consist of a lightweight Al-plastic film, sheet electrodes, and sheet or winding separators, corresponding to planar stacking (i.e., single sheet stacking and Z-stacking) (Figure 4b). Lightweight Al-plastic film has the advantages of reduced additional packaging weight for higher energy density, the ability for deformation, the ability to detect gas inflation, and the universality of the single sheet stacking for all types of SSEs.^[230–232] However, the assembly process for pouch cells is more complicated than that for cylindrical and prismatic cells, such as the accurate cutting of separators and electrodes before stacking to avoid battery shorting caused by side Li deposition and elimination of gas production in the activation process due to the absence of a gas valve in the cell itself.

We have described conventional practical battery manufacturing processes for cylindrical, prismatic, and pouch cells. However, the compatibility between the manufacturing process and

properties of SSEs must be considered when applying SSEs to practical batteries. Figure 5 depicts the advantages and drawbacks of different practical cell shapes and their suitability for oxide-, sulfide-, and polymer-based SSEs. For round or flat windings (i.e., assembling cylindrical or prismatic cells), the inherent fragility of oxide-based SSEs cannot be folded or bent; sulfide-based SSEs are not flexible enough for the winding process, and even flexible polymer-based SSEs are not flexible enough in terms of mechanical damage occurring during the winding process. In addition, neither winding process is suitable for brittle Li-metal anodes. Therefore, cylindrical and prismatic winding types have significant limitations in terms of their applicability in ASSLMBs.

The transition from conventional LIBs to ASSLMBs is not only reflected in the differences in battery composition and structure but also the battery manufacturing process.^[233] Unlike the conventional LIB "roll-to-roll" process, the single sheet stacking manufacturing process is the most popular method for ASSLMBs and is important for ASSLMBs commercialization, which can be easily assembled by stacking cathode, SSEs, and anode layers (Figure 6a). This manufacturing is suitable for free-standing SSEs with thicknesses over 30 μm to ensure the mechanical integrity of SSEs. Regarding the interfacial issues that exist in the stacking manufacturing process, different types of SSEs have corresponding solution strategies: polymer-based SSEs (e.g., heating or cold pressing), sulfide-based SSEs (e.g., cold pressing), and oxide-based SSEs (e.g., interface modification and SSE/electrode co-sintering).^[13,233]

In addition to the stacking manufacturing process, other ASSLMBs manufacturing processes such as slurry casting, extrusion, and dry powder have been reported. The slurry casting manufacturing process is a wet chemical process that can overcome the issues of high interfacial resistance and the inability to achieve ultrathin SSEs (<10 μm) in the conventional stacking manufacturing process (Figure 6b).^[14] This process is suitable for automated and large-scale manufacturing applications. However, the current challenges for this process include choice

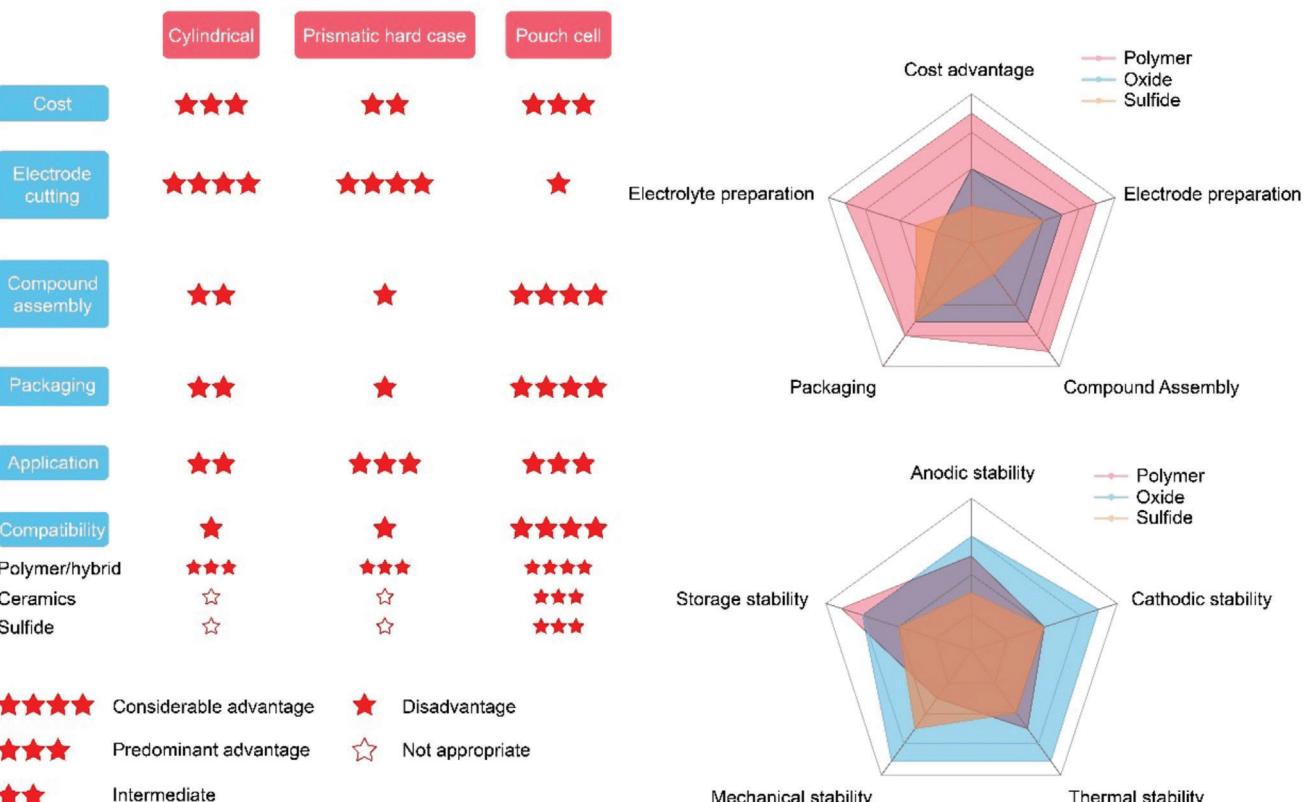


Figure 5. Prospects of different cell formats for ASSLMBs manufacturing, and compatible and stability toward different types of SSEs in battery manufacturing. Reproduced with permission.^[230] Copyright 2020, Wiley-VCH.

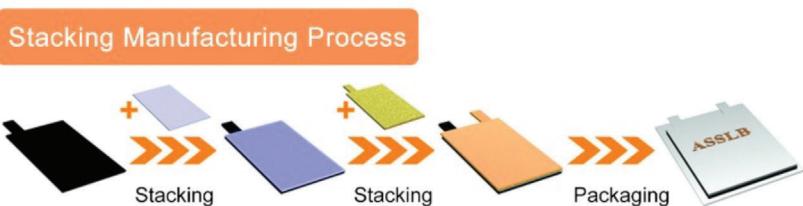
of suitable solvents (stable to SSEs, binders, and substrates) and the abrasion of tools by hard oxide-based SSEs.^[14,233,234] Extrusion manufacturing is a solvent-free process with the following advantages: low porosity, cathode-supported SSEs, low interfacial resistance, environmental friendliness, cost advantages, and automatic production (Figure 6c).^[233,234] However, the problem of limited throughput limitation must be addressed. Dry powder manufacturing is a new process for obtaining high-quality ultrathin SSEs by vapor deposition, aerosol deposition, and other methods (Figure 6d).^[234] However, direct deposition on electrodes remains challenging and requires the electrode substrate to possess high thermal stability. In addition, for the manufacturing process of each ASSLMB, based on the high adhesion of Li metal, it is necessary to replace the traditional cutting technology with a laser cutting process. To achieve intimate contact between the different components inside ASSLMBs, SSEs must be thoroughly mixed with electrode materials (except Li metal anodes) as composite electrodes to form a continuous ion transport network.^[2,235]

3.2. Gaps in the Scale-Up of ASSLMBs

Current lab-level ASSLMBs have not reached levels comparable to those of commercial LIBs in terms of cycling stability and cycling life. In addition, there are still significant challenges in transferring these lab-level achievements to practical batteries, such as the cost and preparation process of SSEs, low loading of

active materials in cathodes, and thick Li–metal anodes, which will lead to a sharp decrease in the energy density and safety issues for ASSLMBs.^[229,230,233,236] Therefore, understanding the gap between lab-level cells and large-scale practical batteries is important for their commercialization and sustainable development. Here, we summarize the gaps between lab-and large-scale ASSLMBs applications in three aspects: SSEs, cathodes, and anodes, as shown in Figure 7.

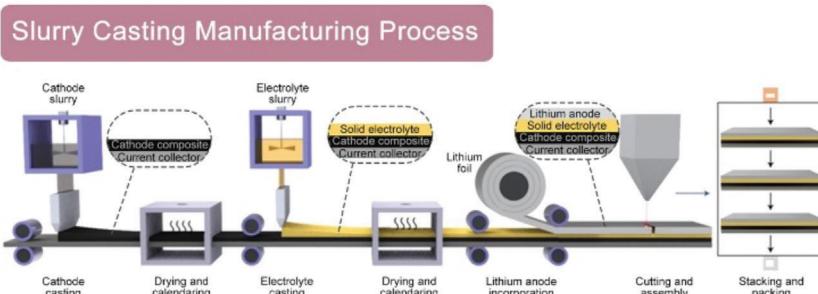
SSEs: As a critical component of ASSLMBs, their performance and physical parameters (e.g., thickness, surface homogeneity, mechanical strength, internal defects, and rare earth elements) are of great importance for the electrochemical performance, energy density, and cost of the battery, etc.^[230,233] Considering the overall energy density and manufacturing cost of batteries, reducing the thickness of SSEs is critical for the commercial development of ASSLMBs. However, the scale-up of ultrathin SSEs poses a great challenge to the industry because the thickness and area of practical batteries are different from those of lab-level cells, which places higher demands on the surface homogeneity, mechanical strength, and internal defect control of SSEs.^[230] The integration of SSEs with electrodes (i.e., battery manufacturing) is also an important step in achieving ultrathin SSEs, requiring attention to interface issues, mechanical properties, and environmental stability. Furthermore, considering that the cost of ingredients is a prerequisite for industrialization, sulfide- and polymer-based SSEs with simple elemental compositions are advocated, whereas oxide-based SSEs are suitable for special

a**Advantage:**

- Easy battery assembly

Disadvantage:

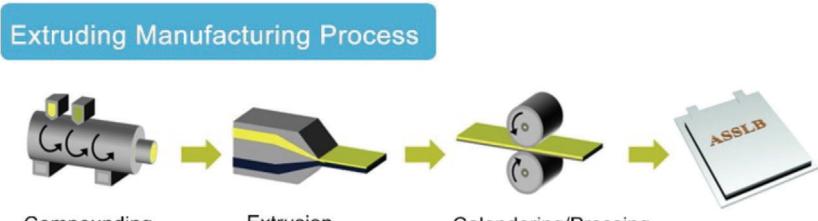
- High interfacial resistance
- Thick SSEs ($> 30 \mu\text{m}$)

b**Advantage:**

- Low interfacial resistance
- Ultra-thin SSEs ($< 10 \mu\text{m}$)
- High throughput

Disadvantage:

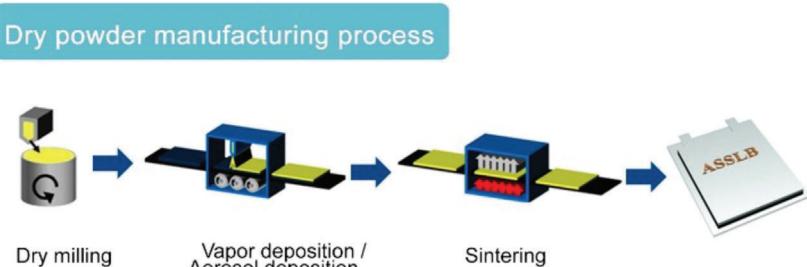
- Selection of suitable solvents
- Hard oxide-based SSEs wear tools

c**Advantage:**

- Low interfacial resistance
- Solvent-free and low porosity
- Automation manufacturing

Disadvantage:

- Limited throughput

d**Advantage:**

- Low interfacial resistance
- High quality ultra-thin SSEs ($< 10 \mu\text{m}$)

Disadvantage:

- Difficulty depositing on electrodes
- Thermal stability electrode substrates
- Immature technology

Figure 6. Manufacturing process of ASSLMBs. a) Stacking manufacturing process. This manufacturing process is suitable for free-standing SSEs. Reproduced with permission.^[233] Copyright 2021, Royal Society of Chemistry. b) Slurry casting (wet chemical process) manufacturing process. Reproduced with permission.^[14] Copyright 2020, Nature Publishing Group. c) Extruding (no solvent process) manufacturing process. Reproduced with permission.^[234] Copyright 2018, Elsevier. d) Dry powder (dry chemical process) manufacturing process. Reproduced with permission.^[234] Copyright 2018, Elsevier. Each manufacturing technology primarily includes three key steps: homogenous slurry preparation, annealing/solvent evaporation and calendaring, and battery stacking assembly.

applications, not for batch production, owing to the presence of a certain amount of rare earth elements (e.g., La and Tb).^[227,230,237]

Cathodes: Achieving high energy density is a prerequisite for the design of practical batteries, and constructing a thick high-mass-loading cathode is a prerequisite to achieving high energy density. However, the rational design of high-capacity cathodes still faces dilemmas (e.g., high loading of active materials and surface homogeneity), and the coupling of different SSEs (e.g., oxide-, sulfide-, and polymer-based SSEs) in ASSLMBs also needs to be considered.^[229,230,233] Currently, binder and current collector support can be avoided in low loading lab-level cathodes by

dense pressing, however, achieving these lab-level key parameters in practical cathodes is extremely challenging.^[230] The dependence on the binder and current collector decreases the limited mass ratio of the active material, and the introduction of high binder content also affects ion conduction, particularly in large-scale batteries with thick cathodes. Furthermore, compared with lab-level cathodes, conventional tape-casting manufacturing procedures leaves too many voids and defects on the surface and inside of large-scale cathodes to obtain reliable uniformity.^[230] Therefore, an ideal manufacturing procedure for large-scale cathodes should simultaneously meet requirements such as high

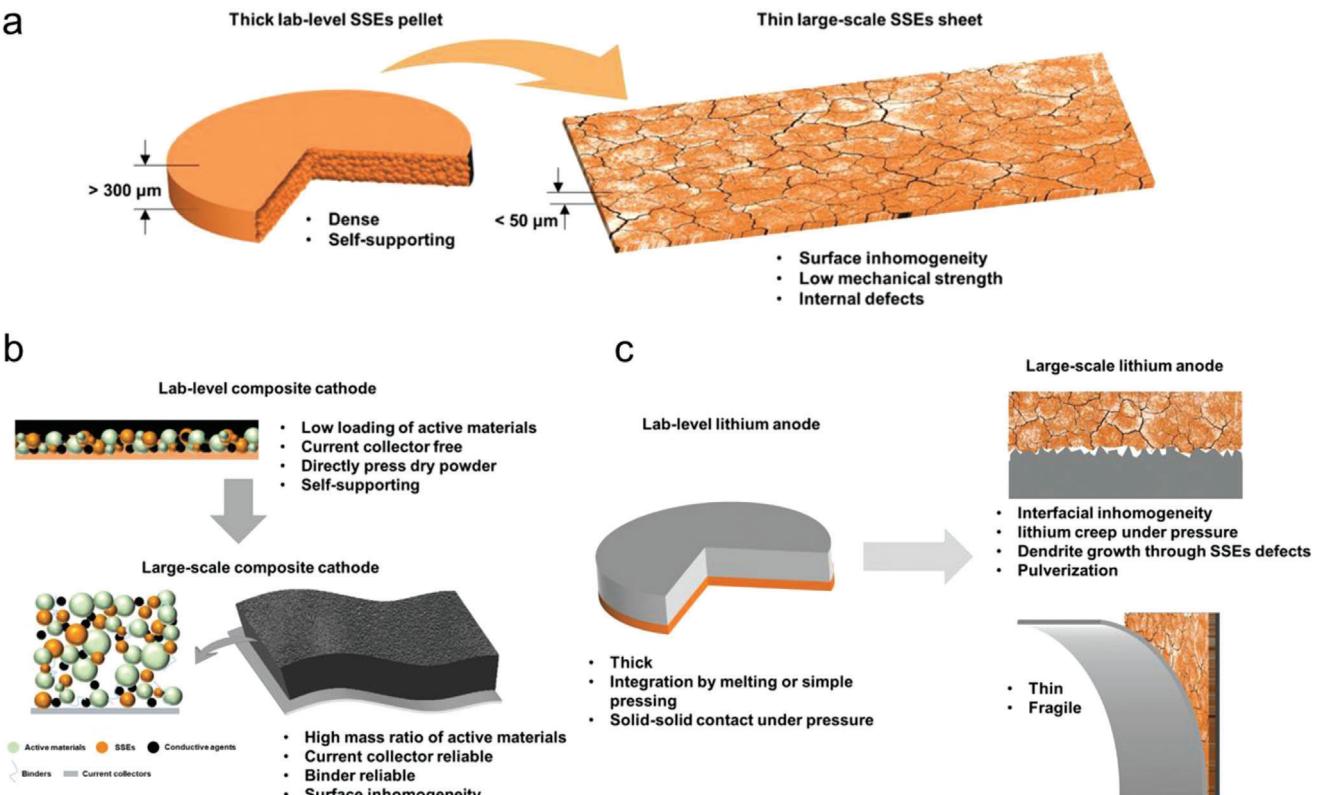


Figure 7. Schematic of the gaps between lab-level and large-scale of a) SSEs, b) cathode, and c) anode. Reproduced with permission.^[230] Copyright 2020, Wiley-VCH.

energy density, surface homogeneity, and assembly compatibility with different SSEs.

Anodes: Lab-level ASSLMBs studies typically employ excess Li-metal (>200 µm) as anodes, which allows for easier integration of SSEs pellets and Li-metal anodes, mainly in the following ways: for polymer-based SSEs, Li-metal is directly stacked on SSEs; for sulfide-based SSEs, Li-metal is attached on SSEs under a certain pressure; for oxide-based SSEs, Li-metal is attached by melting lithium or sputter coating.^[229,230,233] However, for large-scale of ASSLMBs, the thickness of Li-metal (<60 µm) lower than that of regular Li-metal anodes is the basic requirement. Thin Li metal increases the probability of Li creep deformation and pulverization, affecting the SSE/Li interfacial homogeneity, causing the growth of dendrites through SSEs defects, and even inducing battery failure.^[229,230] Furthermore, other inherent physical properties of Li-metal, such as low tensile strength and high adhesiveness, make it unsuitable for roll-to-roll manufacturing processes. Anode-free architecture (i.e., a bare current collector at the anode side without any lithium source) is an exciting and promising approach to reducing material consumption, simplifying the production process, and providing the highest volumetric energy density (>1500 Wh L⁻¹).^[238] However, as anode-free solid-state batteries operate with zero excess lithium, any loss of lithium reflects rapid capacity loss and low coulombic efficiency, influencing the reversibility and cycle-life of the battery. The key challenges impeding the development of anode-free solid-state batteries include low coulombic efficiency (CE), sharp capacity loss, inhomogeneous nucleation, notorious lithium dendrite growth,

and unstable solid electrolyte interphase (SEI).^[238,239] Nevertheless, the failure of anode-free systems is not determined by a single factor but, rather, results from a combination of these factors.^[240–242] In the case of anode-free batteries, lithium is deposited directly on the surface of the anode current collector, which requires overcoming large nucleation barriers. Large overpotentials tend to lead to uneven deposition of lithium and the formation of fragile SEI layers, which aggravate lithium dendrite growth and cause damage to SEI layers during subsequent cycles, ultimately reducing the electrochemical performance of the battery.^[243–245] In contrast to liquid electrolytes, the challenges facing different types of SSEs, including sulfide-, oxide-, polymer-, and halide-based SSEs, differ in anode-free batteries. These batteries are primarily influenced by the physicochemical properties of SSEs, the stability of the SSE/electrode interface, and the mechanical stability to infinite volume changes of the anode.^[238] Hence, the design and scalable strategy for transferring anode-free solid-state batteries from the laboratory to practical application remain challenges. Although some beneficial strategies toward anode-free solid-state batteries have been validated in lab-level cells, they are difficult to apply in practical batteries. However, the lessons learned from the development of ASSLMBs can accelerate the development of anode-free solid-state batteries.

Based on the fact that the commercial feasibility of ASSLMBs depends strongly on various parameters, including the cathode loading level, SSEs and lithium anode thickness, and energy and power density.^[230,246,247] Currently, certain challenges have hindered the transition of laboratory findings to commercial

applications, with few successful lab-based results available for practical applications. In ASSLMBs, the mass ratio of cathode active materials is a critical parameter for realizing high energy density. Generally, the mass ratio of cathode active materials can be adjusted by altering the cathode thickness; a thicker electrode provides a higher mass ratio of active materials in the cell, which results in high energy density.^[248] Energy density approaching 400 Wh kg⁻¹ can be achieved with active material loads up to 20 mg cm⁻² (approximately that of state-of-the-art LIBs). Recently, Liu et al. proposed requirements for 500 Wh kg⁻¹ practical cells by integrating optimal battery materials with cell design parameters.^[249] To achieve this goal, the cell must simultaneously meet the following requirements: specific capacity of cathode > 250 mAh g⁻¹, cathode thickness = 83 μm (active material loading: 26.0 mg cm⁻²), cathode porosity = 25%, N/P ratio = 1, and reduction of inactive materials by > 50%. Under stricter requirements, including further increasing the cathode active material loading, and reducing the N/P ratio and proportion of inactive materials, higher energy density can be achieved. However, current ASSLMB pouch cells that are assembled with thick cathodes have less 20 mg cm⁻² of active material loading due to ion diffusion and volume change issues.^[250] Generally, the electrode active material determines the energy density level of ASSLMBs; reducing the inactive material helps to increase the energy density of the battery. In ASSLMBs, SSEs serve as separators and fill the cathode's porosity to enhance lithium-ion transport. However, these two variables (i.e., SSEs thickness and cathode porosity) have a critical impact on energy density, as the presence of inactive materials significantly impacts battery weight and volume.^[251] Therefore, no excess SSEs are required for ASSLMBs operation. Recently, Huang et al. systematically analyzed the influence of SSE thickness on ASSLMB energy densities based on the practical pouch cell model.^[252] They reported that achieving an energy density > 500 Wh kg⁻¹ in the NCM811/Li system requires SSEs with a thickness < 30 μm, 20 μm, and 10 μm for polymer-, sulfide-, and oxide-based SSEs, respectively. Unfortunately, the conventional SSE thickness surpasses 100 μm, particularly for inorganic SSEs, which increases the internal resistance of the cell and counteracts the advantages of high-energy electrodes for practical applications.^[233] Although it is essential to reduce the SSE ratio in ASSLMBs to achieve high energy density, the mass production of ultrathin SSEs raises new challenges. In addition, while ASSLMBs pouch cells can achieve higher energy density when coupled with an ultrathin lithium metal anode, its excess capacity and thickness present a significant challenge for practical application. To match common oxide cathodes (3–4 mAh cm⁻²), the lithium foil thickness must be < 20 μm.^[249,253,254] However, recent literature shows that the thickness of lithium foil typically exceeds 200 μm, which not only limits energy density but also increases the total cost of the cell. Furthermore, when making lithium foils with a thickness < 20 μm, current fabrication technologies face two major challenges: mechanical fragility and microscale manufacturing capability.^[216,255] Therefore, advanced fabrication techniques are required to ensure its structural integrity. Although anode-free solid-state batteries can achieve high energy density, their low coulombic efficiency and rapid capacity decay restrict their application.^[238] Energy density, one of the most important target performances for cells, is important for ASSLMBs practical application. Conventional LIBs have nearly

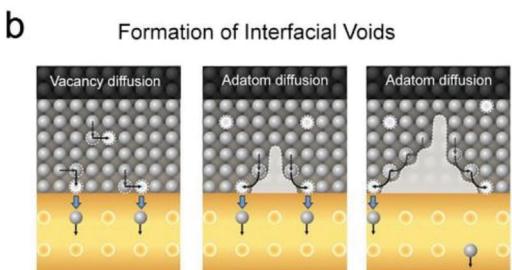
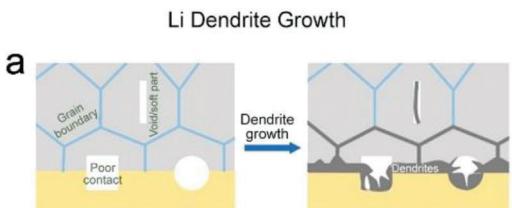
reached their maximum capacity (\approx 300 Wh kg⁻¹) and therefore are unable to meet the requirements for energy and power density. An ideal ASSLMB should simultaneously meet the requirements in terms of high energy density (500 Wh kg⁻¹) and high-power density (500 W kg⁻¹), which would be far superior to LIBs. However, only a few cases have reported energy density in excess of 500 Wh kg⁻¹; to date, no ASSLMBs meet both requirements.^[250] In fact, the current power density is typically <100 W kg⁻¹, which accounts for the considerable challenge associated with achieving high power density. Hence, a long road awaits the achievement of high-performance practical ASSLMBs.

4. Failure Mechanisms of ASSLMBs

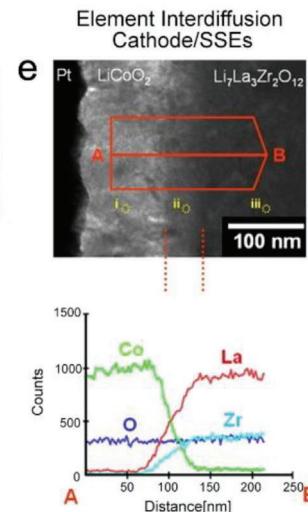
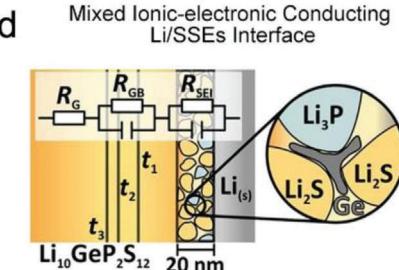
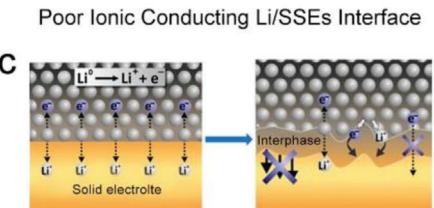
The forthcoming rapid increase in spent ASSLMBs generated from end-of-life or other factors (e.g., battery short-circuiting and battery expansion) will pose greater challenges to the sustainable recycling of batteries worldwide. However, understanding the failure mechanisms of ASSLMBs is a prerequisite for the effective recycling of spent ASSLMBs. The failure of the ASSLMBs is associated with the degradation of the SSE/electrode interface, including electric, chemical, electrochemical, and mechanical failures (Figure 8).^[2,9,242,256] Electric- and mechanical failures are caused by the instability of the interfacial structure of the cell during repeated cycles.^[9,257] Electrical failures mainly manifest as cell short circuits as a result of lithium dendrite growth and high interfacial resistance due to the formation of interfacial voids (Figure 8a,b).^[137,258] Mechanical failures are manifest as large internal stresses due to interfacial fluctuations or interfacial changes, leading to SSEs pulverization or cracking, and cathode cracking or delamination (Figure 8h,i).^[87,259] Chemical and electrochemical failures are caused by the evolution of the composition of the SSE/electrode interface, where most SSEs undergo side reactions with Li metal, leading to the formation of unfavorable interfacial phases and reduced interfacial stability, thus reducing cell capacity (Figure 8c–g).^[94,242,260–263] Moreover, elemental diffusion and interfacial reactions between the cathodes and SSEs tend to lead to poor interfacial stability and high interfacial resistance.^[261,262]

Typically, as ASSLMBs reach the end of their life, Li–metal anodes are completely depleted or a small amount of active lithium remains; therefore, recycling is mainly focused on SSEs and cathodes. For ASSLMBs containing large amounts of residual lithium, it is necessary to discharge the batteries to react all residual lithium before recycling. In conjunction with the failure analysis of ASSLMBs described above, spent SSEs have not undergone structural changes, except for decomposition in the form of a solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI).^[13,14] In addition, previous studies on spent LIBs cathode materials confirmed that degraded cathode materials can be directly regenerated/repaired (i.e., spent cathode materials can be regenerated by replenishing lost elements and repairing the structure) without damaging the structure at the atomic level. It has been proven that even highly degraded cathodes (i.e., with low residual capacity and severe structural defects) resulting from long-term charging/discharging and harsh working conditions can be recycled by means of direct regeneration.^[264,265] Therefore, the battery components of ASSLMBs can be recycled through a gentle physical separation and direct regeneration, where direct

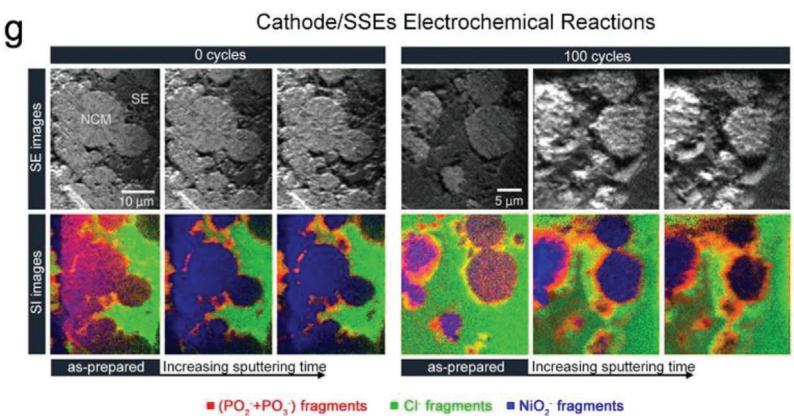
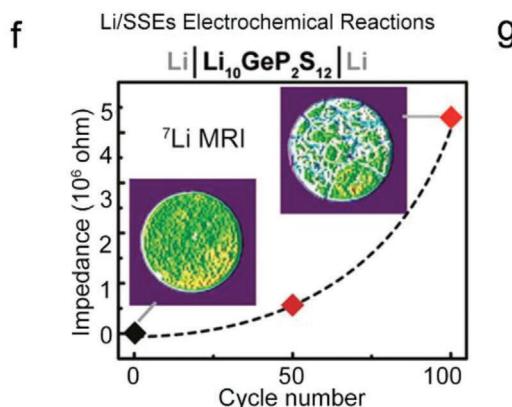
Electric Failure



Chemical Failure



Electrochemical Failure



Mechanical Failure

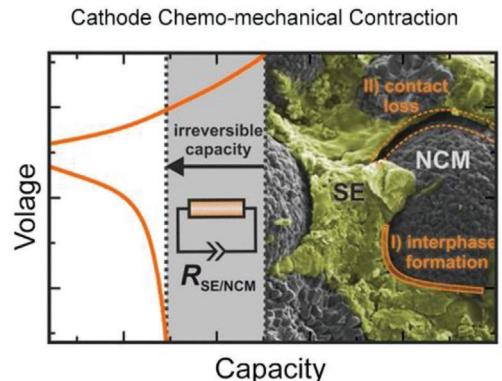
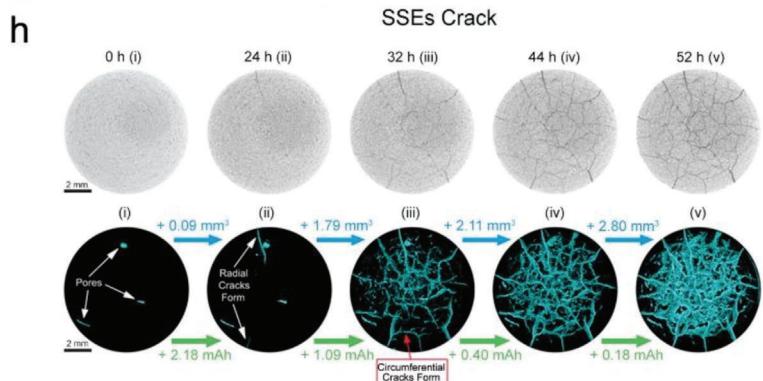


Figure 8. Failure mechanism of ASSLMBs. Electric failure: a) Schematic of Li dendrite growth in SSEs. Reproduced with permission.^[137] Copyright 2020, American Chemical Society. b) Schematic of the mechanism of SSEs/Li–metal interfacial voids. Reproduced with permission.^[258] Copyright 2019, American Chemical Society. Chemical failure: c) Schematic of reactive and thermodynamically unstable interphase formation at Li/SSEs interface (ion-conducting, electron-insulating interphase). Reproduced with permission.^[263] Copyright 2015, Elsevier. d) Schematic of mixed ionic-electronic conducting interphase formation at Li/Li₁₀GeP₂S₁₂ interface. Reproduced with permission.^[94] Copyright 2016, American Chemical Society. e) Cross-sectional

regeneration is considered an environmentally friendly and cost-effective recycling route. Traditional recycling processes such as pyrometallurgy and hydrometallurgy can be used to treat severely damaged battery components. For ASSLMBs, it is important to choose a sustainable recycling technology that maximizes the recovery rates of various battery components.^[13,14]

5. Recycling Processes and Challenges of ASSLMBs

Considering that the current state of LIB recycling technologies is inadequate (e.g., low recovery rate, environmental friendliness, and unsustainability), understanding and learning from LIB recycling practices is of great significance for sustainable battery recycling in the future. Currently, as the market for LIBs continues to grow, so does the waste being generated by discarding them, but there is a lack of economically viable and sustainable recycling systems for spent LIBs. Currently adopted LIB recycling technologies (e.g., pyrometallurgy and hydrometallurgy) typically focus on recovery of valuable metal from cathode materials, resulting in various degrees of loss of the liquid electrolyte and lithium.^[11,266,267] The development of direct regeneration technologies for LIBs is still in the development stage and has not yet achieved widespread industrial application. Compared with LIBs, ASSLMBs have several significant advantages: the discharging process is simple, as there are no liquid electrolytes in ASSLMBs; cells can be assembled in series and parallel directly before packaging, so ASSLMBs can be discharged at the pack level to react with all residual lithium, while LIBs need to be disassembled into unit cells; safety, compared with combustible liquid electrolytes used in LIBs, ASSLMBs have low flammability, reducing safety hazards such as fire and explosion during disassembly; a high recovery rate, SSEs will be recycled, while liquid electrolytes are usually removed.^[10,12–14] However, because of the complex composition and structure of ASSLMBs, recycling technologies that are effective for LIBs may not be suitable for recycling ASSLMBs, or other factors need to be considered (e.g., difficulty in effective separation between SSEs/electrodes, poor air stability of sulfide-based SSEs, and damage to comminution equipment due to hard oxide-based SSEs).

As shown in **Figure 9**, current recycling processes typically include pyrometallurgy, hydrometallurgy, and direct regeneration technologies. Figure 9a depicts the schematic of the process flow of the battery manufacturing chain, from spent to new ASSLMBs. In the first step, considering the different internal chemistries of ASSLMBs systems, the pretreatment technology of packs is divided into two major categories: dissolution-precipitation (for sulfide/polymer-based SSEs) and physical separation in an inert environment (for oxide-based SSEs). Subse-

quently, battery materials must undergo a complex set of physical or chemical processes to produce valuable material streams, including pyrometallurgy (i.e., the reduction of metal oxides to alloys in a high-temperature furnace), hydrometallurgy (i.e., wet chemistry-based methods, chemical decomposition of metal oxides by acid/alkaline leaching, followed by precipitation of metals using counter anions), and direct regeneration (i.e., direct repair by lithium replenishment and heat treatment). The advantages and disadvantages of these recycling technologies are summarized in Figure 9b. Despite the rapid progress in conventional recycling technologies (i.e., pyrometallurgy and hydrometallurgy) because of their prominent advantages, such as simple operation for pyrometallurgy, high metal recovery rate, and high products purity for hydrometallurgy, these recycling technologies have certain disadvantages, including high energy consumption, toxic gas emissions, high cost of high-value metal recovery, complex extraction and separation steps, high cost of wastewater treatment, and low battery recovery rate. Direct regeneration (i.e., direct repair), such as direct solid-state calcination, hydrothermal lithiation, eutectic molten salt lithiation, and dissolution-precipitation, can reconstitute the deficient components of SSEs and cathodes without destroying them. Direct repair of cathodes and SSEs through relithiation and heat treatment not only reduces energy consumption and secondary pollution, but also produces high-value products. The advantages and disadvantages of these technologies provide a reference for the development of new, efficient, safe, and scalable recycling technologies.

Considering the current status of LIBs, recycling technologies are inadequate and unsustainable. Therefore, it is necessary to explore economically viable and sustainable recycling technologies before next-generation batteries enter the market. In this section, we discuss the viability of currently implemented LIB recycling technologies (e.g., pretreatment, pyrometallurgy, and hydrometallurgy) and novel direct regeneration technologies toward ASSLMBs.

5.1. Pretreatment

As the first step in battery recycling, pretreatment mainly involves stabilization, dismantling, and separation, which are necessary processes to improve the recovery rate and reduce subsequent energy consumption.^[10,12,149] To minimize the potential safety hazards caused by the residual power of a battery, the stabilization of spent batteries, that is, discharging, is essential. For LIBs, discharging can be performed using aqueous solutions (e.g., NaCl and Na₂SO₄) and solid electrical conductors (e.g., graphite and copper powder). Of these, NaCl salt solution is the most commonly used discharging treatment.^[12,149] However, the safety issues originating from the above-mentioned

TEM image of Li₇La₃Zr₂O₁₂/LiCoO₂ interface and the EDS line profile obtained from the region A-B. Reproduced with permission.^[261] Copyright 2011, Elsevier. Electrochemical failure: f) 2D cross sections from 3D ⁷Li magnetic resonance imaging (MRI) images of Li₁₀GeP₂S₁₂ SSEs before and after cycled in symmetric Li/Li₁₀GeP₂S₁₂/Li battery. Impedance of symmetric Li/Li₁₀GeP₂S₁₂/Li battery as a function of cycle number. Reproduced with permission.^[260] Copyright 2018, American Chemical Society. g) Time-of-flight secondary-ion mass spectrometry (ToF-SIMS) measurements on crater sidewalls for cathode (NCM622/Li₆PS₅Cl interface) before and after cycling. Reproduced with permission.^[262] Copyright 2019, American Chemical Society. Mechanical failure: h) Mechanical degradation of Li_{1+x}Al_xGe_{2-x}(PO₄)₃ in symmetric Li/Li_{1+x}Al_xGe_{2-x}(PO₄)₃/Li battery during cycling. Reproduced with permission.^[259] Copyright 2019, American Chemical Society. i) SEM images of NCM811/β-Li₃PS₄ interface after cycling. Capacity loss is caused by cathode chemo-mechanical contraction and chemical formation of cathode/SSEs interphase. Reproduced with permission.^[87] Copyright 2017, American Chemical Society.

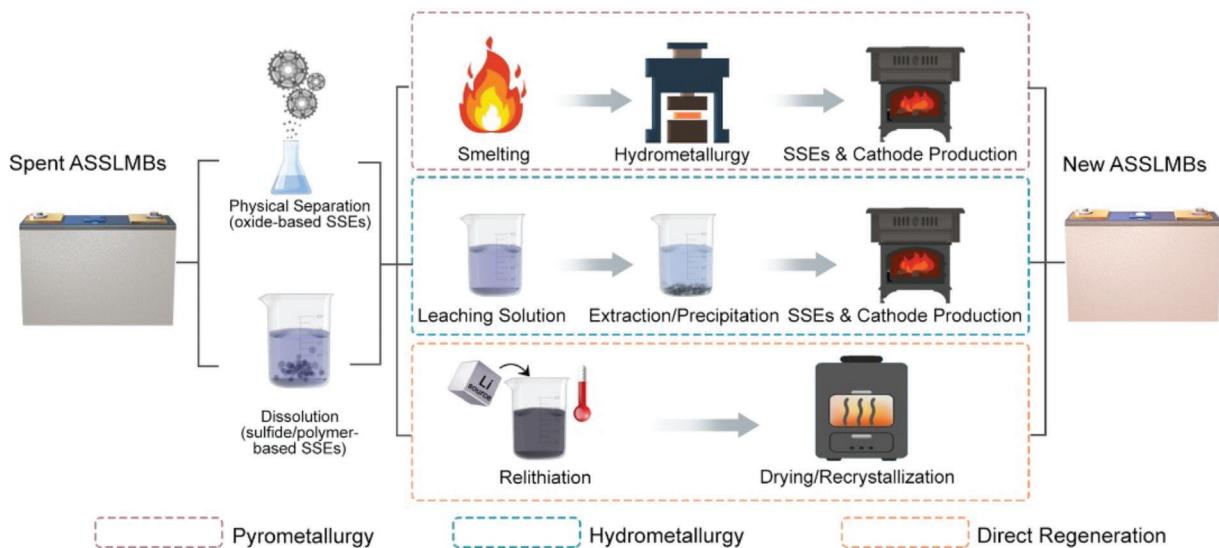
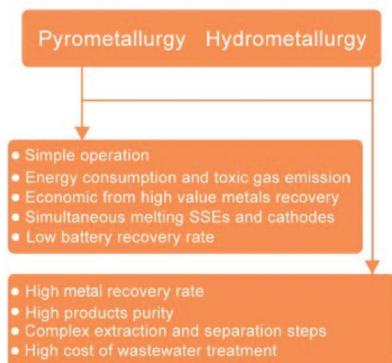
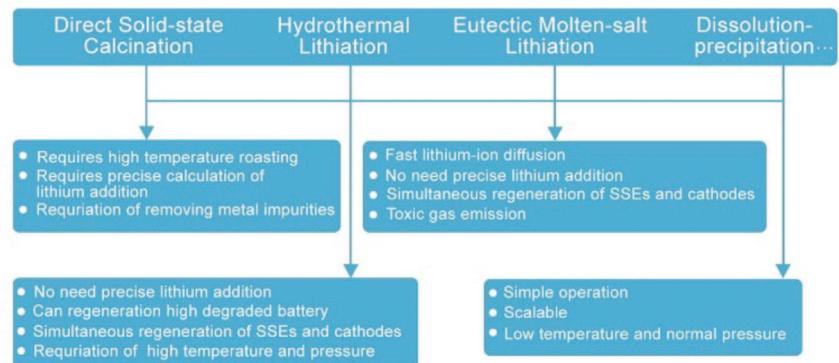
a**b****Extraction of Valuable Metals****Direct Regeneration of SSEs/Cathodes**

Figure 9. Recycling technologies for spent ASSLMBs. a) Schematic and process flow of pyrometallurgy, hydrometallurgy, and direct regeneration recycling technologies for spent ASSLMBs. b) Advantages and challenges of extraction of valuable metals recycling technologies (i.e., pyrometallurgy, hydrometallurgy) and direct regeneration technologies.

discharging treatments include electrolyte leakage and galvanic corrosion for aqueous solution methods, or internal generation of heat and increased risk of explosion for solid electrical conductor methods.^[268,269] Spent LIBs can be dismantled and separated by directly skipping the discharging process through the application of cryogenic (e.g., liquid nitrogen) or inert (e.g., carbon dioxide and argon) atmospheres, which is a widely used technology in industry.^[149,270,271] Differences in the battery structure design and manufacturing technology of ASSLMBs make the required discharge treatment slightly different from that of LIBs. ASSLMBs are not first assembled into unit cells and then connected in series and parallel to achieve high voltage and high capacity, but are directly assembled in series and parallel before packaging, omitting the unit cell sealing process. Based on the stacking assembly form of the ASSLMBs, spent batteries can be directly discharged using LIBs discharge methods at the pack level.^[14,272]

Subsequently, dismantling and separation processes are required to achieve effective separation of various components and

collect effective battery components. Depending on the different physical properties of battery components (e.g., size, density, magnetic properties, and wettability), the effective separation of cathodes, anodes, current collectors, and plastics can be achieved, where the liquid electrolytes are usually removed by heating, organic solvent washing, or supercritical CO₂ extraction.^[10–12,273] Compared with LIBs containing combustible liquid electrolytes, the inherent nonflammability of SSEs in ASSLMBs reduces the safety hazards of the battery pretreatment process. However, owing to the complex composition and structure of ASSLMBs, battery dismantling and separation of valuable components present a greater challenge.^[2,6] For sulfide- and polymer-based ASSLMBs, the pliability of sulfide- and polymer-based SSEs affects the separation efficiency of the cathode/current collector and SSEs/cathode, increasing the difficulty of mesh filtration. For oxide-based ASSLMBs, it is difficult to achieve effective separation of cathode/SSEs by physical methods, and the hardness of the SSEs may cause damage to comminution equipment.^[2,6,13,149]

Recently, Chen et al. recycled sulfide-based ASSLMBs after the removal of packaging materials (without further cell separation) by treating them with ethanol, achieving effective separation of SSEs and cathode, and contributing to the direct regeneration of materials.^[272] In parallel, Liang et al. proposed a charged LIBs precise separation technology in which the disassembly and separation of charged jellyroll LIBs were conducted in water, achieving precise nondestructive separation of LIBs components with no emissions from the batteries.^[273] Water is an excellent fire-extinguishing and oxygen-isolating agent for LIBs; therefore, it is inherently safe to disassemble charged LIBs in water. The precise nondestructive method in water is far superior to the physical separation method of battery pulverization and has notable implications for the pretreatment of ASSLMBs. Because of the differences between ASSLMBs and conventional LIBs, pretreatment technologies developed for LIBs may not be suitable for ASSLMBs, so it is necessary to optimize or develop novel pretreatment technologies, specifically aimed toward ASSLMBs.

5.2. Extraction of Valuable Metals

Currently, LIB recycling technologies mainly involve the destruction of the crystal structure of cathode materials to extract valuable metals, i.e., valuable metals extraction technologies, including pyrometallurgy and hydrometallurgy.^[10,11,149] Pyrometallurgy is a high-temperature smelting process (i.e., recovery or refinement of valuable metals by physical or chemical transformation at high temperature) with simple operation and high production efficiency, and has been widely used in industry.^[274,275] Hydrometallurgy is another mature recycling technology for the extraction of valuable metals from spent LIB materials using an acid/alkali solution and has been used in industrial LIB recycling because of its high recovery rate and low energy consumption.^[276,277] In the case of pyrometallurgy and hydrometallurgy, materials are commonly converted in other formats to extract valuable metals. Considering the complex compositions of ASSLMBs (e.g., various types of SSEs and precious metals), these valuable metal-extraction technologies may not be suitable. The feasibility of these traditional recycling technologies for ASSLMBs is discussed in the following section.

5.2.1. Pyrometallurgy

Pyrometallurgy is the process of melting spent LIBs into alloys (e.g., Co, Ni, Fe, and Cu) using a high-temperature furnace to produce slags (e.g., Li, Al, and Mn) and CO₂ gas.^[10,12,15,278] For pyrometallurgy, the most prominent advantage is that the entire pack or module can be handled directly without sorting or size reduction. However, high-temperature roasting consumes large amounts of energy, and although combustible organic materials in batteries can provide some energy, they can also lead to the irrecoverable loss of these battery components.^[10–12] Furthermore, the residual metals in slags not only waste resources but also cause environmental pollution. These issues have prompted the development of novel processes, including in situ reduction roasting (i.e., the conversion of high-valent metal compounds to low-valent compounds by pyrolysis under vacuum or an inert atmosphere) and salt roasting (i.e., the conversion of metal oxides

into water-soluble salts with the assistance of salt).^[10,149] In situ reduction roasting reduces the roasting temperature and simplifies the recovery process; however, this process still suffers some drawbacks, such as carbothermal roasting generating exhaust gas and thermite roasting generating wastewater.^[279,280] Compared to in-situ reduction roasting technology, salt-assisted roasting technology further reduces the roasting temperature and increases the metal recovery rate, exhibiting good potential for industrial applications.^[275,278] However, remaining challenges, such as the emission of toxic and hazardous gases (e.g., NO_x and SO_x) and relatively high roasting temperatures, restrict their widespread adoption.^[281]

The thermal behavior of the various SSEs is summarized in Figure 10. Oxide-based SSEs exhibited the best thermal stability, followed by sulfide-based SSEs, and all SSEs are superior to LIBs in terms of thermal stability. Note that the onset decomposition temperature of all SSEs decreased when in contact with the electrodes, whereas the reaction mechanisms between SSEs and electrodes are still not clearly understood.^[18] For sulfide- and polymer-based ASSLMBs, SSEs are burned off or turned into slags after high-temperature roasting, which not only prevents the recovery of SSEs but also generates toxic gases.^[2,13,20] Oxide cathodes in the above battery systems are converted to alloys or slags, which is similar to the recycling process for spent LIBs. For oxide-based ASSLMBs, SSEs have chemical compositions similar to those of the cathode materials, where metals (e.g., Li, La, Zr, Ta, Co, Mn, and Ni) in batteries are produced in the form of alloys or slags after high-temperature roasting.^[2,13] Subsequently, the calcined products are further separated and recycled by a complex hydrometallurgical process.^[10,12] However, the large variety of metals in oxide-based ASSLMBs presents a significant challenge for metal separation and recycling. This battery recycling technology has the advantage of high industrial maturity; however, complex operational procedures, low battery recovery, hazardous gases, and wastewater emission, resulting in it having poor industrial potential for ASSLMB recycling. In summary, this technology of extracting valuable metals from spent batteries by destroying the SSEs and cathode crystal structures is not suitable for ASSLMBs.

5.2.2. Hydrometallurgy

Hydrometallurgy is an aqueous chemical treatment technology that extracts valuable metals from spent batteries in two steps: leaching (e.g., using acid, alkali, or deep eutectic solvents as leaching agents) and separation and purification processes (e.g., solvent extraction and chemical precipitation).^[10–12,282] Hydrometallurgy has undergone rapid advances because of its prominent advantages such as high recovery rate, low energy consumption, low CO₂ emission, and high product purity.

Generally, the leaching process can be divided into four major categories: acid leaching, alkali leaching, bioleaching, and green solvent leaching (e.g., deep eutectic solvents and supercritical fluids). Among all leaching processes, acid leaching has drawn the most attention in terms of its high leaching efficiency and low energy consumption. Acid leaching may use either inorganic acids (e.g., HCl, H₂SO₄, HNO₃)^[276,283,284] or organic acids (e.g., citric acid and malic acid).^[285–287] Although

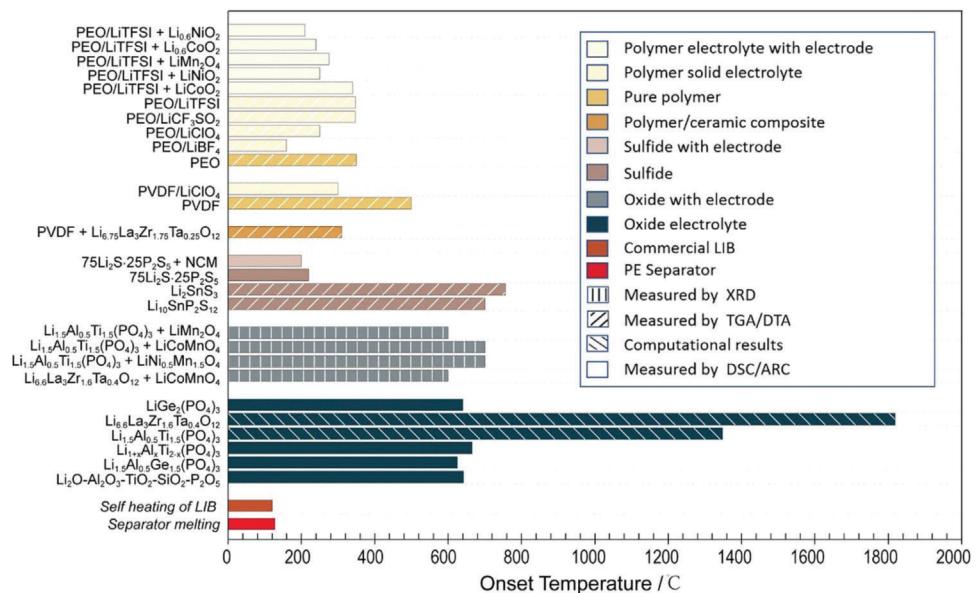


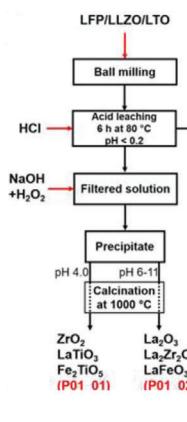
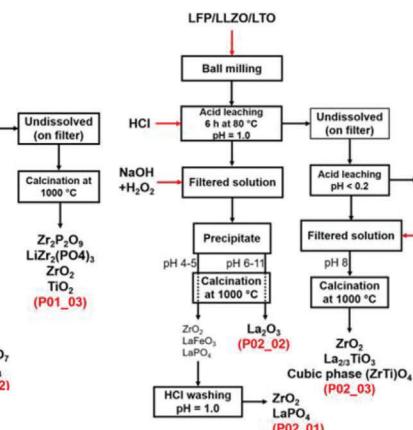
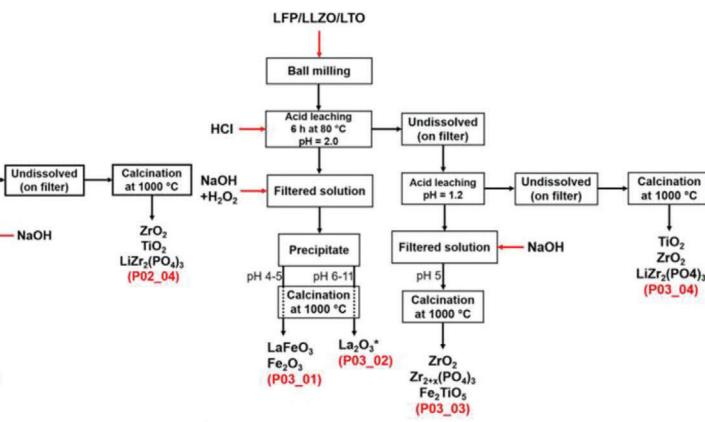
Figure 10. Comparison of onset decomposition temperature of different SSEs. Reproduced with permission.^[18] Copyright 2020, American Chemical Society.

inorganic acids can dissolve almost all metals, the resulting toxic gases (e.g., Cl₂ and SO_x) and acidic wastewater can increase environmental and safety risks.^[288] Compared to inorganic leaching, the biocompatibility and biodegradability of organic acids can effectively alleviate the environmental issues associated with inorganic acid leaching.^[10,149] Given their characteristic of chelate coordination and complex formation, leaching using organic acids deserves further consideration. To further improve the leaching efficiency and reduce the acid dosage, novel strategies such as mechanochemical, electrochemical, and ultrasonic treatment methods have been introduced.^[289–291] For example, after mechanical ball milling, the reduced particle size and increased local temperature (which can promote the destruction of the crystal structure) can lead to a mild leaching process and high leaching efficiency. Unlike acid leaching, alkali leaching (e.g., NH₃, (NH₄)₂CO₃) is a selective leaching method in which the leaching mechanism involves chelation between ammonium ions and certain metal ions (e.g., Li, Ni, and Co) to form water-soluble complexes.^[149,292,293] However, alkali leaching systems suffer from pH changes (affecting the formation of chelates) and the weak complexing ability of ammonium ions and Mn (Mn salts cannot be recycled as valuable products), which remain significant challenges for alkali leaching systems.^[10,149] In addition to alkali and acid leaching, bioleaching, as a complementary technology, is an emerging technology for metal recycling with the advantages of being environmentally friendly and energy-saving; it applies acids (e.g., H₂SO₄, citric acid) produced by microbial metabolism (e.g., *Aspergillus niger*) to convert insoluble metal oxides to soluble metal ions.^[294–297] However, as an indirect acid-leaching recycling technology, bioleaching is limited to large-scale applications because of its low leaching efficiency and slow microbial culturing. Apart from these three conventional leaching technologies, green solvent leaching has attracted significant interest in the recycling of spent LIBs in terms of environmentally friendly solvents, cost-effectiveness, and effi-

ciency. Deep eutectic solvents (DES) are environmentally friendly solvents (i.e., a low eutectic mixture of two or more nontoxic compounds, such as choline chloride + ethylene glycol or choline chloride + citric acid) and effective leaching and reducing agents that enable the extraction of metals from spent LIBs and the separation of battery components.^[298–300] Supercritical fluid (SCF), which is another environmentally friendly solvent (e.g., subcritical water and subcritical methanol), can achieve a higher metal leaching efficiency than conventional leaching methods.^[301,302] Although these green solvent-leaching technologies have been successfully applied to extract metals from spent LIBs, they are still at the laboratory stage and have not been fully explored. The development of novel green leaching solvents with low costs and high leaching efficiencies requires further investigation.

Subsequently, as the next step in the leaching process, the separation and purification processes, such as solvent extraction, chemical precipitation, and resynthesis, play a decisive role in improving the purity of the recycled products.^[10,149] The mechanisms of solvent extraction and chemical precipitation are as follows: metal compounds of different solubilities in two-phase systems (commonly organic and aqueous phases); and of metal compounds different solubilities in different pH solutions.^[303–306] Compared to chemical precipitation, solvent extraction has the advantages of a mild operating environment, short reaction time, and high product purity; however, the high solvent cost and complex process limit its further application.^[149] Future solvent extractions should simultaneously meet the requirements of being inexpensive, environmentally friendly, sustainable, and simple. However, for metal ions with similar properties, these two methods cannot achieve effective separation; therefore, a resynthesis strategy was proposed. Adjusting the ratio of metal ions in the leaching solution to form cathode material precursors by co-precipitation or the sol-gel method not only avoids complicated separation processes but also reduces recycling costs.^[266,277,305–308] Then, the resynthesis of

a

 $pH < 0.2$  $pH = 1.0$  $pH = 2.0$ 

b

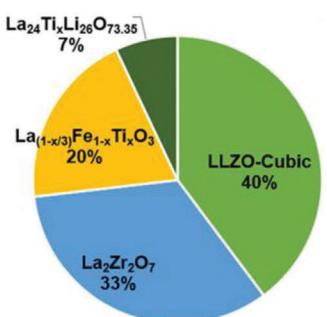
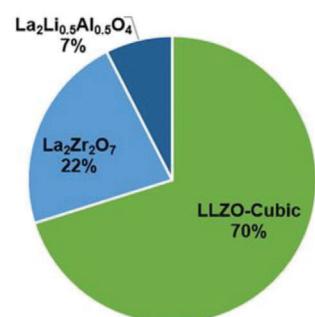
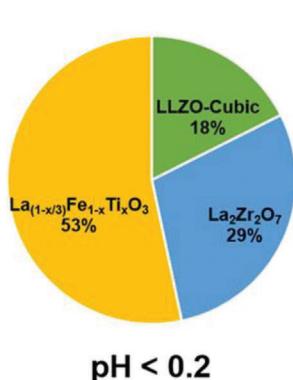


Figure 11. Oxide-based SSEs ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)) recycling schematic by hydrometallurgy technology. a) Recycling process flow of LLZO by acid leaching/alkali precipitation process in HCl (as leaching agent) with different pH values ($pH < 0.2$, $pH = 1.0$, $pH = 2.0$). b) Weight fraction of recycled cubic LLZO at different leaching solutions ($pH < 0.2$, $pH = 1.0$, $pH = 2.0$). Reproduced under the terms of the Creative Commons CC BY license.^[315] Copyright 2022, John Wiley and Sons Publishing.

cathode materials is achieved by drying and sintering. However, this resynthesis strategy is unsuitable for cathode materials containing two main metals, or a mixture of multiple types of cathodes.

Hydrometallurgy is a wet chemistry-based recycling technology that involves solution leaching, separation, and purification processes to recycle metal elements from spent LIBs. However, owing to the complex composition of ASSLMBs, it is challenging to extract valuable metals from spent ASSLMBs by hydrometallurgy and resynthesize cathodes and SSEs. Sulfide-based SSEs are unstable in air and undergo hydrolysis reactions with water to generate H_2S toxic gas, hydrometallurgy is not suitable for sulfide-based ASSLMBs recycling.^[2] For polymer-based SSEs, even small amounts of polymer electrolytes dissolved in aqueous solutions significantly change the solution viscosity and affect the precipitation of metal ions (e.g., Li, Co, Ni, and Mn), making it difficult to recycle valuable metals from spent ASSLMBs using this technology.^[309] For oxide-based SSEs, because the K_{sp} (i.e., solubility product) values of metal hydroxides of metal elements used in SSEs (e.g., La, Zr, and Ti) are lower than those of the cathodes (e.g., Co, Ni, and Mn), metal ions can be se-

lectively precipitated by adjusting the pH of the leaching solution, extraction agents, and precipitation conditions.^[13,310,311] For some oxide-based SSEs that can be prepared by co-precipitation, SSEs, and cathode materials can be recovered separately by a co-precipitation process and subsequently resynthesized by simple heat treatment and chemical re-lithiation.^[277,312,313] Recently, Friedrich et al. proposed a recycling concept suitable for oxide-based solid-state batteries, including inert crushing, heat treatment, sorting pretreatment, and a multistep hydrometallurgy process.^[314] Subsequently, Nowroozi et al. recycled $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) SSEs from a $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ system via hydrometallurgy using HCl as the acid leaching agent and $\text{NaOH}+\text{H}_2\text{O}_2$ as the precipitation agent, as shown in Figure 11.^[315] They also found that changes in the leaching solution concentrations significantly influenced the purity of the final recycled products. Although hydrometallurgy has progressed rapidly for LIBs, only a limited number of studies have been conducted on its effectiveness in ASSLMB recycling. Therefore, it is of great significance to develop suitable hydrometallurgy technologies for recycling spent ASSLMBs before a large number of batteries are scrapped.

5.3. Direct Regeneration of SSEs/Cathodes

Direct regeneration is a direct repair technology that avoids the destruction of SSEs/cathode crystal structures, allowing them to be reused through heat treatment and lithium replenishment.^[10,12,149] Compared with traditional recycling technologies, direct regeneration has the advantages of a simple process, low cost, environmental friendliness, and high recovery rate, and therefore has been rapidly developed for the recycling of spent LIBs, mainly including solid-state calcination, hydrothermal, and eutectic molten-salt.^[316–320] Recently, Chen et al. analyzed the energy consumption and greenhouse gas (GHG) emissions of LiCoO₂ from upstream processing to achieve complete recovery through the EverBatt model.^[272] Compared to traditional pyrometallurgical and hydrometallurgical recycling technologies, direct regeneration requires less energy and generates lower amounts of GHGs. Therefore, from an economic perspective, it is important to develop direct regeneration technologies for ASSLMBs. In Section 4, we have described how SSEs are not destroyed, except in the form of SEI/CEI layer decomposition, and that even highly degraded cathode materials can be directly regenerated/repaired.^[13,14,321] Therefore, instead of destroying SSEs and cathode materials to the atomic level for recycling, they can be regenerated by direct repair. Compared to the direct regeneration of LIBs, SSEs in ASSLMBs increase the complexity and challenges of this process. In the following section, we discuss the feasibility of using direct regeneration technologies intended for LIBs on ASSLMBs and currently invented direct regeneration technologies for ASSLMBs.

5.3.1. Solid-State Calcination

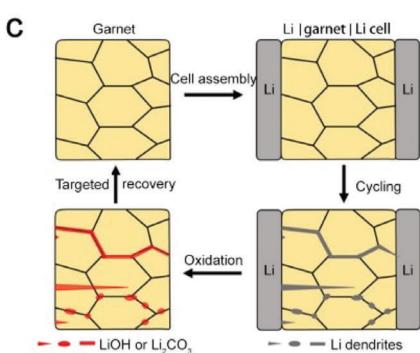
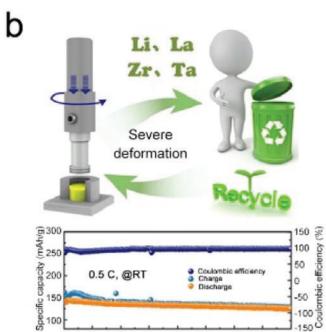
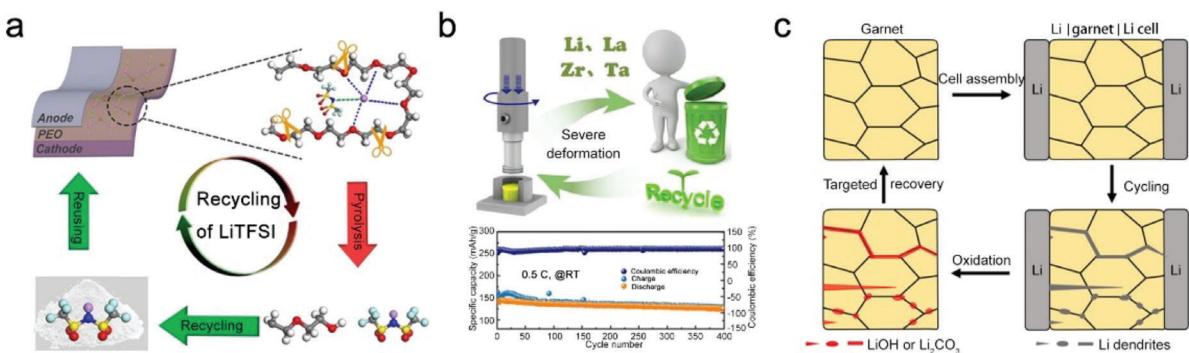
Solid-state calcination is a technology commonly used with or without the addition of lithium salts (e.g., Li₂CO₃) for the direct regeneration of spent LIBs cathodes, mainly for single-component cathode materials (e.g., LCO, NCM, and LFP).^[319,322–324] Numerous studies have confirmed that this recycling technology can repair the crystal structure of the cathode and achieve good electrochemical performance. However, solid-state calcination technology can be challenging for recycling spent ASSLMBs. In sulfide- and polymer-based ASSLMBs, at high temperatures, SSEs are destroyed, burned off, or converted into slags.^[2,13] Therefore, for both types of SSEs, a milder temperature is required to achieve direct regeneration of SSEs. Recently, Zhou et al. proposed a low-cost strategy for the reclamation of Li salts (LiTFSI) from polymer electrolytes using an SnF₂ catalyst (Figure 12a).^[325] Around 96% by weight of the initially added PEO is separated from the spent PEO-LiTFSI electrolytes in ethylene glycol at 60 °C (lower than the melting point of PEO) prior to roasting the spent polymer electrolyte. The presence of the SnF₂ catalyst can widen the thermal decomposition temperature gap between the polymer and the Li salt, allowing the selective fracture of the polymer without affecting the highly thermally stable LiTFSI. For oxide-based ASSLMBs, effective separation between SSEs and cathodes is a prerequisite for the direct regeneration of ASSLMBs, as solid-state calcination requires the precise calculation of the amount of additional lithium required for the waste material.^[322,323] However, effective separation of oxide-

based SSEs and cathodes remains challenging. In addition, because regenerated SSEs and cathode materials are sensitive to metal impurities, the removal of impurities to a satisfactory purity is another major issue to be considered in the recycling of spent ASSLMBs.^[322] Recently, Huang et al. proposed a green sustainable deformation-driven re-sintering (DDR) technology for recycling of garnet-type SSEs (LLZO) of spent ASSLMBs (Figure 12b).^[326] In parallel with this, Luo et al. found that short-circuit garnet-type Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂ SSEs can be directly regenerated by one-step annealing at 900 °C (Figure 12c).^[327] Garnet grains in Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂ SSEs can in situ react with dendritic Li and its derivative at 900 °C, which leads to the rapid recovery of short-circuit SSEs.

5.3.2. Hydrothermal Relithiation

Hydrothermal relithiation is a wet chemical regeneration method performed in an autoclave reactor to regenerate spent SSEs and cathode materials by lithium supplementation in an aqueous solution followed by heat treatment. The feasibility of this technology for recovering spent LIBs cathodes was demonstrated, and the results show that it is simple, environmentally friendly, and economical.^[328,329] For example, Chen et al. proposed a nondestructive process (i.e., hydrothermal relithiation at 220 °C for 4 h followed by annealing at 850 °C for 4 h) to directly regenerate degraded NCM cathode materials, achieving perfect reconstitution of new active particles in terms of chemometrics and microphase purity.^[329] Recently, Cheng et al. proposed the use of environmentally friendly ethanol (as a solvent and reducing agent) and CH₃COOLi (as a Li source) to directly repair spent LiFePO₄ in spent LIBs via hydrothermal treatment and sintering (i.e., hydrothermal relithiation at 180 °C for 5 h followed by annealing at 700 °C for 5 h).^[264] Furthermore, they introduced polyvinylpyrrolidone (PVP) into the recycling process to improve the cycling stability of regenerated LiFePO₄ by introducing N atoms to regulate the position of the d-band center of Fe near the cathode surface. Compared to solid-state calcination, hydrothermal relithiation allows for the direct regeneration of spent cathode materials with different lithium consumption levels without the need for precise calculations of the lithium salt addition.^[328,329] Due to the complex structure of ASSLMBs, this recycling technology is not applicable to all types of ASSLMBs. For ASSLMBs assembled with oxide-based SSEs, hydrothermal relithiation can be used to directly regenerate both spent SSEs and cathodes without the need for precise separation, mainly because of the following reasons: similar chemical properties of SSEs and cathodes (i.e., metal oxides), some oxide-based SSEs can be prepared by hydrothermal method, and there is no need for precise calculations regarding the amount of lithium salt to be added.^[13] For regenerated powders obtained after hydrothermal relithiation, additional SSEs or cathode powder must be added to achieve the desired SSE/cathode ratio. Finally, heat treatment is required to establish intimate contact between the SSEs and cathode, and the regenerated materials obtained can be reintegrated into new ASSLMBs. However, for ASSLMBs assembled with sulfide-based SSEs, this hydrothermal relithiation recycling technology is not suitable due to the instability of sulfide-based SSEs and the generation of toxic H₂S gas in water.^[2] For

Solid-state Calcination



Dissolution-precipitation

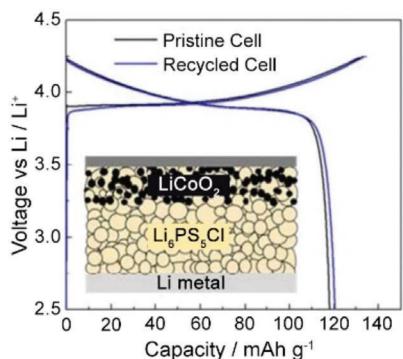
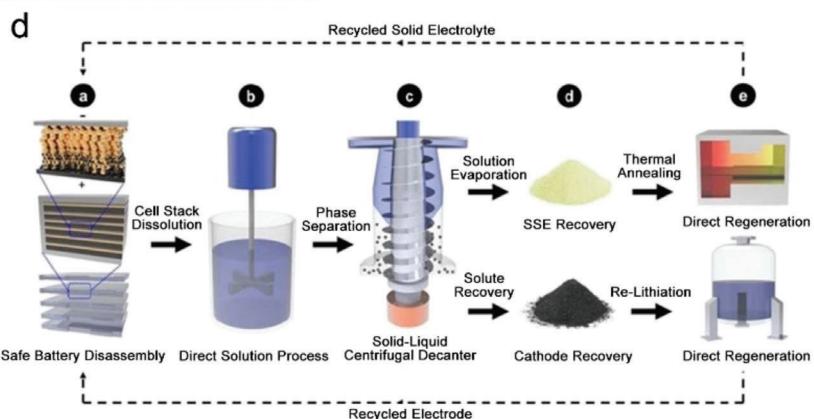


Figure 12. Direct regeneration of SSEs from spent ASSLMBs. a) Schematic of recovery of Li-salt (LiTFSI) from PEO-based polymer electrolytes by thermally depolymerizable technology. Reproduced with permission.^[325] Copyright 2022, Wiley-VCH. b) Schematic and recycling process flow of $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO) SSEs from spent solid-state lithium batteries by deformation-driven re-sintering (DDR) technology. Reproduced with permission.^[326] Copyright 2022, Elsevier. c) Schematic and recycling process flow of $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO) SSEs from spent ASSLMBs by an in situ one-step annealing. Reproduced with permission.^[327] Copyright 2022, Elsevier. d) Left: schematic and recycling process flow of $\text{Li}_6\text{PS}_5\text{Cl}$ SSEs and LiCoO_2 cathode materials from spent LiCoO_2/Li -metal ASSLMBs by dissolution-precipitation technology. Right: Voltage profile of $\text{LiCoO}_2/\text{Li}_6\text{PS}_5\text{Cl}/\text{Li}$ -metal ASSLMBs in the pristine and recycled state. Reproduced with permission.^[272] Copyright 2020, Springer Nature.

polymer-based SSEs, such as PEO-based SSEs (the most frequently applied polymer electrolytes), dissolve into monomers when immersed in water for a certain period of time.^[13] Some polymer-based SSEs may significantly change the solution viscosity and affect the recycling of spent SSEs and cathodes. Recently, Jing and Evans proposed a recyclable solid polymer electrolyte (i.e., a PEO network containing dynamic boronic ester crosslinks) that can be dissolved in water within 30 min to recover the starting polymer monomers.^[330] The dissolution of polymer electrolytes in polar solvents is usually achieved at room temperature or with slight heating; however, hydrothermal methods require high temperatures and pressures, and are therefore not suitable for polymer electrolytes.

5.3.3. Dissolution Precipitation

Dissolution precipitation is a direct regeneration technology applicable to some soluble SSEs, where SSEs are dissolved in

solution and cathodes act as precipitates and are separated by filtration or gravity.^[13,272] Subsequently, the recovered SSEs and cathodes are dried and regenerated through heat treatment and relithiation, respectively. Previous studies have shown that some sulfide-based SSEs (containing PS_4^{3-} thiophosphate units) can be solubilized in polar solvents (e.g., ethanol and acetonitrile) without structural damage.^[331,332] Recently, Chen et al. used ethanol as a solvent to separate $\text{Li}_6\text{PS}_5\text{Cl}$ SSEs and LiCoO_2 cathode materials from spent $\text{LiCoO}_2/\text{Li}_6\text{PS}_5\text{Cl}/\text{Li}$ -metal ASSLMBs, which were then regenerated by heat treatment and hydrothermal relithiation, respectively (Figure 12d).^[272] In addition, dissolution-precipitation recycling technology is also suitable for some polymer-based SSEs, such as PEO-based SSEs, which are currently the most studied polymer electrolytes because of their stable contact with Li metal, good electrode interfacial wettability, and good lithium salt solubility.^[20] PEO and LiTFSI have good solubility in polar solvents such as acetonitrile and ethylene glycol, and effective separation of SSEs and cathodes can be achieved using the dissolution-precipitation

recycling technology.^[13,20] The obtained polymer-based SSEs and cathodes can be regenerated by evaporating the solvent and hydrothermal relithiation, respectively. However, dissolution-precipitation recycling technology is not suitable for ASSLMBs based on oxide-based SSEs because of the chemical similarity between oxide-based SSEs and cathode materials.

5.3.4. Eutectic Molten-Salt Relithiation

Eutectic molten-salt relithiation technology provides another unique platform for the regeneration of spent SSEs and cathodes at normal pressure with the advantages of fast ion diffusion and no requirement for the precise calculation of lithium salt addition.^[333–335] In 2019, Chen et al. successfully demonstrated that a eutectic Li⁺ molten-salt solution (LiOH + LiNO₃) is useful for the ambient-pressure relithiation of degraded LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM523) cathode material.^[334] This technology has been demonstrated the spent LIB cathode recycling in eutectic molten salt systems, such as LiOH+LiNO₃ and LiOH+Li₂CO₃.^[333,334] Subsequently, Cheng et al. selected a eutectic Li-LiOH salt (the system with the lowest eutectic point in binary eutectic molten salt systems) to directly regenerate oxide cathode materials (LiCoO₂ and LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂) in spent LIBs.^[265] This combination of eutectic molten salt relithiation (decreases the temperature and time of the direct recycling process) and a one-step heating strategy simplifies the recycling process and realizes the replenishment of lithium and structural ordering. These results show that the use of eutectic Li⁺ molten salt solutions for atmospheric pressure relithiation has promising applications in the recovery and remanufacturing of degraded LIB cathode materials. Therefore, eutectic molten salt is a promising direct regeneration medium for recycling spent ASSLMBs. Based on the similar chemistry of oxide-based SSEs and cathode materials, it is possible to use this technology to recover ASSLMBs based on oxide-based SSEs using a method similar to hydrothermal relithiation without precise separation of the SSEs and cathodes. However, eutectic molten salts can change the composition of polymer electrolytes and are difficult to remove; therefore, they are unsuitable for polymer electrolyte systems.

In addition, other direct regeneration technologies, such as electrochemical relithiation (e.g., lithium as a counter electrode to supply lithium for spent cathodes, functionalized prelithiation separator),^[316,336] and deep eutectic solvent relithiation,^[335] have also been demonstrated to be practical for the recovery of spent LIBs cathodes. These studies also have certain reference importance for future ASSLMB recycling. Compared with conventional recycling processes, direct regeneration, as a non-destructive repair technology, can maximize the conversion of aged or degraded materials into components ready for new SSE or electrode fabrication by a relatively straightforward and simple recycling process. Although several direct recycling methods for solid-state batteries have been demonstrated at the laboratory scale, significant efforts are required to address existing challenges. These include effective separation of SSEs from other battery components, appropriate separation and direct recycling technologies for the distinctly different chemistries of SSE and cathodes, and challenges associated with residual lithium metal. The high viscosity of lithium metal presents challenges in mechanical sepa-

ration, while rapid exothermal reactions pose a significant safety hazard. SSEs also present safety hazards as sulfide-based SSEs generate toxic H₂S gas in moist conditions, halide-based SSEs are humidity-sensitive, polymer-based SSEs absorb moisture in air, and oxide-based SSEs form various lithium salts on their surfaces that harm comminution equipment. Furthermore, the lack of standardization in battery module shape, size, and weight presents hurdles for automation at an industrial level. **Table 2** lists some SSE materials recycled by direct regeneration technologies that exhibit electrochemical performance comparable to that of commercial materials.

As mentioned above, many challenges complicate the recycling of ASSLMBs unless the batteries are intentionally designed for recycling, and sustainable recycling technologies that can alleviate these problems are developed. Combined with the experience of LIB recycling technologies, the recycling technologies and processing of spent ASSLMBs can be divided into three categories: pyrometallurgy, hydrometallurgy, and direct regeneration. **Figure 13** summarizes and compares the feasibility and challenges of the three different recycling technologies described above for the recovery of ASSLMBs. As conventional recycling technologies for LIBs, pyrometallurgy and hydrometallurgy primarily involve the destruction of the crystal structure of the material at the atomic level and the extraction of valuable metallic elements. Although these two recycling processes are relatively mature and simple to operate, they are not sustainable because of their low recovery rates and the severe pollution caused by them. In addition, as an important component of ASSLMBs, SSEs undergo no structural changes at the end of their life, except for decomposition into SEI/CEI; therefore, the conventional recycling processes are not applicable to ASSLMBs. If full recyclability of ASSLMBs is to be achieved, there is an urgent need to find alternative methods, rather than optimizing conventional recycling technologies, to recover only the most economically valuable battery components. In the management hierarchy of spent ASSLMBs, direct regeneration is considered superior to conventional recycling technologies in terms of maximizing economic value and minimizing environmental impact. However, the number of studies conducted to date is relatively small and there are many opportunities for further research in this area. To accelerate the development of ASSLMBs recycling technologies, it is necessary to optimize and design novel recycling technologies to achieve unique applications and economic benefits.

Vehicle electrification will fundamentally change the automotive industry and bring about significant changes in the lithium-based battery industry, where the management of end-of-life batteries is a global challenge due to resource management, environmental, and safety reasons. With the impending surge in the number of retired LIBs, many recycling companies have emerged to jointly promote the sustainable use of spent batteries. The representative industrial LIB recycling technologies are listed in **Table 3**, and include pyrometallurgy (commercial plant), hydrometallurgy (commercial plant), and direct regeneration (pilot plant). However, these traditional recycling technologies are not designed for the recovery of spent LIBs, only the recovery of valuable metals can be achieved. Direct regeneration technology, which is still in the laboratory development stage, provides an excellent solution for the sustainable recycling of spent LIBs. Future industrialization of ASSLMBs recycling can draw on the

Table 2. Examples of direct regeneration of SSEs from spent ASSLMBs.

Regenerated production	Regenerated strategy	Ionic conductivity [S cm ⁻¹]	Critical current density [mA cm ⁻²]	Electrochemical performance of full cell	Refs.
Li ₆ PS ₅ Cl	Dissolution-precipitation	1.48 × 10 ⁻³ (RT)	—	≈ 80 mAh g ⁻¹ after 100 cycles at 0.1 C at RT, similar capacity retention compared to the pristine (Li/LiCoO ₂ cell, mass loading of LiCoO ₂ is 10 mg cm ⁻²)	[272]
Li _{6.5} La ₃ Zr _{1.5} Ta _{0.5} O ₁₂	Solid-state calcination	6.3 × 10 ⁻⁴ (RT)	1.0 (RT)	127.1 mAh g ⁻¹ after 100 cycles at 0.5 C at RT (LiAl/LiFePO ₄ cell, mass loading of LiFePO ₄ is 4.6 mg cm ⁻²)	[327]
Li _{6.5} La ₃ Zr _{1.5} Ta _{0.5} O ₁₂	Solid-state calcination	3.55 × 10 ⁻⁴ (RT)	1.24 (RT)	126.7 mAh g ⁻¹ after 400 cycles at 0.5 C at RT (Li/LiFePO ₄ cell, mass loading of LiFePO ₄ is 2 mg cm ⁻²)	[326]
LiTFSI (from PEO-LiTFSI electrolyte)	Solid-state calcination	4.22 × 10 ⁻⁶ (RT) ^a	—	≈ 135 mAh g ⁻¹ after 200 cycles at 0.15 C at 62 °C (Li/LiFePO ₄ cell, mass loading of LiFePO ₄ is 3.2 mg cm ⁻²)	[325]

^{a)} Similar ionic conductivity to PEO containing commercial LiTFSI.

lessons learned from these industrial LIB recycling processes to develop a sustainable ASSLMBs recycling process.

6. Recycling-Oriented ASSLMBs Design

Currently, because LIBs are not designed with recycling in mind, issues originating from the recycling of spent LIBs, including safety, low recovery rates, and high recycling costs, remain troublesome obstacles. To address these issues, the U.S. Department of Energy's ReCell Center proposed core principles for LIB recycling, including materials designed for recycling, direct cathode recycling, recycling of other battery components, and modeling and analysis. (<https://www.recellcenter.org/research>) Taking ReCell's goals as a starting reference point, a battery-recycling-oriented design for ASSLMBs is urgently required to ensure their

recyclability and sustainability. The targeted design of the cell and electrode structure, active electrode materials, and solid-state electrolytes will facilitate spent ASSLMBs recycling and maximize profitability. A future recycling-oriented ASSLMBs design is introduced in the following section (Figure 14).

6.1. Sustainable Cathode Material Design

Sustainable electrode material design is essential for the sustainability of the ASSLMBs industry. Considering the supply risk, toxicity, and high cost of cobalt (Co), the future trend is toward low-Co and Co-free batteries, which is expected to realize the decoupling of energy storage devices from the Co content. Li-rich Mn-based cathodes (>250 mAh g⁻¹) and Ni-rich cathodes (200 mAh g⁻¹) can provide high energy density and mitigate the

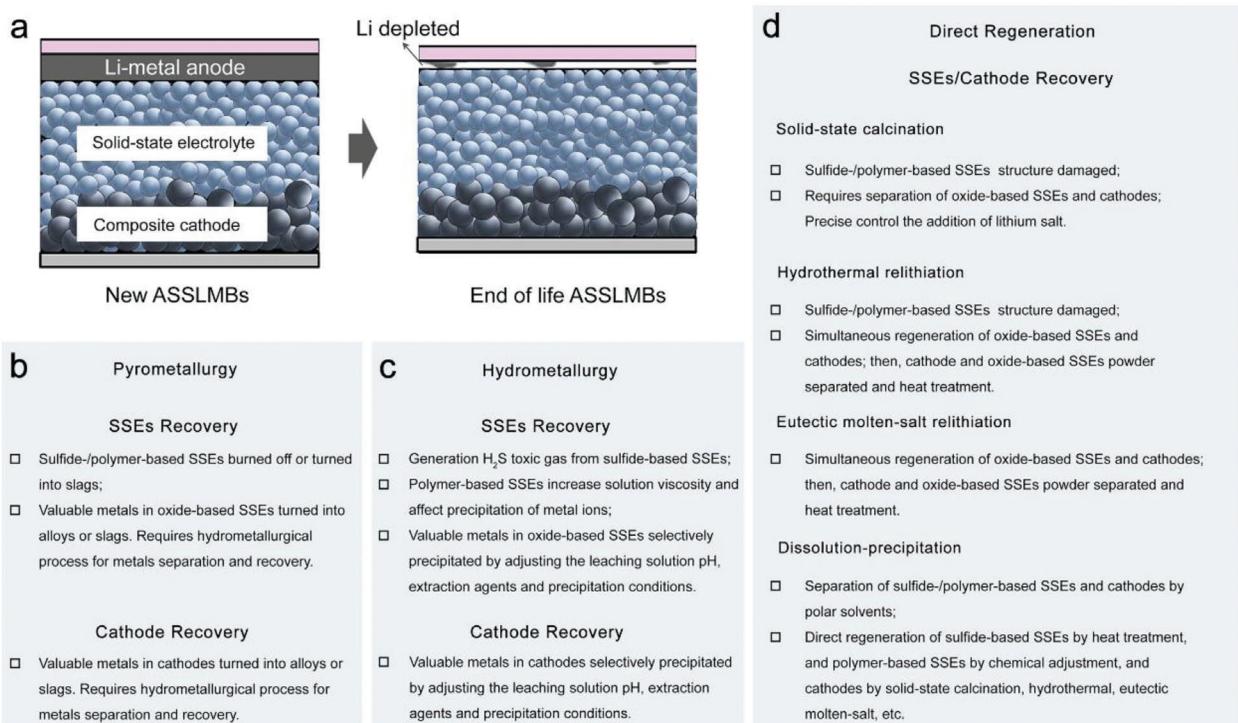
**Figure 13.** Overview of feasibility and challenges of different recycling technologies for ASSLMBs.

Table 3. Current LIBs recycling industrial technologies.^[10,11,281,337]

Company	Location	Recycling process	Annual capacity (tonnes/year)	Recycled elements
Sony-Sumitomo	Japan	Pyrometallurgy	150	Co, Ni, Cu
Glencore	USA, Canada, Norway	Pyrometallurgy	7000 (Norway)	Co, Ni, Cu
Inmetco	USA	Pyrometallurgy	6000	Co, Ni, Fe
Umicore	Belgium	Pyrometallurgy	7000	Co, Ni
Accurec	Germany	Pyrometallurgy	6000	Co, Li
Akkuser Ltd	Finland	Pyrometallurgy	4000	Co, Cu, Fe
SungEel HiTech	South Korea	Hydrometallurgy	8000	Co, Ni, Mn, Li
Brupn	China	Hydrometallurgy	25000–30000	Co, Ni, Cu, Al
GEM	China	Hydrometallurgy	20000	Co, Ni
Bangpu Ni/Co High-Tech Co	China	Hydrometallurgy	3600	Cathode power, Co
Huayou Cobalt	China	Hydrometallurgy	60000	Co, Cu
Highpower International	China	Hydrometallurgy	10000	/
Retriev	Canada, USA	Hydrometallurgy	/	Co, Li
Recupyl	France	Hydrometallurgy	110	Co, Li
TES-AMM	Singapore	Hydrometallurgy	1000	/
Batrex Industrie AG	Switzerland	Hydrometallurgy	200	/
Farasis Energy	USA	Direct regeneration	/	Cathode powder
OnTo Technology	USA	Direct regeneration	/	Cathode powder

Co supply risk, increasing battery sustainability and exhibiting commercial viability.^[338] Nevertheless, the disadvantage of these high-energy-density cathode materials, that is, irreversible phase transitions (e.g., layered to spinel, cubic to tetragonal), results in poor cycling and thermal stability.^[339] Consequently, modification strategies have been applied to boost the stability of these cathode materials, including selecting suitable binders, interface modifications, atomic doping, and single crystals^[146,338,339] Furthermore, the rapid growth in the demand for Ni will ultimately limit its availability and increase its cost until more attractive cathodes emerge. Based on limited mineral resources, shifting from inorganic compounds to sustainable materials (e.g., polymeric cathode materials) is another sustainable electrode material design. Generally, organic electrodes have certain advantages such as no high-temperature roasting process, no mining requirements, and sustainable recycling processes (e.g., some organic electrodes can be dissolved in water or ethanol).^[340–342] However, their poor electronic conductivities and low tap densities significantly restrict their application in ASSLMBs. Advancements in cathode materials, such as oxygen/air and sulfur cathodes, can significantly improve battery energy density and reduce costs and CO₂ emissions (e.g., no transition metals in cathodes) during production and recycling.^[5,141] However, the degradation of electrolytes in air and insoluble discharge products hinder the air diffusion in cathodes of Li–oxygen/air batteries; the presence of polysulfide shuttles in Li–sulfur batteries reduces the feasibility of active sulfur cathodes and decreases the battery cycling efficiency. Sustained efforts should be made to overcome these challenges for the cathode material

technologies and further enhance the sustainable development of ASSLMBs.

In practice, recycling-friendly retrofits need to maintain the performance specifications of existing ASSLMBs, simultaneously use cost-effective materials and allow for easy material separation and subsequent recycling of electrode materials. Potential ways to achieve these goals include: at the electrode level, the use of water or alcohol-soluble binders and organic cathode materials to reduce the use of hazardous substances in material separation and to control cathode material costs; at the cathode recycling level, the use of single crystal cathodes are easier to implement for direct regeneration and exhibit higher reversible capacity and more stable cycling performance compared to polycrystalline cathode materials. In addition, innovative designs are also needed at the level of existing electrodes and cells. A new electrode design that allows for quick and easy separation of active electrode materials from other inactive components, minimizing the time and costs involved in recycling. Research direction can be directed towards seeking binder-free, current collector-free cathode designs that achieve almost 100% recovery without releasing toxic wastes. Therefore, it is essential to consider these requirements during the design phase for retrofits to create efficient and sustainable ASSLMBs.

6.2. Sustainable Anode Material Design

In a lab-level ASSLMBs assembly, the integration of Li–metal anodes and SSEs, such as compression, direct stacking, melting,

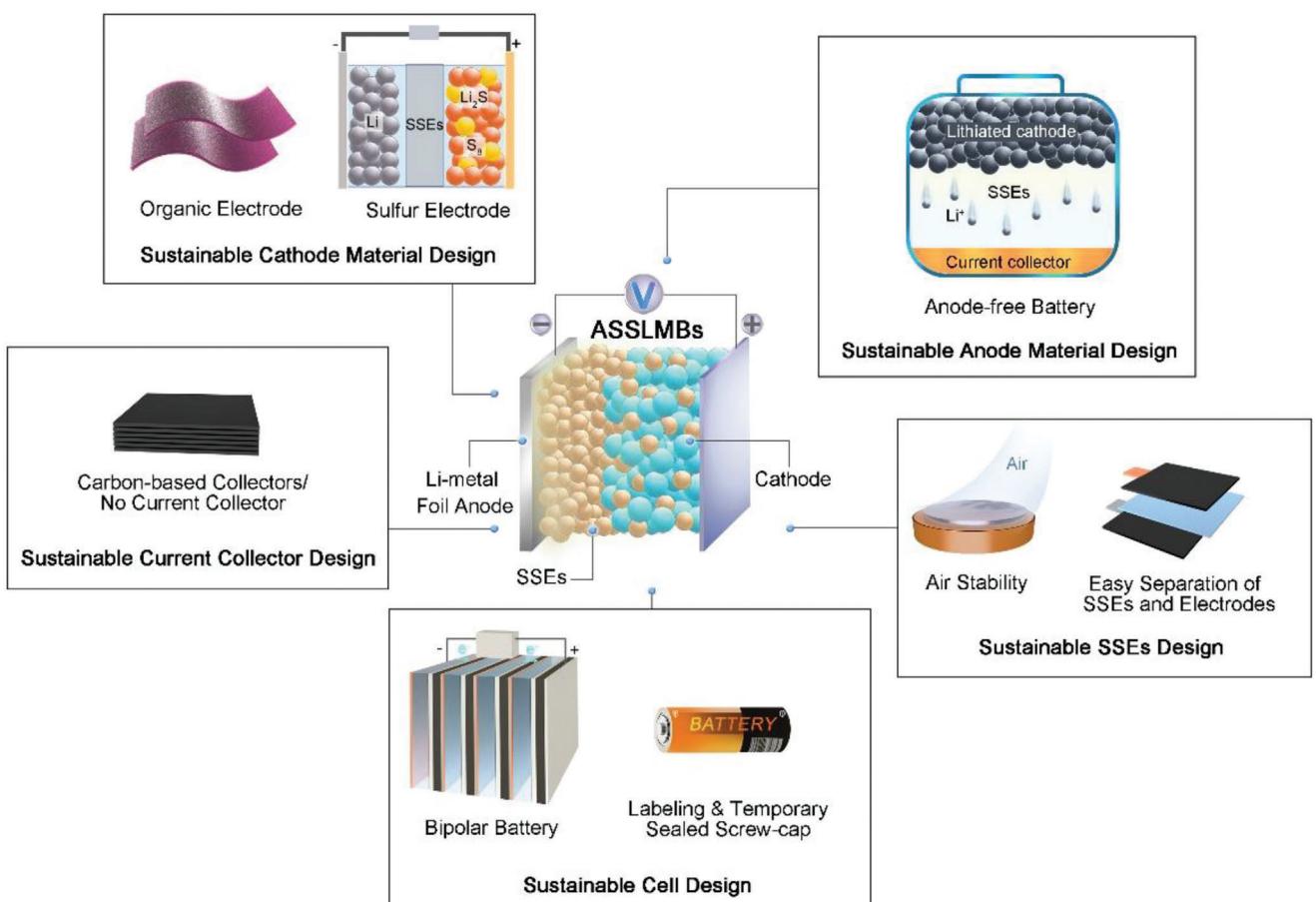


Figure 14. Schematic of future hypothesized recycling-oriented ASSLMBs design.

and sputtering, is technically easy.^[230] From lab-level to large-scale, challenges such as interfacial inhomogeneity of the Li–metal interface, the fragility of Li–metal during conventional roll-to-roll processes (owing to the low tensile strength of Li–metal), permeation of Li–metal into SSEs (due to creep behavior of Li–metal), and pulverization limit their practical application in industrial-scale batteries.^[137,230] Although various beneficial strategies toward Li–metal anodes have been confirmed at the laboratory level, rational application techniques are highly significant for large-scale applications. Furthermore, the high reactivity and strong adhesion originating from the Li–metal anode in ASSLMBs result in safety issues (e.g., fire, explosion) and difficult separation processes (e.g., crushing, sieving, shredding) for spent battery recycling.^[218] However, from a theoretical analysis, anode-free Li metal batteries (i.e., no Li-ion insertion host at the anode) can provide a higher energy density because of the reduction in the weight and thickness of the battery. Furthermore, anode-free Li–metal batteries have significant manufacturing advantages, including low process cost, being less error-prone, higher production efficiency, and lack of major safety risks.^[238] However, challenges for anode-free Li–metal batteries, such as insufficient coulombic efficiency (CE), interfacial issues, and inhomogeneous nucleation, remain troublesome obstacles for their transfer from lab-scale to industrial-scale.

Today, in the realm of battery design, product performance enhancements reign supreme. However, as new energy products become increasingly prevalent, resource consumption, elevated costs and environmental pollution all exert a significant impact on battery design. Therefore, it is necessary to consider material recycling in the early stages of battery design, not only to alleviate the difficulties of material recycling in later stages but also to optimize the reuse of recycled battery materials in new manufacturing processes. Despite the challenges associated with lithium metal anode and anode-free battery configurations, it must be acknowledged as significant strides towards replacing graphite anodes for the purpose of enhancing energy density, mitigating the complexity and expense of recycling spent batteries, and accomplishing sustainable development of solid-state batteries.

6.3. Sustainable Current Collector Design

The exploration of lighter current collectors is a promising way to further increase the energy density of ASSLMBs. Metal-on-plastic foil is one strategy facilitating lighter current collectors (i.e., metal is sputtered or evaporated onto a thin plastic foil) that is being explored in the industry.^[343,344] Low-density plastic current collectors not only reduce the overall mass and increase the energy density of the battery, but also allow for

functional designs such as fire retardancy to enhance battery safety. However, the development of advanced processing techniques for their integration into industrial manufacturing remains a challenge. Additionally, because battery materials are sensitive to metal impurities such as copper (Cu) and aluminum (Al), removing impurities to a satisfactory degree is an important consideration for battery recycling. Replacing conventional Cu or Al foil current collectors with low-cost, environmentally friendly, lightweight, and low-corrosion carbon-based collectors has been recognized as a promising method to overcome these issues.^[345] To solve the challenge of separating electrode materials from current collectors, freestanding electrode materials have attracted great interest.^[346] This not only simplifies the process of separating the electrode material from the current collector during the pretreatment steps of battery recycling, but can also further improve battery energy density.

With the optimization of electrode and electrolyte materials in high specific energy ASSLMBS, there is an alluring opportunity to further augment the energy density of batteries while achieving sustainable recycling of solid-state batteries by reducing the weight of current collectors and optimizing their structural design. The potential and incentives for improvement are clear, while producing them on a large scale continues to pose challenges. It is undeniable that carbon-based current collectors and freestanding electrode have obvious advantages over other current collector structure designs for solid-state battery recycling, making them an attractive option for potential future use. They not only prevent battery materials from being affected by metal impurities but also simplify the process and reduce the cost of separating electrode materials from collectors during recycling. Overall, the use of carbon-based current collectors and freestanding electrode presents a promising avenue for the development of more sustainable, efficient, and cost-effective ASSLMBS in the field of energy storage.

6.4. Sustainable SSEs Design

Although SSEs still face some problems and challenges in practical applications, some practical attempts have been made to shorten the distance from lab-scale to large-scale. However, recyclable and reprocessable SSEs are crucial for achieving sustainable ASSLMBS. For the SSEs, the structure was not destroyed, except for decomposition in the form of SEI/CEI layers.^[13,14,321] Therefore, the regeneration of spent SSEs can be achieved by direct regeneration technology. However, there are still problems with SSEs in terms of sustainability. Considering the supply issue, toxicity, and high cost of rare earth elements (e.g., La and Tb) toward oxide-based SSEs, realizing the decoupling of rare elements from SSEs is an important step for the large-scale application of ASSLMBS.^[227,237] In addition, the optimization of ceramic pellets or film frangibility is another challenge for industrial applications. Toward sulfide-based SSEs, their simple elementary composition (e.g., Li_xP_yS_z, Li₆PS₅X (X = Cl, Br I)) has led to widespread interest and advocacy for their practical application, while the higher ionic conductivity of LGPS may prevent their large-scale application due to the high cost of feedstock GeS₂.^[230] It is also important to consider their sensitivity to moisture, which leads to bottlenecks in the mass produc-

tion of sulfide-based SSEs.^[347] Polymer-based SSEs are among the most promising in terms of mass production, where both lithium salts and polymer matrices can be industrially produced, and the similarities between polymer-based SSEs and liquid electrolytes reduce the complexity of the production process design. However, their limited ionic conductivity at room temperature restricts their application in ASSLMBS. While current research efforts have focused primarily on oxide-, sulfide- and polymer-based SSEs, an undesired trade-off has been observed between ionic conductivity and SSE stability. However, recent advancements in halide-based SSEs have improved certain variables, including the instability to oxygen, poor chemical/electrochemical stability toward traditional oxide cathodes, low ionic conductivity, low deformability, and unscalable synthesis routes.^[23,110] Specifically, some halide-based SSEs have gained attention due to their stability in an oxygen atmosphere with no deterioration of the structure/composition, high lithium-ion conductivity up to 10⁻³ S cm⁻¹ at room temperature (possibly up to 10⁻¹ S cm⁻¹), compatibility with cathode materials without extra surface coating, suitability for large-scale water-mediated synthesis, as well as their low manufacturing cost, high deformability and flexibility with electrodes.^[23,105,110,348] By comprehensively addressing these issues, halide-based SSEs are recognized as highly promising. Despite being an alternative to oxide-, sulfide- and polymer-based SSEs for ASSLMBS large-scale deployment, few halide-based SSEs, namely, Li₃YBr₆ and Li₃InCl₆, can achieve room temperature ionic conductivity of 10⁻³ S cm⁻¹.^[23,56] Consequently, the exploration of other high ionic conductivity halide-based SSEs is required. Additionally, effective strategies to protect halide-based SSEs from reduction by the lithium metal anode are needed to avoid side reactions at the SSEs/lithium anode interface. Further efforts are also required to scale up the liquid-phase synthesis methods for halide-based SSEs and other types of SSEs.

The development of ASSLMBS relies on the design of highly conductive and (electro) chemically stable SSEs. An essential aspect of this design process is the use of cost-effective materials and easily scalable preparation methods of preparing SSEs. By designing SSEs with high conductivity and stability, it is possible to enhance the overall performance and lifespan of the batteries. The selection of cost-effective materials and scalable preparation methods allows for the cost-efficient production of SSEs, which is important for the commercialization and sustainability of ASSLMBS. Therefore, the strategic selection of materials and preparation techniques is crucial in the development and implementation of ASSLMBS. Polymer-based SSEs offer distinct advantages in waste recycling due to their relatively lower preparation and recycling costs and good processability, as well as their renewability. The recycling strategies can be either physical separation methods (e.g., green solvent dissolution separation) to facilitate subsequent recycling and reuse processes, or thermal pyrolysis and decomposition of the spent SSEs at a certain temperature to generate basic units for the regeneration process. Additionally, recycled polymer-based SSEs can be modified by adding filler and plasticizer to improve performance and expand their applicability to other scenarios. Overall, polymer-based SSEs have comparable recovery value in terms of sustainability. Recently, halide-based SSEs have emerged as a strong contender due to their unique combination of sulfide- and oxide-based SSEs

benefits. These materials have both mechanical sinterability and excellent (electro)chemical stability. Furthermore, they can be easily produced using a scalable, water-mediated synthesis method, which is ideal for use in practical manufacturing processes and sustainable recycling efforts. As a result, halide-based SSEs show a lot of promise in the field of sustainable ASSLMBs. However, this does not mean that the other type of SSEs cannot be recycled. Although recycling oxide-based SSEs poses several challenges due to their hardness, chemical stability, and close integration with other components, valuable metal elements like lithium, lanthanum, and zirconium can still be recovered using chemical leaching and precipitation. For sulfide-based SSEs chemically unstable in air and moisture, which causes structural and compositional deterioration. Recovery of these materials can be achieved by processing in an inert or dry environment and using organic solvents to separate the electrolyte from the battery components. With further research, it is likely that more environmentally friendly and efficient recycling technologies will emerge, even in the face of current challenges.

6.5. Sustainable Cell Design

In the context of sustainable cell design, issues that need to be addressed include the simplification of cell openings, electrode material separation, and battery configuration and components. Although mechanical treatment (e.g., crushing, grinding, and separation) is a widely adopted method in industrial LIB recycling, poor selectivity and inevitable interpenetration of different battery components remain as obstacles. For example, a variety of assumptions have been made for sustainable battery case design, such as replacing permanently sealed canisters/prismatic cells with temporarily sealed screw caps or internal vacuum-release valves and lightweight shape-memory alloys as smart battery casings.^[342,349,350] As such, it can be expected that casings can be feasibly separated from other battery components. Furthermore, connection parts and module manufacturing can use reversible insulating rings, sealants, and shape-memory polymers to achieve nondestructive modules and pack openings.^[342,351] Decoupling electrode materials from current collectors is expected to be achieved in a sustainable manner, through the design of free-standing electrode materials and water-soluble binders. By embedding these chemical designs into a sustainable ASSLMB design, more competitive and convenient material separation and product purity assurance can be achieved.

At the level of cell packaging and stacking, it is important to modify designs to achieve easier dismantling of individual cells, either manually or by automation. Additionally, the safe dismantling and component separation of high-volume and hazardous ASSLMBs would be best accomplished with automation, as it could minimize the risks and exposure to workers. Such adaptations need to be made to ensure efficient and safe handling of cells during dismantling processes. Therefore, the design of packaging and stacking of ASSLMBs should be carefully considered to promote safer and more efficient cell dismantling while minimizing possible damage or contamination. Considering the complex structure of conventional LIBs, simplifying the ASSLMBs configuration and components could facilitate

a streamlined battery material separation for sustainable battery recycling. Recently, the bipolar electrode structure has been applied as an interesting strategy to simplify the battery structure, where the cathode and anode using a unified current collector not only reduce the battery manufacturing cost but also increase the battery energy density.^[352,353] Furthermore, through these optimized battery structures and intelligent designs, battery identity and state of health monitoring can be achieved, and safety issues originating from spent battery transport and recycling can be reduced. Although there is a long way to go to achieve sustainable production of ASSLMBs, a strong drive towards global sustainability will incentivize sustainable battery manufacturing.

7. Conclusion and Future Perspective

We reviewed the sustainability of ASSLMBs, including battery technology, battery recycling processes and challenges, and recycling-oriented battery designs. In the future, the development of Li-based batteries will shift from LIBs to ASSLMBs owing to their high energy density and safety. To acclimate to this trend, long-term considerations and circumventing of recycling challenges are crucial for the development of sustainable ASSLMBs. Additionally, the development of recycling-oriented battery designs and sustainable recycling technologies is important for the sustainability of ASSLMBs. Although some lab-level strategies can alleviate the issues mentioned above, scaling up from the lab scale to commercial deployment remains challenging in most cases. Immense efforts are still required to achieve sustainable recycling of ASSLMBs, as shown in Figure 15. These include the following:

1) Technical aspects: ASSLMBs technology and recycling technologies are in a dynamic state of development; therefore, great efforts are needed for battery manufacturers and recyclers to achieve sustainability of ASSLMBs. For battery manufacturers, recycling-oriented battery designs, such as environmentally friendly battery materials (e.g., electrode materials, solid-state electrolytes, binders, current collectors, and casings) and design of a sustainable battery structure to streamline battery collection, sorting, and separation, have been recognized as significant points for battery remanufacture, repurposing, or entering the recycling stream to realize sustainable ASSLMBs. For battery recyclers, sustainable ASSLMB recycling technologies, such as gentle pretreatment required to prevent the original crystal structure (e.g., cathode and SSEs) from being destroyed at the atomic level, effective separation of various battery components, obtaining consistency and satisfactory purity of regenerated materials, and recycling different types of ASSLMBs, are of great significance for the sustainability of ASSLMBs and achieving maximum economic benefits. The development of sustainable ASSLMBs from technical level includes the following specific aspects:

- 1) Easy-to-recycle battery materials: For example, in order to reduce the environmental impact of recycling process, low toxicity or degradable SSEs can replace rare and toxic materials. The development of green binders has gained attention as a way to reduce the environmental impact of adhesive materials. Therefore, fluoride-free binders have been investigated as



Figure 15. Schematic of future strategy and principle for sustainable recycling of ASSLMBs in the future.

potential substitutes for conventional binders that contain fluoride. In addition, the solubility of green binders in water or ethanol is also critical for their eco-friendliness, as it affects their ease of application, viscosity, and residue formation. In addition, it is essential to minimize binder usage and clearly specify the type and distribution of binders, which determines material separation.

- 2) Designing recyclable cell structures: One critical aspect of designing batteries is the facilitation of their component effective separation. The design stage of ASSLMBs should focus on more recyclable components, such as the use of detachable structure, easily separated materials, etc. For example, various battery materials can be effectively separated using green solvents such as water or alcohol, with no need for additional chemicals. This represents a significant advantage over traditional methods that typically involve the use of multiple hazardous chemicals, which can be costly and environmentally harmful. By employing green solvents, the separation process can be accomplished in a more environmentally sustainable and cost-effective manner. As such, the use of green solvents is an important step forward in promoting environmentally responsible battery production. In addition, to simplify the recycling process for ASSLMBs and reduce resource consumption, it is recommended to implement a standardized industry practice for designing battery packaging that is easy to disassemble. Another area of research worth exploring is the development of automation technology to facilitate the battery recycling process.
- 3) Developing efficient recycling technologies: To enhance the recycling efficiency and resource utilization, it is vital to develop efficient recycling technologies. This includes the need for advanced physical and chemical methods to effectively separate the battery components. Subsequently, direct regeneration technologies are applied to recovered battery components, such as SSEs and cathode. This design demonstrated

reduced energy costs and greenhouse gas emissions in comparison to traditional pyrometallurgical or hydrometallurgical methods. Additionally, it is possible to minimize waste and support the transition toward a circular economy. Thus, the development of efficient recycling technologies for ASSLMBs is urgently required.

- 4) Reutilization and regeneration: Optimizing the use of valuable materials from spent batteries by repurposing them for other applications is critical in reducing the demand for raw materials. For example, directly transforming spent ASSLMBs into high-quality functional materials (e.g., catalytic system) can eliminate the energetically costly and inefficient steps of recycling, purification, and synthesis. Furthermore, repurposing these materials reduces the cost of extracting new raw materials, which can be both economically and environmentally beneficial in the long run. The practice of reusing valuable materials is also in line with the principles of circular economy and sustainability.
- 5) Intelligent recycling managements: Intelligent management of spent ASSLMBs recycling can be achieved by utilizing advanced technologies such as big data and artificial intelligence. These technologies can significantly enhance the efficiency of the recycling process. For example, big data can be utilized to analyze the data collected from various sources, such as battery production and use stages, to identify potential areas for improvement in the recycling process. Furthermore, artificial intelligence can be used to automate tasks such as sorting and separating recyclable materials, thus reducing the need for manual labor and increasing the speed and accuracy of the recycling process. Therefore, the integration of these technologies can lead to a more sustainable and effective spent ASSLMBs management system.
- 6) Interdisciplinary cooperation: The researchers from multiple fields, such as materials science, environmental science, and

chemical engineering, collaborate to study ASSLMBs recycling technology and techniques.

Through the above research direction, the advancement of ASSLMBs recycling technologies in both academic and industrial settings can be facilitated. By exploring different avenues to increase the efficiency of recycling processes, the academic community can contribute to the improvement of these recycling technologies. In turn, the industry can benefit from technological advancements by implementing them in their recycling practices, which can result in more efficient and cost-effective recycling solutions. Overall, the implementation of the research direction outlined above can promote the sustainable development of ASSLMBs recycling technologies across different fields.

(2) Policy support aspects: Beyond industrial-level technical challenges, policy-level support is needed to establish a sustainable ASSLMBs recycling system. Several specific aspects are involved in the development of sustainable ASSLMBs at the policy level:

- 1) Comprehensive policy frameworks: A battery policy requires the establishment of a comprehensive ASSLMBs management platform encompassing all stages of the battery life cycle, including battery manufacturing, sale, use, collection and transportation of retired batteries, battery remanufacturing (i.e., replacement of inferior cells or modules in battery packs), repurposing (i.e., use of energy-demanding equipment), and recycling. Such frameworks should outline clear targets and sustainability indicators, and establish mechanisms to monitor and evaluate progress towards these targets. In addition, the development of sustainable ASSLMBs requires the integration of sustainability considerations across all policy domains and levels of government and the establishment of effective governance structures to support implementation.
- 2) Standardization and supervision: The development of national or industry standards for the recycling of ASSLMBs is crucial for ensuring a safe, efficient, and environmentally friendly recycling process. These standards provide a framework for ensuring that the recycling process adheres to strict safety protocols, minimizing the risk of accidents that could potentially cause harm to workers or the environment. Furthermore, standard procedures in place can improve the overall efficiency of the recycling process, reducing costs and improving the overall speed of the process. Governments should formulate relevant battery manufacturing standards and specifications, such as cell design (e.g., size and labeling), binder types, cell joining mechanisms, and responsibility for the collection and treatment of retired batteries.
- 3) Cooperation of various stakeholders: Sustainable ASSLMBs development must involve engagement and collaboration with a diverse range of stakeholders, including society, industry, and academia. To establish a comprehensive and well-defined battery recycling industry, it is essential to create a clearly delineated industry chain that can assign roles and responsibilities to each participant. These responsibilities should include outlining how spent batteries are collected, transported to the recycling facility, processed, and safely disposed of. A standardized and efficient battery re-

cycling industry chain will ensure that all participants play their roles. For battery remanufacturing, policies and regulations are required, including diagnostic criteria for retired batteries, composition of battery components, and the performance of reassembled new battery packs. Repurposing requires the replacement of damaged cells or modules and the building of new battery management systems (BMSs) for other, less energy-demanding equipment. It is necessary to establish policies and regulations to regulate the design of repurposed batteries and performance metrics, and clearly define the risks and liabilities of battery use to reduce consumers' concerns regarding repurposed batteries. Remanufacturing and repurposing only delay the recycling horizon, and retired batteries are ultimately recycled, by which valuable materials are returned to the value chain. ASSLMB packs are complex, not only because of the multiplicity of battery material chemistries, but also because the architecture of battery systems varies significantly from manufacturer to manufacturer. However, sustainable battery recycling technologies need to accommodate all designs of ASSLMB packs and recycle more valuable battery materials to achieve sustainable battery recycling ecosystems. For battery recycling, policies and regulations are required to evaluate retired ASSLMBs and to set standards for the performance and reliability of recycled battery materials. Furthermore, other aspects of battery recycling, including collection, transportation, and storage, must be regulated by policies and regulations to avoid safety hazards caused by improper handling that result in thermal runaway. This can facilitate the innovative solutions and strategies, as well as increase public awareness and enhance the feasibility of achieving a sustainable ecosystem for spent ASSLMBs.

(3) Environmental and safety aspects: Environmental and safety issues originating from ASSLMBs can be divided into two aspects: battery manufacturing and recycling. Generally, spent Li-based batteries are considered hazardous waste because they contain a variety of chemicals, including heavy metals, reactive salts, inorganic/organic electrolytes, and additives. In the future, reducing the heavy metal content of batteries, selecting environmentally friendly materials for components such as electrodes, electrolytes, and binders, and optimizing the battery structure will help reduce the environmental and safety impacts of ASSLMBs. Given the complex composition of ASSLMBs, on the premise of ensuring the battery recovery rate, there may be potential hazards (e.g., the aggressive reaction of lithium metal with water, thermal runaway, and explosions caused by short circuits) and secondary pollutants (e.g., wastewater, waste gas, and residues) in the recycling process. At the environmental and safety level, the development of sustainable ASSLMBs involves several specific aspects:

- 1) Source control. The choice of materials for ASSLMBs is an important factor to consider in order to develop sustainable and environmentally friendly battery systems. It is desired that nontoxic elements be used as substitutes for toxic materials, without compromising on the performance of the batteries. Such materials have the potential to reduce the pollution associated with battery production and disposal, and can also

make batteries safer to use. For example, cobalt-free cathodes are known to be less polluting and more sustainable. Additionally, realizing the decoupling of rare elements (e.g., La and Tb) from SSEs is also an important step to achieve pollution source control. By using nontoxic materials, researchers can develop batteries that are not only more sustainable but also more affordable and accessible for large-scale.

- 2) End-treatment control: When it comes to the recycling process, it is recommended that nontoxic reagents and technologies with low emissions and energy consumption be utilized. This approach should be prioritized, as it can significantly reduce the environmental impact of recycling. As the last resort for spent ASSLMBs disposal, end-treatment should be implemented to minimize pollution emissions. By following these guidelines, we can ensure that the recycling process is as environmentally friendly as possible.
- 3) Evaluating whole lifecycle cost and environmental effects: Scaling up lab-scale technologies is often difficult due to the associated high capital costs, high energy consumption, and environmental concerns. As such, it is essential to evaluate the cost of recycling a process and determine its economic and environmental feasibility before proceeding in order to achieve sustainable solid-state batteries.
- 4) Consumer behavior aspects: In addition to technical, policy support, environmental, and safety considerations, consumer behavior is also critical in developing sustainable battery recycling. Recycling waste batteries can be facilitated by providing popular education on their environmental benefits and hazards. It is essential to educate the masses about the toxic components of batteries, such as electrolyte and heavy metals, which can contaminate soil and water, causing severe health risks. Simultaneously, promoting the benefits of recycling batteries, such as conserving natural resources and reducing pollution, can also raise awareness about their importance. By creating public awareness about the significance of battery recycling, it contributes to sustainable ASSLMBs. At the Consumer behavior level, the development of sustainable ASSLMBs involves several specific aspects: improving consumer policies and regulations for the disposal of spent batteries, establishing a sound recycling infrastructure and creating a paid recycling mechanism for spent ASSLMBs.

In the future, the increasing number of discarded ASSLMBs will pose serious waste management challenges to society, environment, economy, and human health. Nevertheless, spent batteries represent a valuable resource containing strategic elements and critical materials for battery manufacturing. Overall, given the global nature of the battery industry, global participation in the battery life cycle, including governments, battery manufacturers, distributors, consumers, and battery recyclers, is required to support a concerted push towards sustainable ASSLMB recycling and a circular economy of battery materials, which is essential to ensure supply chain stability, environmental safety, and human health. To achieve this, recycling-oriented battery design and sustainable recycling technologies must be developed to ensure the sustainability of ASSLMBs. With this review, we hope to create synergies between battery and sustainable recycling technologies surrounding ASSLMBs to further stimulate interest and promote the sustainable development of ASSLMBs.

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Conflict of Interest

The authors declare no conflict of interest.

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Xiaoxue Wu (Ph.D. 2021) is a postdoctoral researcher at the Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University. Before taking this position, she received her Ph.D. under the supervision of Prof. Chilin Li at the Shanghai Institute of Ceramics, Chinese Academy of Sciences. Currently, she works with Prof. Zheng Liang (Shanghai Jiao Tong University) and Prof. Guangmin Zhou (Tsinghua-Berkeley Shenzhen Institute & Tsinghua Shenzhen International Graduate School, Tsinghua University) on lithium-based battery solid electrolyte design and its recycling.



Guangmin Zhou is an associate professor at the Tsinghua Shenzhen International Graduate School, Tsinghua University. He received his Ph.D. degree from the Institute of Metal Research, Chinese Academy of Sciences in 2014 under the supervision of Prof. Hui-Ming Cheng & Prof. Feng Li, and then worked as a postdoc at UT Austin with Prof. Arumugam Manthiram during 2014–2015. After that, he was a postdoc fellow at Stanford University with Prof. Yi Cui from 2015 to 2019. His research mainly focuses on the development of advanced energy-storage devices and battery recycling.



Zheng Liang is an associate professor at the Frontiers Science Center for Transformative Molecules, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University. He received a Bachelor's degree from both the University of Michigan Ann Arbor (2011) and Shanghai Jiao Tong University (2011). Afterwards, he earned a Ph.D. from Stanford University (2018) and continued working as a postdoctoral researcher at Lawrence Berkeley National Laboratory. His research focuses on fast-charging Li secondary batteries and spent battery recycling.