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Dimensional Strategies for Bridging the Research Gap between Lab-Scale and Potentially Practical All-Solid-State Batteries: The Role of Sulfide Solid Electrolyte Films

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The absence of liquid components in all-solid-state batteries (ASSBs) based on sulfide solid electrolytes (SSEs) significantly impacts manufacturing processes and performance, particularly concerning mechanical properties and evolution. SSE films play vital roles in this context. This review provides a comprehensive analysis of SSE film design strategies, emphasizing their significance in the cell assembly and operation of practical ASSBs. Essential SSE film components are examined, including SSEs, binders, and scaffold or substrate materials, and key characteristics related to ASSB assembly and operation are addressed, such as conduction properties, electrochemical stability, and mechanical properties. Various SSE films fabricated using different binders and scaffold or substrate materials are explored through slurry-casting or solvent-free methods, and ASSBs employing SSE films with diverse form factors and components are presented, emphasizing their ability to operate under low-pressure conditions. Additionally, the importance of establishing test protocols for assessing SSE film performance metrics is highlighted and strategies for enabling Li metal anodes are introduced. By deepening the understanding of the electrochemo-mechanical phenomena and engineering processes in ASSBs, it is anticipated that the gap between lab-scale research and practical goals can be bridged through design strategies that leverage the hybridization of various compositions and the immiscible nature of solid-state materials.

1. Introduction

Lithium-ion batteries (LIBs) are crucial for modern life owing to their rechargeability and high energy and power densities, which allow them to be used for a variety of applications, such as mobile electronics, electric vehicles (EVs), and energy storage systems.^[1-4] However, the energy densities of conventional LIBs based on liquid electrolytes (LEs) and intercalation-type electrodes have reached their theoretical limit.^[5–7] Furthermore, safety concerns stemming from the use of flammable organic

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LEs and polyolefin-based separators have been a significant issue, as evidenced by the occurrence of thermal catastrophes, which are mainly caused by internal short circuits (ISCs) and thermal runaway.^[8-10] While safety measures such as thermal meltdown can be implemented for the separator, thermal shrinkages in the separator can contribute to the risk of an ISC, increasing the likelihood of thermal incidents or battery explosion.^[11–13] However, despite various approaches, including ceramic coating, polymer blending, and multilayer design by surface coating or surface grafting, aimed at enhancing the thermal stability and dendrite-suppression capability of separators,^[12–14] tackling the challenges posed by organic LE materials, which act as fuel sources in the event of thermal runaway, remains challenging.^[3,8,9]

In this context, all-solid-state batteries (ASSBs) employing non-flammable inorganic solid electrolytes (SEs) are attracting significant attention.^[15–22] Furthermore, solidifying electrolytes has a potential to stabilize alternative electrode materials such as Li metal, thus enhancing

energy density. Various classes of SEs that exhibit ionic conductivities of $\geq 1 \text{ mS cm}^{-1}$ at room temperature (RT) have been developed for ASSBs, including sulfides (e.g., $\text{Li}_{6-\gamma}\text{PS}_{5-\gamma}X_{1+\gamma}$ (X = Cl, Br; $\gamma = 0.0-0.5$), max. $\approx 10 \text{ mS cm}^{-1}$),^[23,24] oxides (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, max. $\approx 1 \text{ mS cm}^{-1}$),^[25] halides (e.g., Li_3MX_6 (X = Cl, Br), max. $\approx 1 \text{ mS cm}^{-1}$),^[26–28] and closo-borates (e.g., $0.7\text{Li}(\text{CB}_9\text{H}_{10})-0.3\text{Li}(\text{CB}_{11}\text{H}_{12})$, 6.7 mS cm⁻¹).^[29,30] In particular, sulfide SEs (SSEs) are the primary option for practical applications owing to their high ionic conductivities at RT, which are comparable to those of LEs ($\approx 10 \text{ mS cm}^{-1}$), and mechanical sinterability.^[15,16,23,31,32] In this review, we focus on SSE-based ASSBs, specifically discussing SSE-based separators (hereinafter referred to as "SSE films").

In **Figure 1**a, conventional LIB and SSE-based ASSB test cells are compared. In SSE-based ASSBs, SSE films replace the conventional separators in LIBs that contain pore-filling LEs.^[6,33–35] The LIB cell components of laboratory-scale coin cells and practical pouch-type cells are comparable; for example, their electrodes and separators have comparable thicknesses. In contrast, for



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Figure 1. Comparison of conventional lithium-ion batteries (LIBs) and all-solid-state batteries (ASSBs) with separators of varying thicknesses. a) Schematic comparison between conventional LIBs (NCM||Gr) and ASLBs (NCM||Li), for lab-scale cells (coin cells for LIBs and uniaxial pressurized cell for ASSBs) and pouch-type cells. b) Gravimetric energy densities and c) volumetric energy densities of ASSBs with varying thicknesses of sulfide solid electrolyte (SSE) films. d) Comparison of compositions and cost splits for conventional LIBs and ASSBs with various SSE film thicknesses (20, 30, and 40 μ m).

SSE-based ASSBs, there are significant gaps between laboratoryscale uniaxial pressurized cells and potentially practical pouchtype cells.^[36,37] Specifically, concerning expectations for performance in practical applications,^[18,38] reliance on laboratory-scale uniaxial pressurized cells—which utilize SSE-powder-based separator layers with thicknesses in the range of 400–600 µm, and are tested under exceedingly high external pressures in the tens of megapascals (e.g., 70 MPa),^[15,16,39,40]—might lead to the oversight of certain aspects, such as energy density calculation and contact loss.^[41] Therefore, the development of large-area and thin SSE films is imperative.^[18,19]

To exhibit energy densities equivalent to that required for a minimum driving range of 500 km for EVs, ASSBs need to achieve a gravimetric energy density of 350 Wh kg⁻¹ and a volumetric energy density of 750 Wh L⁻¹ at the cell level.^[5] Reducing the thicknesses of SE films is highly effective in enhancing the energy density of ASSBs, as well as utilizing advanced anode systems (e.g., Li metal anode, Si anode, anodeless system), bipolar stacking, and ultrathick electrodes.^[6,15,17,37,42] Figure 1b,c shows the gravimetric and volumetric energy densities of NCM811 (LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂)||Li and NCM811||anodeless ASSB unit cells with varying SSE film thicknesses, respectively; for detailed calculations, see the Supporting Information. The results emphasize the importance of developing SSE films with a minimum thickness of 30 µm; the gravimetric and volumetric energy densities exhibited by the NCM811||Li system were 397 Wh kg⁻¹ and 1277 Wh L⁻¹ and by the NCM811||anodeless system were 406 Wh kg⁻¹ and 1481 Wh L⁻¹, respectively. However, when considering inactive components of pouch-type cells, such as housing materials, SSE films with a thickness of $\approx 20 \,\mu\text{m}$ may be required.^[5,18,33]

Moreover, as LEs are replaced by SSEs, the material cost distribution for cells changes remarkably, mainly originating from the significantly higher estimated cost of SSE materials (Li₆PS₅Cl (LPSCl): \approx 319 USD kg⁻¹) compared to that of conventional LEs (10 USD kg⁻¹).^[5,6,27,43,44] The cost distribution of ASSB unit cells (areal cost values) fabricated using a 70 µm-thick NCM811 cathode, 20 µm-thick Li metal anode, and SSE films with varying thicknesses are displayed in Figure 1d (for detailed calculations, see the Supporting Information). The results were compared with those of an NCM811||graphite (Gr) LIB system.^[5,45-47] In contrast to the LIB, wherein the cathode constituted the largest proportion of cost and the separator was more expensive than the LEs, the cost of the SSE material was the highest compared to those of the components in the ASSB system, even when considering only SSE materials within SSE films. SSEs account for approximately 63% of the total materials cost in the unit cell when using a 20 µm-thick SSE film, mainly owing to the high cost of the precursor Li₂S. Not surprisingly, reducing the thickness of SSEs could lead to a drastic decrease in the cost portion (Figure 1d). Developing alternative cost-effective precursors and/or production methods for SSEs, such as liquid-phase synthesis, may decrease the cost portion of SSEs in the cost distribution.[16,48-52]

For practical ASSBs, several key characteristics of SSE films should be considered, including ionic conductivity, electrochemical stability, mechanical properties, and thickness.^[16,53] It is worth noting that the mechanical requirements for SSE films during the cell assembly and operation of ASSBs are more challenging to achieve compared to those for separators in LIBs.^[54]

Specifically, the mechanical properties and evolution in SSEbased ASSBs are critical for achieving practical ASSBs that can be operated under low or no operating pressures.^[39,54–56] The electrochemical stability of SSE films toward high-voltage cathodes and Li metal anodes, as well as their air and thermal stabilities, should be carefully considered.^[17,53,57–59] Moreover, design factors, such as components, fabrication methods, and form factors, are key considerations. However, a comprehensive review on the design strategies of SSE films, particularly from the perspective of cell assembly, has yet to exist.^[34,60]

This review aims to bridge the gap between lab-scale and practical research by shedding light on the critical role of SSE films in assembling practical ASSBs. We provide a comprehensive overview of the essential components of SSE films, including SSEs, binders, and scaffold or substrate materials. We also discuss the necessary properties that SSE films must possess, such as low thicknesses, high Li+ conductivities, electrochemical stability, and thermal and air stabilities. In particular, we analyzed the mechanical requirements of SSE films in terms of assembly and operation of ASSBs under low pressures. Furthermore, we review the design strategies for versatile SSE films, employing various components through different fabrication methods from the perspective of fabricating pouch-type ASSB cells. Considering the mechanical properties of SSE films, we focused on pouch-type cells, which are assembled using a stacking process, as opposed to other cell formats such as prismatic or cylindrical cells. By delving into these key aspects, we hope to contribute to the development and optimization of SSE films, which can facilitate the successful integration of ASSBs into practical applications.

2. Components of Sulfide SE (SSE) Films

In this section, we discuss the components required for the fabrication of SSE films and their specific requirements. We categorize the components of SSE films into four groups, as illustrated in **Figure 2**: SEs (SSEs and solid polymer electrolytes (SPEs)), binders, scaffold materials, and substrate materials. While SSEs and binders are mixed to form the main structure of the SSE film, scaffold and substrate materials provide structural integrity by acting as a mechanical backbone.

2.1. Sulfide Solid Electrolytes (SSEs)

The electrochemical properties (ionic conductivity, anodic, and cathodic stabilities) and chemical stability (toward atmosphere and processing solvent) of SSE films are intrinsically linked to the SSE materials they are composed of.^[61] Despite their high ionic conductivities and mechanical sinterability, SSEs face challenges in large-scale applications owing to H₂S evolution and their narrow intrinsic electrochemical stability windows.^[16,42,58,59] As such, understanding the electrochemical and chemical properties of SSEs is crucial for enhancing the performance and processability of ASSBs that utilize SSE films.

Among the various functions of SSE films, the most crucial is serving as an efficient ionic pathway.^[61–63] Arrhenius plots of the ionic conductivities of major SSEs and other types of



Figure 2. Schematic of SSE film consisting of SE (SSE and SPE), binder, scaffold material, and substrate material.

SEs are provided in **Figure 3a**.^[15,24,25,32,64–75] Since the initial research on SSEs in the 1980s–1990s with glassy materials ($\approx 0.1 \text{ mS cm}^{-1}$), significant progress has been made in developing crystalline sulfide Li⁺ superionic conductors, such as thio-LISICON (lithium superionic conductor) (Li_{3,25}Ge_{0,25}P_{0,75}S₄, $\geq 1 \text{ mS cm}^{-1}$).^[76] In 2011, the development of Li₁₀GeP₂S₁₂ (LGPS) sparked renewed interest in this field, as it exhibited an ionic conductivity level (12 mS cm⁻¹) comparable to those of LEs.^[64] Since then, various classes of SSEs have been reported, including argyrodite, phosphorus-free, and glass or glass–ceramic groups.^[20,23,32,64,69,71,77–79] Table 1 provides a summary of the properties of each SSE group.

It is important to note that achieving ASSBs with high power and energy densities cannot solely rely on the high ionic conductivities of SSEs. Ensuring that the operating voltages of the electrodes are within the stability windows of the SEs or that stable passivating interfaces are formed between the SEs and electrodes is also essential.^[57,80-82] Studies revealed that SSEs have narrow electrochemical stability windows (Figure 3b).[82,83] When SSEs are combined with 4 V-class layered oxide cathodes without protective coating layers, such as LiNbO₃, Li₂O-ZrO₂, and Li₃BO₃-Li₂CO₃, ASSB cells exhibit poor electrochemical performance.^[22,84-86] Additionally, SSEs at the anode react with Li metal to form decomposition products as interphase layers.^[17,57] If the layers formed are of a mixed ionic and electronic conducting (MIEC) nature, the decomposition process would extend into the bulk of the SSEs. However, if the layers are electronically insulating but ionically conducting, the interphase layers would remain stable, as is the case with the solid electrolyte interphase (SEI) layers in conventional LIBs.^[17,87] For example, LGPS forms a MIEC interphase layer when in contact with Li metal anodes, leading to increased interfacial resistance and degraded electrochemical performance in ASSB cells.^[82,83,88] In contrast, LPSCl and $Li_7P_3S_{11}$ form relatively favorable interphases, limiting further side reactions.^[89,90] Additionally, achieving stable interfaces also requires careful consideration of ionic passivation in terms of kinetic stability. Strategies such as mechanical constriction or the implementation of core-shell structures have been explored to expand the electrochemical stability window of SSEs while addressing the kinetic stability concerns (Figure 3c).^[91–93]

The mechanical and physical properties of SSEs play a vital role in designing SSE films that possess excellent mechanical properties, electrochemo-mechanical stabilities, and Li dendrite tolerance.^[35,54,94] It is worth noting that glass or glass–ceramic SSEs group tend to be more deformable than those with crystalline structures (e.g., argyrodite and LGPS groups).^[95–97] As the mechanical properties of SSE films directly influence the use of Li metal anodes or cathodes with low interfacial resistance, the choice of SSE for SSE film fabrication should be carefully considered.^[22,54,94] In addition, researchers have explored various approaches to control the physical characteristics of SSEs, such as particle size and distribution and morphologies, which impact the thicknesses and uniformity of SSE films. Synthetic techniques such as liquid-phase synthesis, wet-milling, and jet-milling have been used to achieve these advancements.^[16,48,49,68,98–103]

The chemical instability of SSEs toward air and solvents is a critical factor that affects the processability and electrochemical stability of SSE films;^[42,58,59,104] this is discussed later. It is crucial to note that most SSEs react with polar solvents, resulting in irreversible side reactions. However, unique SSEs exhibit distinctive solution processability.^[16,49] Some SSEs, for example, can dissolve in specific solvents to form homogeneous SE solutions, which can then be recovered via a drying process and subsequent heat treatment. These SSEs are known as solution-processable SSEs (e.g., Li₄SnS₄, LiI–Li₄SnS₄, LPSCl, and Li_{6+x}P_{1-x}M_xS₅I (M = Ge, Sn)),^[20,105–110] and they have been applied as uniform SE coatings on active materials or the infiltration into slurry-cast porous electrodes used in conventional LIBs.^[49,106–108,110]

2.2. Binders and Processing Solvents

To achieve acceptable mechanical properties of SSE films, the use of polymeric binders is essential.^[54] Binders that exhibit flexibility and elasticity effectively anchor SE particles together and readily fill void spaces within composite structures.^[111,112] Unfortunately, conventional binders used in LIBs, such as polyvinylidene fluoride (PVDF) and styrene-butadiene rubber (SBR)/carboxymethyl cellulose (CMC), are not suitable for SSE slurry systems owing to the chemical sensitivity of SSEs toward conventional protic or highly polar processing solvents, such as *N*-methyl-2-pyrrolidinone (NMP) and water.^[16,58,113–115] As a result, researchers have explored alternative binder–solvent

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Figure 3. Characteristics of SSE film components. a) Arrhenius plots of ionic conductivities for various types of SSEs. Data for other SEs including oxides, SPEs, and LEs are also shown for comparison. b) Electrochemical stability windows of various types of SEs. Reproduced with permission.^[83] Copyright 2015, American Chemical Society. c) Li10 GeP2S12 decomposition energy, ground state pressure, and ground state capacity versus voltage at different effective modules (K_{eff}). Reproduced with permission.^[91] Copyright 2020, John Wiley and Sons. d) XRD patterns and Li⁺ conductivities of Li argyrodite (Li₆PS₅Cl_{0.5}Br_{0.5}) after exposure to various solvents (NMP, EA (ethyl acetate), BA (benzyl acetate), BB (butyl butyrate), and IAE (isoamyl ether)). Reproduced with permission.^[111] Copyright 2022, Elsevier. e) Ion conduction mechanism in LiX–PEO. Reproduced with permission.^[127] Copyright 2015, The Royal Society of Chemistry. f) Photograph and FESEM images of PPTA NW scaffold. Reproduced with permission. [138] Copyright 2015, American Chemical Society.

systems that utilize non-polar or less polar solvents, such as xylene, toluene, benzyl acetate, and anisole (Figure 3d).^[58,111,116–120] Polymeric binders that are soluble in those types of solvents such as rubber-type binders (e.g., butadiene rubber (BR), nitrile butadiene rubber (NBR)), and acrylate-type binders are commonly used in research on SSE-based ASSBs.^[112,121] The major bindersolvent system candidates for SSE-based ASSBs are summarized

in Table 2. It is worth noting that cosolvent systems can be used to tune the solubility and dispersion of binders, reactivity of SSEs, and solubility of additives (e.g., Li salts).[37,112,122] Furthermore, given that solvents could cause the degradation of SSEs and cathode active materials (e.g., Ni-rich layered oxides),[111,118,119] there has been a growing interest in solvent-free processable binders such as polytetrafluoroethylene (PTFE).^[37,123,124] To attain stable

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Table 1. Properties of SSEs (sulfide solid electrolytes).

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SSEs		lonic conductivity at 25 °C [S cm ⁻¹]	Bulk modulus [GPa]	Shear modulus [GPa]	Specific density [g cm ⁻³]	Li concentration [mol L ⁻¹]	Echem window [V vs Li/Li ⁺]	Ref.
Phosphorus-free	Li ₂ SnS ₃	1.5 × 10 ⁻⁵	-	-	3.51	30.66	-	[240]
group	Li ₄ SnS ₄	$7.0 imes 10^{-5}$ (20 °C)	-	-	-	37.13	-	[71]
	0.4Lil-0.6Li ₄ SnS ₄	4.1 × 10 ⁻⁴ (30 °C)	-	-	2.64 (measured)	33.80	-	[20]
	Li _{3.833} Sn _{0.833} As _{0.166} S ₄	1.39×10^{-3}	_	-	-	-	0–5	[241]
	Li _{3.85} Sn _{0.85} Sb _{0.15} S ₄	$8.5 imes 10^{-4}$ (30 °C)	_	-	2.56	35.92	_	[171]
LGPS group	Li ₁₀ GeP ₂ S ₁₂	1.2×10^{-2}	27.3 ^[95]	7.9 ^[95]	2.08	35.33	0–5	[64]
	Li ₁₀ SiP ₂ S ₁₂	2.3×10^{-3}	_	-	1.86	34.18	_	[242]
	$Li_{10}SnP_2S_{12}$	$4 imes 10^{-3}$ (27 °C)	_	-	1.80	28.35	_	[243]
	Li ₁₀ Si _{0.3} Sn _{0.7} P ₂ S ₁₂	8 × 10 ⁻³	_	-	-	-	_	[244]
	Li ₁₀ Ge _{0.95} Si _{0.05} P ₂ S ₁₂	8.6×10^{-3}	_	-	2.02	34.43	_	[245]
	Li ₁₁ AlP ₂ S ₁₂	0.802×10^{-3}	_	-	2.18	43.60	0–5	[246]
	Li _{9.54} Si _{1.74} P _{1.44} S _{11.7}	2.5×10^{-2} (hot sintered)	-	-	1.86	33.24	_	[15]
	Li _{10.35} (Sn _{0.27} Si _{1.08}) P _{1.65} S ₁₂	1.1×10^{-3}	-	-	2.000	36.31	0–5	[247]
	Li _{9.6} P ₃ S ₁₂	1.2×10^{-3}	_	-	1.91	33.69	-	[15]
Argyrodite group	Li ₆ PS ₅ Cl	1.3×10^{-3}	28.7 ^[95]	8.1 ^[95]	1.64	36.70	0–7	[66]
	Li ₆ PS ₅ Br	6.2×10^{-4}	29 ^[95]	9.3 ^[95]	1.90	36.44	0–7	[66]
	Li ₆ PS ₅ I	1.9×10^{-4}	29.9 ^[95]	11.3 ^[95]	2.22	37.02	0–7	[66]
	Li ₇ PS ₆	$1.6 imes 10^{-6}$ (40 °C)	-	-	1.80	46.33	-	[248]
	Li ₇ P _{2.9} Mn _{0.1} S _{10.7} I _{0.3}	5.6×10^{-3}	-	-	-	-	0–5	[249]
	Li _{6.6} Si _{0.6} Sb _{0.4} S ₅ I	1.48×10^{-2}	-	-	1.81	29.90	-	[67]
	Li _{5.35} Ca _{0.1} PS _{4.5} Cl _{1.55}	10.2×10^{-3}	-	-	1.92	37.89	0–5	[250]
	Li _{6.75} Sb _{0.25} Si _{0.75} S ₅ I	1.31×10^{-2}	-	-	2.33	40.73	0.04-6.55	[251]
	Li _{6.6} P _{0.4} Ge _{0.6} S ₅ I	$5.4 imes 10^{-3}$	-	-	2.41	40.80	-	[79]
	Li _{5.5} PS _{4.5} Cl _{1.5}	9.4×10^{-3}	-	-	1.88	38.78	-0.1-5	[65]
	$Li_{6.35}P_{0.65}Si_{0.35}S_5Br$	2.4×10^{-3}	-	-	2.06	41.61	-	[252]
Glass or	β -Li ₃ PS ₄	1.6×10^{-4}	23.3 ^[95]	11.4 ^[95]	1.85	30.82	-0.2-5	[68]
Glass-ceramic	Li ₄ PS ₄ I	1.2×10^{-4}	-	-	2.44	31.14	-	[253]
group	${\sf Li}_{3.45}{\sf Si}_{0.45}{\sf P}_{0.55}{\sf S}_4$	6.7×10^{-3}	-	-	1.92	36.49	0–5	[245]
	Li _{5.3} PS ₄ (BH ₄) _{2.3}	1.1×10^{-2}	-	-	-	-	0–5	[254]
	Li _{3.25} Ge _{0.25} P _{0.75} S ₄	2.2×10^{-3}	-	-	-	-	0–5	[76]
	Li ₇ P ₂ S ₈ I	$6.3 imes 10^{-4}$	-	-	-	-	0–10	[70]
	0.8Li ₂ S-0.2P ₂ S ₅	7.2×10^{-4}	-	-	-	-	-	[255]
	0.7Li ₂ S-0.3P ₂ S ₅	3.2×10^{-3}	23.9 ^[95]	8.1 ^[95]	1.87	26.49	-	[69]
	80(0.7Li ₂ S-0.3P ₂ S ₅)-20Lil	5.6×10^{-4}	-	_	-	_	0-10	[256]

electrochemical performance in ASSBs, it is critical to consider not only the mechanical stability but also the electrochemical stability of the binder.^[112] However, research specifically dedicated to the electrochemical stability of binders in SSE-based ASSBs remains rather limited. For instance, certain studies have noted disparate amounts of CO₂ gas evolution influenced by varying oxidation stability, depending on the type of binder utilized.^[125,126] Additionally, while research has been conducted on a limited selection of solvent and polymeric binder combinations compatible with SSE, there is a compelling need to expand this scope to include research on environmentally friendly solvents and binders.^[114]

2.3. Solid Polymer Electrolytes (SPEs)

SPEs are composed of Li salts (e.g., LiClO₄, lithium bis(trifluoromethanesulfonyl)imide) (LiTFSI)) dissolved into various types of polymeric matrices and are considered promising candidate SE materials for the practical application of ASSBs owing suto their unique properties, such as excellent flexibility, intimate contact with electrodes, and compatibility with Li metal.^[127,128] SPEs can also serve as a viable binder component for SSE films, providing additional ionic pathways. The ion conduction mechanisms of SPEs differ by their type and crystallinity.^[129] Figure 3e illustrates the various mechanisms

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Table 2. Basic properties of binder materials and processing solvents for SSEs.

Binder	T_{g} [°C]	T _m [°C]	Note	Compatible solvent	Solvent b.p. [°C]	Compatible SSE	Ref.
SEBS	-	-	Low polarity	Heptane	98.4	Li ₃ PS ₄	[257]
				n-decane	174.1	Li ₃ PS ₄	[258]
SBS	-57.5	-	-	Anisole	153.8	Li ₃ PS ₄	[257]
SBS-COOH click binder	-	-	Polarity of SBS controlled by thiol-ene click reaction	p–xylene	138.4	Li ₆ PS ₅ Cl	[119]
SBR	-56.7	-	Low polarity, spot adhesion	Anisole	153.8	Li ₃ PS ₄	[216]
				o-xylene	144.0	Li ₃ PS ₄	[126]
PIB	-64	-	-	Toluene	110.6	Li ₃ PS ₄	[144]
NBR	-62	-	Excellent chemical and heat	THF	66.0	Li ₂ S-P ₂ S ₅	[259]
			resistance, strong	Xylene	138.4	Li ₆ PS ₅ Cl	[193]
			adhesion properties	DBM ^{a)}	97.0	Li ₆ PS ₅ Cl	[117]
				p-xylene	138.4	Li ₃ PS ₄	[118]
NBR-LiTFSI	-	-	Li–ion conductive binder	DBM + hexyl butyrate	208.0	$\mathrm{Li}_{6}\mathrm{PS}_{5}\mathrm{Cl}_{0.5}\mathrm{Br}_{0.5}$	[122]
NBR-poly(1,4-butylene adipate)-LiTFSI	-	-	Li-ion conductive binder	Benzyl acetate	214.0	$\rm Li_6PS_5Cl_{0.5}Br_{0.5}$	[111]
HNBR	4	-	Excellent chemical and heat	Toluene	110.6	Li ₁₀ SnP ₂ S ₁₂	[184]
			resistance	o-xylene	144.0	Li ₃ PS ₄	[126]
BR	-105	-	Low polarity	p-xylene	138.4	Li ₆ PS ₅ Cl	[119]
				Butyl butyrate	166.0	Li ₆ PS ₅ Cl	[260]
PPC	28	-	Thermally decomposable polymer	Anisole	153.8	Li ₃ PS ₄	[202]
PMMA	105	-	-	Toluene	110.6	Li ₁₀ SnP ₂ S ₁₂	[184]
PVdF-HFP	-35	143	mechanically and	THF	66.0	Li ₇ PS ₆	[169]
			electrochemically favorable	Ethyl acetate + hexyl butyrate	205.0	$\mathrm{Li}_{6}\mathrm{PS}_{5}\mathrm{Cl}_{0.5}\mathrm{Br}_{0.5}$	[194]
Ethyl cellulose	-	-	-	Toluene	110.6	Li ₆ PS ₅ Cl	[187]
PTFE	119	327	Dry fabrication process available	-	-	_	[123]

^{a)} DBM, dibromomethane.

involved in ion transport in poly(ethylene oxide) (PEO), such as intrachain hopping, interchain hopping, intrachain hopping via ion cluster, and interchain hopping via ion cluster.^[127] **Table 3** summarizes several SPEs and their properties. However, SPEs exhibit low ionic conductivities at RT, typically $\leq 10^{-5}$ S cm⁻¹, limiting their practical use.^[130,131] Several strategies have been proposed to improve the ionic conductivities of SPEs, such as adding Li⁺-conductive fillers or additives that can control their crystallization behavior.^[74,132–135] In addition, most SPEs exhibit poor electrochemical oxidative stability at high voltages (>4.0 V vs Li/Li⁺), although extensive research has been conducted to address this issue.^[127,136] When hybridizing SSEs and SPEs for SSE films, it is important to consider different ion conduction mechanisms, transference numbers, and interfacial phenomena to prevent overpotential.^[137]

2.4. Scaffold Materials and Substrate Materials

The use of polymeric binders alone in thin SSE films is insufficient to meet the mechanical properties required for handling and cell assembly processes, such as roll-to-roll processing.^[7,14,19,38,54] As a solution, SSE films can be fabricated by embedding SSEs within porous scaffold materials or by attaching SSE films onto substrate materials. Several candidates for scaffold and substrate materials and their properties are summarized in **Table 4**.

SSE films embedded with scaffold materials exhibit good mechanical properties, and a free-standing form can be achieved, particularly with ultralow thicknesses. Porous scaffold materials such as non-woven (NW) fabric, mesh-type materials, and fiber-type materials have previously been used (Figure 3f).^[138-142] For the design of scaffold materials, effective ionic conduction and embedding capacity should be considered. To minimize Li⁺ transport hindrance by the scaffold materials, the tortuosity and amount of the scaffold material should be minimized while maintaining the required mechanical properties.^[11] Moreover, the porosity and tortuosity of the scaffold material are factors that affect the fabrication method (e.g., slurry casting and infiltration), which is discussed in detail in Section 4.2. The thermal stability of the scaffold materials is also important for the safety of ASSBs.

SSE films can also be integrated into ASSB cells through transfer or peel-off processes using substrate materials. Substrate

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Table 3. Properties of SPEs.						
SPE	Li salt	Additive	lonic conductivity at 25 °C [S cm ⁻¹]	Echem window [V vs Li/Li ⁺]	T _g [°C]	Ref.
PEO	LiTFSI	_	1.01 × 10 ⁻⁵ (30 °C)	≈5.7	-37	
		TiO ₂	$0.7 imes 10^{-4}$ (30 °C)	≈5		[261]
		Silica nanotubes	$4.4 imes 10^{-4}$ (30 °C)	>5	-51.3	[262]
	LiClO ₄	-	1.0×10^{-4} (RT)	-	-32.1	[263]
		TiO ₂	$6.0 imes 10^{-4}$ (RT)	-	-29.1	
PEO-TEGDMA ^{a)} -TEGDME ^{b)}	LiTFSI	-	$2.7 imes 10^{-4}$ (24 °C)	≈5	-78	[264]
PAN ^{c)}	LiCF ₃ SO ₃	-	3.04×10^{-4} (RT)	-	-	[265]
PAN-PEO	LiClO ₄	-	6.8×10^{-4}	≈4.8	-	[266]
PAN-PVC ^d	LiTFSI	-	$4.4 imes 10^{-4}$ (30 °C)	-	-	[267]
PVC	LiCF ₃ SO ₃	-	$4.8 imes 10^{-5}$ (50 °C)	-	-	[268]
PMA ^{e)}	LiTFSI	-	$1.4 imes 10^{-4}$ (65 °C)	-	-	[269]
PEC ^{f)}	LiFSI ^{g)}	Montmorillonite	3.5×10^{-4} (RT)	≈4.6	-52.3	[270]
^{a)} TEGDMA: tetraethylene glycol c poly(ethylene carbonate); ^{g)} LiFS	limethacrylate; ^{b)} TEr I: lithium bis(fluoros	GDME: tetraglyme; ^{c)} PAN: ulfonyl)imide.	polyacrylonitrile; ^{d)} PVC: poly	y(vinyl chloride); ^{e)} PMA: բ	ooly(N-methyl-malon	ic amide); ^{f)} PEC:

materials not only provide a mechanical backbone for SSE film on top but also contribute to the mechanical properties required for handling and cell assembly processes (e.g., transfer or peeloff method). The detailed fabrication method for SSE films is discussed in Section 4.2. For the transfer or peel-off method, various substrate materials, such as metal foil, poly(ethylene terephthalate) (PET) film, Teflon plate, and Mylar foil, are used.^[37,143–145] For a uniform casting process, surface uniformity and smoothness of the substrate material are essential. Additionally, the substrate material must be inert when in contact with SSEs and processing solvents, and good thermal properties are required owing to the drying process involved in the slurry casting method.^[111,117] In particular, for the subsequent peel-off and transfer processes, it is critical to optimize the adhesion properties between the substrate material and SSE film.

3. Required Properties of SSE Film

Given its position between the cathode and anode, the SSE film must be versatile in terms of electrochemical stability and mechanical properties. While SSE films need to satisfy certain requirements that are in common with those of the separators used in LIBs, such as electronic insulation, mechanical stability, chemical resistance, and uniformity, some properties such as wettability that are essential for LEs are not needed for SSE films.^[7,14] However, air stability upon exposure to moisture is a crucial aspect for SSEs.^[42,58,59] This section provides a summary of the major requirements for SSE films, with a particular emphasis on the need to carefully monitor their mechanical properties during the fabrication and operation of pouch-type ASSBs (Figure 4a).

3.1. Thickness and Li+ Conductivity

Low thicknesses and high ionic conductivities of SSE films are primary requirements for achieving high energies and power densities in ASSBs.^[18,33,42,53] SSEs with high ionic conductivities play a key role in determining the ionic conduction of the resulting SSE films.^[11,15,65,146] Moreover, the content of insulating materials, such as binders, additives, and scaffold materials, is responsible for the reduced ionic conductivities of SSE films compared to SSE materials. Mechanical defects (i.e., pores, cracks) and Li⁺ tortuosity of SSE films also influence their ionic conductivities.[11,147,148]

Scaffold/substrate materia	s	T _g [°C]	T _m [°C]	Thickness	Mechanical property	Ref.
				μπη		
Scaffold materials	PPTA NW	-	-	16	-	[138]
	EVAP film	300	338-355	-	Strong adhesion properties	[188]
	PINW	>200	>400	-	Good mechanical strength	[140]
	Nylon mesh	40–50	20	-	_	[170]
	Cellulose skeleton	-	-	29	Tensile strength 13.2 MPa	[141]
	NW fiber glass	-	-	-	_	[271]
Substrate	PET film	73	248.9	75	_	[37]
materials	Mylar foil	-	250	-	_	[144]

Table 4. Properties of scaffold and substrate materials.

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Figure 4. Key characteristics for SSE films regarding high energy and safe ASSBs. a) Selected (structural, (electro)chemical, and mechanical) requirements for SSE films. b) Areal specific resistances of SSE films with varying thicknesses and ionic conductivities. c) Photograph of PI-Li₆PS₅Cl_{0.5}Br_{0.5}

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For a fair evaluation of the ionic conduction performance of SSE films, both the extensive properties, areal specific resistance ($\Omega \text{ cm}^2$) and Li⁺ conductance (S), and the intensive property, Li⁺ conductivities (S cm⁻¹), should be provided.^[60] In Figure 4b, areal specific resistance is plotted against SSE film thickness with different ionic conductivities. For example, both a 20 µm-thick SSE film with an ionic conductivity of 1.0×10^{-3} S cm⁻¹ and a 200 µm-thick SSE film with an ionic conductivity of 1.0×10^{-2} S cm⁻¹ exhibit the same areal specific resistance value of 2 Ω cm². It is also important to note that the total resistance value measured using ion-blocking symmetric cells can be affected by the contact resistance between the electrode and SSE film. Several strategies have been proposed to measure ionic conductivity without the interference of contact resistance, such as the use of Ag-based conductive discs.^[139,145]

The successful fabrication of SSE films with low thicknesses (<30 μ m) and high uniformity depends on the choice of fabrication method, as well as the average particle size, particle size distribution, and morphology of the SSEs.^[99,100,106] Finer particles may be beneficial for achieving lower thickness and higher uniformity. However, it is necessary to strike a balance between ionic conductivity and particle size, as contact and/or grain boundary resistances between SSE particles increase with decreasing particle size.^[103] Maintaining the uniformity of SSE films is crucial for stable cycling, particularly when Li metal anodes are employed. Poor uniformity can result in localized high current densities and subsequent Li dendrite formation, leading to capacity loss and safety issues.^[17,149,150]

3.2. Electrochemical Stability

The electrochemical stability of SSE films is crucial since they are in direct contact with both the cathode and anode in ASSBs.^[80,81] SSEs, as a major component, play a decisive role.^[83] Similar to other types of SEs, SSEs are also unstable when in contact with Li metal anodes, leading to penetrating growth and ISCs.[17,53,57,80] To address this issue, various approaches have been employed, including doping with elements such as O and F, and surface coating with stable layers (e.g., lithium phosphorus oxynitride (LiPON) and Al₂O₃).^[151,152] Alternatively, surface modification of Li metal with inorganic Li compounds (e.g., LiF, LiI, Li₃N) and lithiophilic metal (e.g., In, Mg) has also been introduced.^[45,153–156] Robust inorganic compounds with high interfacial energies are known to constrain the formation of Li dendrites, while lithiophilic metals promote uniform Li+ flux. Additionally, carbonbased materials have been suggested to address the Li metal-SSE compatibility issue.^[37,139] Further details about stabilizing the SSE film-Li metal interfaces are discussed in Section 5.3. Unlike LE-based LIBs, ASSBs can accommodate a bilayer design where two different SE layers with good oxidation and reduction stabilities, respectively, can be stacked.^[15,27,157–160] This design allows for improved electrochemical stability by leveraging the strengths of each SE layer while mitigating their weaknesses. For example, an SSE layer design, wherein a less-stable SSE is sandwiched between layers of more-stable SSEs, was reported to improve compatibility with Li metal.^[91,92]

3.3. Thermal and Air Stability

The safety of ASSBs may have been overestimated.^[13] Recent studies have reported the possibility of ignition and exothermal behaviors in SSE-based ASSBs under abusive conditions.^[161–167] Additionally, the potential evolution of toxic and flammable H₂S from SSEs is also an important safety factor for ASSBs. SSE films, which constitute the largest portion of SSEs within the cell and prevent electrical contact between electrodes, play a critical role.^[37] Considering that ASSB manufacturing occurs under dry room conditions, wherein small amounts of humidity are inevitable,^[104] it is imperative for SSE films to exhibit air stability. This section discusses the thermal and air stability of SSE films, which can be crucially related to the safety and operational stability of ASSBs.

The thermal stability of SSE films is important for both the safety and performance of ASSBs, as their contraction at high temperatures can lead to ISCs.^[8,14] Although SSEs are inorganic materials, the thermal stability of SSE films should be carefully examined owing to the presence of organic components, such as binders and scaffold materials. Various protocols have been used to evaluate the thermal stability of SSE films, with thermogravimetric analysis (TGA) being one of the most common.^[140,142,168] Li et al. compared the TGA results of PVDF-LiTFSI SE films without and with Li₇PS₆, demonstrating the positive effect of Li₇PS₆ incorporation on the thermal stability of the films.^[169] Direct heat exposure or flammability tests are also employed to assess the thermal stability of SSE films. Oh et al. evaluated the thermal stability of an SSE film comprising Li argyrodite Li₆PS₅Cl_{0.5}Br_{0.5} (LPSClBr), NBR, and SPE-type binder poly(1,4-butylene adipate) with Li salts (referred to as NA-LiTFSI) by subjecting it to thermal shock at 200 °C for 1 h, and found that it did not exhibit shrinkage.^[111] Liu et al. conducted a flammability test on an SSE film composed of Li₁₀GeP₂S₁₂ (LGPS) and triethylene glycol diacrylate (TEGDA) by directly exposing it to flame, and found that it exhibited superior thermal stability compared to the commercial Celgard separator.^[170] In addition to concerns about the shrinkage or degradation of SSE films under thermal stress, the electrochemical performance of ASSBs employing SSE films at high temperatures is also crucial. Kim et al. investigated the thermal stability of SSE films comprising Li argyrodite LPSClBr

membrane, SEM image of an electrospun porous PI NW scaffold material, and charge–discharge voltage profiles for NCM||Gr all-solid-state full-cells employing PI–Li₆PS₅Cl_{0.5}Br_{0.5} membranes at 0.1C and 30 °C before and after exposure to 180 °C for 1 h. Reproduced with permission.^[140] Copyright 2020, American Chemical Society. d) H₂S gas measurement setup and amount of H₂S released over time for composites comprising Li₇P₃S₁₁ and hydrophobic SEBS polymer. Reproduced with permission.^[143] Copyright 2019, American Chemical Society. e) Schematic and photographs of F-POS@LATP|LPSCI|F-POS@LATP membrane and bare Li₆PS₅Cl membrane upon exposure to extreme conditions and continuous water-drop attack. Reproduced with permission.^[177] Copyright 2021, John Wiley and Sons. f) H₂S concentration over time for LPSCI-based SSE film (4 cm², uncompressed, 40 µm-thick) exposed to dew points between 10 and -50 °C (TWA: time-weighted average; STEL: short-term exposure limit for personnel) Schematic of production process of SSE films and relevant properties of intermediate products and processes regarding H₂S gas formation. Reproduced with permission.^[178] Copyright 2022, American Chemical Society.

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and thermally stable polyimide (PI) NW by exposing NCM|PI–LPSClBr|Gr ASSB cells to a temperature of 180 °C (Figure 4c).^[140] After the exposure, the voltage profiles nearly overlapped with those obtained prior to exposure, demonstrating the excellent thermal stability of the fabricated SSE film.

SSE films, owing to the intrinsic properties of SSE materials, are susceptible to hydrolysis upon exposure to air, which can lead to the evolution of toxic H₂S gas.^[58] Several approaches have been developed to enhance the air stability of SSE materials, such as doping and surface coating,^[99,105,171-175] as documented in multiple comprehensive reviews.^[42,58,59,81] The air stability of SSE films can be improved by introducing intrinsically air-stable components.^[99,171] Tan et al. demonstrated that SSE films fabricated using Li₇P₃S₁₁ and a hydrophobic binder polystyrene-block-polyethylene-ran-butyleneblock-polystyrene (SEBS) produced lower amounts of H₂S gas in air compared to SSE powders without SEBS (Figure 4d).^[143] Additionally, surface protection layers can be applied onto SSE films to enhance their air stability.^[176] Xu et al. developed an SSE film coated with a hydrophobic protection layer consisting of Li₁₄Al₀₄Ti₁₆(PO₄)₃ (LATP) nanoparticles and fluorinated polysiloxane (F-POS) formed using a spray coating method (Figure 4e).^[177] The surface-coated SSE film exhibited a much higher static contact angle of a water droplet compared to the bare LPSCl-based film. Furthermore, the electrochemical performance of the ASSB using the surface-coated SSE film surpassed that of the ASSB using the bare LPSCl-based film, even after exposure to extreme conditions. Recently, Singer et al. investigated the hydrolysis of Li argyrodite-based SSE films under practically relevant dry room conditions.^[178] They measured the H₂S formation rates of SSE films exposed to dew points between -50 °C and 10 °C (Figure 4f), suggesting acceptable processing conditions of dry rooms. Furthermore, they proposed a process to address H₂S gas formation during SSE film production.

3.4. Mechanical Properties

The absence of liquid components and low amounts of soft components in SSE films make them susceptible to mechanical and electrochemo-mechanical issues.^[54] Mechanical failure can occur during the handling and assembly of large-format pouch-type ASSB cells. The latter could arise due to the electrochemically accelerated mismatch in mechanical properties between SSE films and electrodes, which becomes highly critical under no or low operating pressure conditions.^[40,55,56,99,179] Therefore, it is crucial to develop SSE films with favorable mechanical properties in multiple aspects, including flexibility, tensile strength, shear strength, and compressive strength. This section provides insights into the required mechanical properties of SSE films for pouch-type cell assembly and low-pressure cell operation.^[54]

3.4.1. For Cell Assembly Process

The assembly process for pouch-type ASSBs involves several steps that can affect the structural integrity of SSE films, as illustrated in **Figure 5a**.^[6,38,180] These steps include winding, calen-

dering, stacking, and pressurization, and the corresponding requirements for SSE films are discussed in this section. Detailed pouch-type cell assembly processes for ASSBs employing various forms of SSE films are discussed in Section 5.1.

Winding: Efficient material transport is crucial in the assembly process of pouch-type cells, which typically involves the roll-to-roll process where SSE films are subjected to bending and tensile stress during winding.^[6,7] To withstand these stresses, SSE films must possess flexibility, tensile strength, and robustness.

Calendering: In conventional LIBs, electrodes undergo a calendering step for porosity control before cell stacking.^[6,180,181] SSE films for ASSBs must be densified via the calendering process to facilitate 2D ionic contact, as well as to control porosity and thickness.^[38,182] Additionally, the calendering process can also be used in the transfer and peel-off methods used in ASSB cell manufacturing, which will be discussed in Section 5.1. SSE films need to possess sufficient mechanical properties to withstand the shear stresses and compression forces during calendering.^[7]

Stacking (Folding): The stacking process in SSE-based pouch-type ASSBs proceeds after preparing all the components, including the anode, cathode, and SSE films, during cell assembly.^[6,38,180] Whether to fold SSE films during this process depends on their processability.^[38,138] Alignment of the cell components, including electrodes and SSE films, is crucial, considering that the subsequent step is pressurization with pressures of hundreds of megapascals, which may cause mechanical failure and subsequent ISC in ASSBs.^[54,183] In this regard, SSE films with robustness and flexibility (if folding is involved) are needed.

Pressurization: Pressurization of pouch-type cells is carried out as the final step after stacking, welding of the current collectors, and pouch sealing.^[6] Additionally, SSE films can be subjected to pressurization prior to the final pressurization step for purposes such as achieving densification and transferability.^[37,55,123] During pressurization, there may be side effects such as embrittlement, depending on the degree of pressure. Therefore, the mechanical properties of SSE films before and after the pressurization process should be thoroughly investigated.^[55,149,150] To withstand the brittleness that can occur after pressurization, SSE films with both robustness and compressive strength, as well as mechanical integrity, are required.

As SSE films undergo multiple processing steps, whether their mechanical properties and ionic conductivities are maintained after being subjected to mechanical abusive conditions should be carefully evaluated. Nam et al. performed bending tests of SSE films using rods with different diameters (Figure 5b) along with field-emission scanning electron microscopy (FESEM) measurements, assessing their mechanical integrity retention.^[138] Riphaus et al. conducted the Mandrel bend test on SSE films prepared using various types of binders, investigating the influence of binder content and densification on the bending properties of the films (Figure 5c).^[184] Tensile strength is one of the most important mechanical properties for SSE films, particularly for winding and calendering;^[7,14] binders, scaffold materials, and substrate materials can significantly impact tensile strength as well as bendability.[115,141,142,185,186] Cao et al. conducted tensile tests on SSE films composed of LPSCl and ethyl cellulose (Figure 5d).^[187] The SSE films exhibited a high tensile strength of 495 kPa and a Young's modulus of 12.56 MPa, likely attributable to the high mechanical strength of the ethyl cellulose binder.

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Figure 5. Mechanical requirements for SSE films and methods for evaluating compliance. a) Schematic of assembly process of pouch-type cell with SSE films. b) Photographs and FESEM image of bendable NW–SSE films before and after bending tests using rods with diameters of 1 and 3 cm. Reproduced

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3.4.2. For Low-Pressure Operation and Prevention of Li Dendrite Growth

The porosities of SSE films must be minimized to ensure effective ionic conduction and prevention of Li dendrite growth.^[147-150] Several strategies have been introduced to achieve this. Riphaus et al. demonstrated that the porosities of SSE films could be altered by using different types of binders (Figure 5e).^[184] Despite maintaining the same binder content (2.5%), the porosities of SSE films employing hydrogenated NBR (HNBR) and polyisobutene (PIB) were found to be different, with values of 15% and 10%, respectively. Lee et al. presented a method for preventing pinhole defects in SSE films by using cosolvents in the slurry process (Figure 5f).^[37] In contrast to the morphologies of SSE films prepared with xylene alone, employing isobutyl isobutyrate as a cosolvent yielded pinhole-free SSE films. Furthermore, warm isostatic pressing (WIP) at 490 MPa allowed for SSE film densification, imparting the film with a compact microstructure (Figure 5f). Recently, Emley et al. examined the quality of tape-cast SSE films, including pinhole defects and homogeneity, using an imaging technique with a light emitting diode (LED) lightboard (Figure 5g).^[145] They comparatively evaluated the images of backside-illuminated SSE films prepared using casting slurries with different solid loadings, based on the extended Derjaguin-Landau-Verwey-Overbeek theory.

To ensure low-pressure operation of ASSBs, the elasticity of SSE films and the integrity of interface adhesion between SSE films and electrodes are crucial, considering the significant volume changes of electrode materials during charging and discharging processes.^[54–56,94,188,189] Moreover, sufficient moduli and hardness of SSE films are required to prevent Li dendrite growth.^[17,53,54] The design of SSE films in terms of elasticity and interface adhesion primarily depends on polymeric materials such as binders.^[113,115,190–192] On the other hand, the physical properties required to inhibit Li dendrite growth are reliant on the inorganic solid components, including SSEs and additives.^[17,54,95]

4. Design Strategies of Versatile SSE Films

To fabricate SSE films with the required properties discussed previously, it is crucial to select the right combination of components. The characteristics and functions of SSE films can vary depending on the materials employed and the fabrication approach. In this section, we discuss the design strategies for preparing SSE films, focusing on aspects of composition and fabrication method.

4.1. SSE Films with Various Compositions

We examined three different compositional approaches for SSE films: SSE films employing various types of binders, hybrid SSE films, and SSE films fabricated using scaffold materials.

4.1.1. SSE Films Employing Various Types of Binders

SSE films can be prepared using various types of binder materials.^[111,112,117,119] Riphaus et al. investigated slurry-based processing of SSEs for the preparation of SSE films using diverse binders, including PIB, SBR, poly(methyl methacry-late) (PMMA), poly(ethylene vinyl acetate) (PEVA), and HNBR (**Figure 6**a); the films exhibited different morphologies, mechanical properties, and ionic conductivities.^[184]

As conventional binders disrupt ionic conduction pathways, imparting ionic conductivity to binders or other components can be effective.^[116,193] Oh et al. developed Li⁺-conductive polymeric binders using solvate ionic liquids (complex of triethylene glycol dimethyl ether (G3) and LiTFSI, referred to as LiG3) and fabricated LPSCl–NBR–LiG3 films at a weight ratio of 95.0:1.5:3.5, respectively. These films exhibited a Li⁺ conductivity of 3.3 × 10^{-3} S cm⁻¹ at 30 °C and a thickness of 70 µm.^[117] In subsequent research, Oh et al. improved the SSE films by using SPEbased binders without liquid components, fabricating LPSClBr– NBR–poly(1,4-butylene adipate)–LiTFSI films with a thickness of 80 µm (Figure 6b).^[111] They demonstrated the processability of the chosen solvent, benzyl acetate, which has the ability to dissolve both the polymeric binder (NBR) and Li salts (LiTFSI) without causing damage to the SSE (LPSClBr).

Researchers have also developed novel binders specifically tailored for use in SSE films.^[55,111,117,119,194] Cao et al. developed SSE films using ethyl cellulose as a binder, achieving a high ionic conductance of 291 mS and thickness of 47 μ m, as well as good thermal stability and mechanical properties (Figure 6c).^[187] The unique amphipathic molecular structure of ethyl cellulose facilitated uniform dispersion within the SSE (LPSCI) when toluene was employed as the solvent.

An effective strategy to address ion blocking caused by binders is to minimize the amounts of binders used while maintaining outstanding mechanical properties.^[195-200] In more radical approaches, the complete removal of binders can result in optimal ionic conduction in SSE films.^[123,138,142,201] Yamamoto et al. demonstrated a proof-of-concept for binder-free SSE films using volatile poly(propylene carbonate) (PPC)-based binders, which could be removed after fabrication through simple heating (Figure 6d).^[202] They prepared 59 μ m-thick SSE films using anisole as the processing solvent and confirmed that binder removal positively impacted the electrochemical performance of ASSB cells.

with permission.^[138] Copyright 2015, American Chemical Society. c) Mandrel bend testing of calendered SSE films with 2.5 wt% HNBR (left) and 10 wt% SBR (right). Reproduced with permission.^[184] Copyright 2018, The Electrochemical Society. d) Tensile stress–strain curve of SSE film. The inset photographs show the samples before and after the tensile test. Reproduced with permission.^[187] Copyright 2021, John Wiley and Sons. e) Relationship between the minimum amount of binder required to obtain a free-standing and processible SSE film (blue) and the resulting porosity after calendering (red) for films with different binders: SBR, PEVA, HNBR, and PIB. Reproduced with permission.^[184] Copyright 2018, The Electrochemical Society. f) Effect of solvents on the uniformity of SSE films and SEM images of SEs before and after WIP (490 MPa). Reproduced with permission.^[174] Copyright 2020, Springer Nature. g) Schematic of lightboard imaging technique for quantitative analysis of SSE films. Reproduced with permission.^[145] Copyright 2021, Elsevier.



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Figure 6. SSE films employing various types of binder materials. a) Photographs of cast SSE films containing 10 wt% of different binders: PIB, SBR, PMMA, PEVA, and HNBR. Reproduced with permission.^[184] Copyright 2018, The Electrochemical Society. b) Schematic illustrating reactivity with LPSX for i) hydrocarbon solvents (e.g., o-xylene), ii) Lewis-basic solvents with bulky hydrocarbons (e.g., BA), and iii) Lewis-basic solvents with small hydrocarbons (e.g., EA), and photographs of SSE films (LPSX–NA–LiTFSI). Reproduced with permission.^[111] Copyright 2022, Elsevier. c) Photographs of SSE dispersions with/without ethyl cellulose and SSE film consisting of LPSCI and ethyl cellulose. Reproduced with permission.^[187] Copyright 2021, John Wiley and Sons. d) Photographs of flexible and free-standing PPC-containing SSE film with 6 and 8 wt% PPC. Reproduced with permission.^[202] Copyright 2018, Springer Nature.

The selection and optimization of binders in SSE films play a crucial role in improving the performance of ASSBs. Future research should aim to strike a balance between enhancing ionic conductivity, maintaining mechanical integrity, and exploring binder-free alternatives.

4.1.2. Hybrid SSE Films

Hybridizing SSEs with polymeric materials such as SPEs can impart unique characteristics that cannot be achieved with SSEs alone.^[128,136,190,203] Efforts to address the limited electrochemical stability of SSEs with Li metal anodes have led to the investigation of hybridization with SPEs such as PEO-LiTFSI.^[168,204–206] However, most SPEs exhibit low ionic conductivities, typically $<10^{-5}$ S cm⁻¹ at RT.^[130,131] Through the proper hybridization of SSEs and SPEs, it is possible to overcome the issue of low ion conductivity in SPEs. For example, Li et al. recently produced 150 µm-thick SSE films employing poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF-HFP) (and LiTFSI), with tetrahydrofuran (THF) as a processing solvent.^[169] Despite the low con-

tent (10 wt%) of SSE (Li₇PS₆), the film exhibited a moderate ionic conductivity of 1.11×10^{-4} S cm⁻¹ at RT. Additionally, since the ion conduction mechanism of SPEs differs from that of SSEs, a detailed mechanistic study of these hetero-structured materials is necessary.^[127,130,131,137] Recently, Li et al. studied the Li⁺ conduction mechanism and electrochemical behavior of hybrid SSE films made of PEO/LGPS composites, and found that the composition affected the structure and Li⁺ conduction behaviors of the films (**Figure 7**a).^{[197] 6}Li magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy measurements were performed on ⁶Li|SSE film|⁶Li cells before and after cycling; the results demonstrated an enrichment of ⁶Li in ceramic domains, which increased with increasing ceramic content.^[195]

Polymeric components in hybrid SSE films can also influence their mechanical properties, offering potential advantages for stabilizing Li metal.^[127,128] Pang et al. developed hybrid SSE films using polydimethylsiloxane (PDMS) as a polymeric filler (Figure 7b).^[207] They fabricated β -Li₃PS₄-PDMS hybrid films with thicknesses of 2–4 µm by slurry casting β -Li₃PS₄ using THF as a solvent and subsequently spin coating a PDMS solution onto the cast film. The as-prepared SSE films were utilized

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Figure 7. SSE films hybridized with polymeric materials. a) SEM images (top) and photographs (inset) of PEO/LGPS films with different LGPS fractions; schematic illustrating the corresponding Li⁺ transport pathways (bottom). Reproduced with permission.^[197] Copyright 2021, American Chemical Society. b) Photograph and SEM images of β -Li₃PS₄–PDMS film. Reproduced with permission.^[207] Copyright 2018, The National Academy of Sciences. c) Schematic of the formation of an SSE film with a self-healing polymer matrix membrane and photograph of the resulting free-standing hybrid SSE film. Reproduced with permission.^[209] Copyright 2015, John Wiley and Sons. d) Self-healing of hybrid SSE films after cycling and mechanical breakdown. Reproduced with permission.^[210] Copyright 2021, John Wiley and Sons.

with Li-metal anodes with LEs; they demonstrated stable cycling owing to the high elasticity of PDMS and its insolubility in LEs.

Repeated charge–discharge cycling of ASSBs can cause delamination between the solid components, resulting in increased impedance.^[56] This is a critical issue for the practical application of ASSBs, particularly under low-pressure operational conditions.^[54,55] One promising approach to maintaining the mechanical integrity of the SSE films against electrode volume changes is hybridizing them with self-healing polymers.^[208] Whiteley et al. reported hybrid SSE films with a self-healing polymer matrix, fabricated using variations of polyimine by replacing the monomer diethlyene triamine with penta-ethylene hexamine or 3,3'-diaminodipropyl-*N*-methylamine (Figure 7c).^[209] The resulting hybrid SSE films exhibited an ionic conductivity of 0.092 mS cm⁻¹ at 25 °C, a thickness of 100 μm, and enhanced electrochemical performance in FeS₂ cells. Ren et al. developed self-healable hybrid SSE films by combining Li_{3.85}Sn_{0.85}Sb_{0.15}S₄ with ureidopyrimidinone methacrylate monomer (UPy-MA) using poly(styrene-butadiene-styrene) (SBS) as a binder by grafting (UPy-MA) to both Li_{3.85}Sn_{0.85}Sb_{0.15}S₄ and SBS (Figure 7d).^[210] The hybrid SSE films had a thickness of 30 µm and an ionic conductivity of 0.27 mS cm⁻¹ at 25 °C, and exhibited self-healing after cycling and mechanical breakdown.

4.1.3. SSE Films Fabricated Using Scaffold Materials

Several studies have been conducted to enhance the free-standing ability of large-area SSE films, as scaffold materials play a crucial role in achieving the desired mechanical properties, particularly



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Figure 8. SSE films with scaffold materials as a structural backbone. a) Schematic illustrating the fabrication of SSE films with two different structures (SE–NW–SE and NW–SE–NW) and their corresponding FESEM images and photographs. Reproduced with permission.^[138] Copyright 2015, American Chemical Society. b) Cross-sectional SEM image of ASSB employing an SSE film with NW fabric as a scaffold material. Reproduced with permission.^[139] Copyright 2021, John Wiley and Sons. c) Schematic of the fabrication procedure of LPSCl@P(VDF-TrFE) film and photograph of the film. Reproduced with permission.^[142] Copyright 2022, John Wiley and Sons. d) Photograph and cross-sectional SEM images of SSE film based on a cellulose skeleton as the scaffold material. Reproduced with permission.^[141] Copyright 2021, John Wiley and Sons. e) Photographs and cross-sectional SEM images of SSE film based on a scaffold material. Reproduced with permission.^[170] Copyright 2022, Elsevier.

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Table 5. Fabrication methods for SSE films.

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Fabrication methods	Advantages	Issues/challenges
Slurry casting	 Suitable for mass production Continuous processing Can be used with various types of binders Flexible control of SSE film thickness 	 Degradation of SSEs by processing solvents Environmental/safety concerns related with processing solvents Expensive drying process
Solvent-free	 Free from issues related to processing solvents (e.g., degradation of SSEs, environmental/safety concerns) Minimal amount of binder required (e.g., PTFE) No need for drying process using solvents 	 Challenging to develop a scalable process Shortage of binders that can be processed without solvents. Chemical stability issues regarding PTFE binder toward Li metal anode
Infiltration	 Scalable process using liquefied SSE solution Intimate ionic contact enabled by SSE solution Available for use with tortuous or micro-sized substrates Minimal amounts of SSEs can be utilized 	 Requires high temperature heat treatment for crystallization of SSEs Shortage of scaffold materials that can withstand high temperature heat treatment Shortage of binders that can be used with solution-processing solvents
Spin coating	 High throughput Enables the fabrication of ultra-thin (e.g., sub-micrometer) SSE films Various factors can be controlled (e.g., spin speed, solution concentration) 	 Challenging to apply during mass production Limited processing area for SSE film
Vacuum filtration	 Scalable production Cost-effective Can be used with various types of binders 	• Time-consuming process for mass production

for thin SSE films.^[211–213] SSE films with scaffold material can be fabricated by various methods, including slurry casting and hot pressing. Detailed fabrication methods will be discussed in Section 4.2.

Nam et al. developed an SSE film using poly(paraphenylene terephthalamide) (PPTA) NW as a scaffold material through a transfer method (Figure 8a).^[138] They cast an SSE slurry on an Ni foil substrate and subsequently transferred the cast SSE layer onto a PPTA NW, resulting in a free-standing SSE film. They also demonstrated a bilayer design, LGPS-NW-LPS films with two different SE layers (LGPS and Li₃PS₄ (LPS)), which exhibited a high ionic conductivity of 0.34 mS cm⁻¹ at 30 °C and thickness of 90 µm.^[157] Owing to the flexibility of the PPTA NW scaffold material, the resulting SSE films exhibited excellent bending properties. Suzuki et al. demonstrated ASSBs based on thin carbon black layers with self-standing ≈60 µm-thick SSE films supported by NW fabric as the scaffold material, which were fabricated using the slurry casting method (Figure 8b).^[139] Various types of scaffold materials have also been employed for fabricating SSE films. Liu et al. fabricated a thin SSE film with an ionic conductivity of 1.2 mS cm⁻¹ at RT and a thickness of 30-40 µm using the slurry casting method and a poly(vinylidene fluoride-cotrifluoroethylene) (P(VDF-TrFE)) network skeleton as a scaffold material (Figure 8c).^[142] They employed a facile electrospinninginfiltration-hot-pressing technique to create a porous P(VDF-TrFE) framework, which was then used for the slurry casting of an LPSCl-toluene slurry. Zhu et al. presented a free-standing SSE film (6.3 \times 10⁻³ S cm⁻¹ at RT and 60 μ m thick) comprising a cellulose skeleton as the scaffold material (Figure 8d).^[141] They proposed a self-limited assembly of solid particles on the cellulose skeleton, which could be achieved owing to the presence of hydroxyl groups in cellulose. Consequently, the thickness of the

SSE film could be directly linked to that of the cellulose skeleton. Additionally, Liu et al. demonstrated a flexible hybrid SSE film comprising PEO–LGPS composites and using nylon mesh as the scaffold material (Figure 8e).^[170]

The use of scaffold materials in the fabrication of SSE films enables the production of free-standing SSE films with enhanced mechanical properties. Various scaffold materials have been explored, showcasing the potential of scaffold-based approaches for the development of flexible and high-performance SSE films for ASSBs.

4.2. Fabrication Methods

In this section, we discuss fabrication methods for SSE films, which significantly influence the form factors and electrochemomechanical characteristics of the films, and the applications of the corresponding ASSBs.^[6,178] Factors to consider during SSE film fabrication include SSE processibility, binders, processing solvents, and the properties of scaffold or substrate materials (such as thermal stability, porosity, and tortuosity).^[112] We classify SSE film fabrication methods into three categories: slurry casting, solvent-free fabrication, and alternative methods (**Table 5**).

4.2.1. Slurry Casting Method

The slurry casting method for fabricating SSE films is a continuous flow process suitable for scalable production.^[85,112,119,198,214,215] Factors to consider during this process include the selection of appropriate processing solvents

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Figure 9. Slurry casting methods for fabrication of SSE films. a) Schematic illustrating the slurry casting method for SSE film fabrication with electrodes, scaffold materials, and substrate materials. b) Cross-sectional FESEM image of pouch-type NCM622||Gr full-cell using an SSE film cast on a Gr electrode. Reproduced with permission.^[193] Copyright 2018, Elsevier. c) Photographs of SSE film production by slurry casting on Mylar foil as a substrate material and cathode–electrolyte assembly by cold-pressing. Reproduced with permission.^[144] Copyright 2019, Elsevier. d) Photographs of SSE film on PET film as a substrate material before and after WIP. Cross-sectional SEM image of the ASSB employing the SSE film is also provided. Reproduced with permission.^[37] Copyright 2020, Springer Nature.

to avoid affecting the components (SSEs, binders, etc.), porosity control of the SSE films, and ensuring the binders are soluble or dispersible in the processing solvents.^[37,112,116,117] Slurry casting of SSE films can be performed on scaffold materials, substrate materials, or directly on electrodes, as illustrated in **Figure 9**a.

Nam et al. demonstrated SSE film formation on Gr electrodes using slurry casting, achieving a 30 µm-thick film (Figure 9b).^[193] However, while the method allows for scalable production, achieving precise thickness and uniformity control is limited owing to electrode unevenness. To address this, SSE films can be prepared on substrate materials with homogenous surfaces, such as metal foil and polymeric materials, which allows for better film thickness control.[37,55,216] Additionally, free-standing SSE films can be obtained by peeling them from the substrate materials. For example, Tan et al. fabricated a Li₇P₃S₁₁-SEBS film using the slurry casting method.^[143] The resulting $\approx 50 \,\mu\text{m}$ -thick SSE film was then peeled from the Al current collector or Teflon plate substrate, and was found to exhibit an ionic conductivity of 0.34 mS cm⁻¹ at RT. Hood et al. successfully fabricated a 12 μ m-thick SSE film with an ionic conductivity of 7.2 \times 10⁻⁵ S cm⁻¹ at 20 °C by dip-coating a polished Ni foil substrate with a β -Li₃PS₄·2acetonitirle (ACN) suspension, followed by drying and peel-off processes.^[201] Additionally, SSE films cast on substrates can be transferred to electrodes or other substrates using pressure or heat treatment. For example, Ates et al. transferred an SSE film cast on Mylar foil to a cathode for cell assembly (Figure 9c).^[144] Lee et al. also demonstrated the transfer method using WIP, preparing the SSE film via slurry casting on a PET film substrate (Figure 9d);^[37] after pressurization, the SSE film thickness was 30 µm. For the transfer method, the adhesion between the binder in the SSE film and substrate material should be carefully controlled, particularly under varying conditions, such as temperature and pressure. Moreover, substrate materials with controlled surface properties can be employed. For instance, Emley et al. investigated the quality of SSE films prepared by slurry casting on silicone-coated PET films.^[145] The hydrophobic surfaces of substrate materials such as silicone-coated PET films and Teflon plates can offer different adhesion properties between the SSE films and substrate materials.^[200]

Additionally, free-standing SSE films can be directly obtained by slurry casting on porous scaffold materials.^[139,141,142] In this case, the porosity (pore size) and tortuosity of the scaffold materials must be carefully engineered, taking into account the particle sizes of the SSEs and the rheology and viscosity of the SSE slurry. Utilizing scaffold materials for the slurry casting method is advantageous in achieving a free-standing form.^[138] However, it is essential to choose a scaffold material with an appropriate structure, as its thickness can set the lower limit for the SSE film thickness.

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Figure 10. Solvent-free methods for fabrication of SSE films. a) Schematic of solvent-free fabrication of SSE films, which involves the mixing of SSEs and binders, followed by shearing and/or calendering. b) SEM image of a free-standing SSE film based on a PTFE binder. Reproduced with permission.^[123] Copyright 2019, Elsevier. c) Photograph of the hot-calendering process and an SSE film dry-fabricated using a PTFE binder. Reproduced with permission.^[182] Copyright 2021, American Chemical Society. d) Schematic of the solvent-free preparation process of SSE film using nylon mesh as a scaffold material, and cross-sectional SEM image of the resulting SSE film. Reproduced with permission.^[217] Copyright 2021, Elsevier. e) Schematic (top) and SEM image (bottom left) of SSE film fabricated using the SBR-175 g binder, and SEM image of the interface between the anode and film after 400 cycles (bottom right). Reproduced with permission.^[218] Copyright 2022, John Wiley and Sons.

4.2.2. Solvent-Free Method

Given the chemical reactivity of SSEs toward solvents, alternative methods for SSE film preparation that do not require organic solvents are attractive.^[16,58] In this section, we review the solvent-free method for SSE film fabrication. **Figure 10**a provides a schematic illustration of the solvent-free process, which involves

mixing, shearing, and subsequent calendering.^[38] Hippauf et al. demonstrated a solvent-free method for SSE film fabrication using PTFE as a binder (Figure 10b).^[123] They mixed SSEs (LPSCl) with PTFE in a heated mortar, which formed flakes that were subsequently rolled out. When the PTFE content was 0.15 wt%, a free-standing SSE film with an ionic conductivity of 2.7 mS cm⁻¹ at 25 °C and thickness of 150 μ m was formed. Similarly, Zhang





Figure 11. Alternative fabrication methods for SSE films with versatile characteristics. a) Schematic illustrating the fabrication of SSE films by infiltration of electrospun porous PI NWs with solution-processable SEs (top). Photograph and surface SEM image of a $PI-Li_6PS_5Cl_{0.5}Br_{0.5}$ SSE film (bottom). Reproduced with permission.^[140] Copyright 2020, American Chemical Society. b) Schematic of SSE film fabrication through spin coating; top-view and cross-sectional SEM images of the resulting SSE film. Reproduced with permission.^[226] Copyright 2022, John Wiley and Sons. c) Schematic of the binder-assisted vacuum filtration method and photograph of the resulting SSE film. Reproduced with permission.^[187] Copyright 2021, John Wiley and Sons.

et al. reported an SSE film with a high ionic conductivity of 8.4 mS cm⁻¹ at 25 °C and a thickness of 30 µm using PTFE as a binder (Figure 10c).^[182] They incorporated a hot calendering step to facilitate the scale-up of the production process. Jiang et al. fabricated an SSE film by employing a solvent-free method with a nylon mesh as a scaffold material (Figure 10d).^[217] Nylon mesh was covered with a PTFE-LGPS composite and rolled between two rollers. Recently, Li et al. presented a solvent-free method to synthesize SSE films using a modified SBR as a novel type of dry binder (Figure 10e).^[218] They introduced an SBR paraxylene solution into NaCl granules to reduce the packing compactness and enhance the dispensability of the bare SBR binder. They synthesized an SSE film using modified SBR and SSEs (LPSCl), mixing 1.96 wt % modified SBR with SSEs in a heated mortar and subsequently roll pressing at 80 °C. The resulting SSE film exhibited an ionic conductivity of 2.34 mS cm⁻¹ at 25 °C with a thickness of 80 µm.

While solvent-free methods help alleviate concerns regarding the chemical stability of SSEs, they present limitations in terms of binder options, cost, and scalability for the fabrication of large-area and thin films. Therefore, it is vital to investigate various fabrication methods based on conventional solvent-free techniques, such as spray coating, for producing LIB electrodes.^[124] Additionally, supplementary approaches, such as interlayer engineering, are required to address the instability of Li metal when using PTFE binders. This topic is discussed in Section $5.3.^{\left[182,219\right]}$

4.2.3. Alternative Methods

Kim et al. developed SSE films by employing a solutionprocessable Li argyrodite LPSClBr in conjunction with electrospun PI NWs as scaffold materials (**Figure 11**a).^[140] A homogeneous SSE solution, formed by dissolving LPSClBr in anhydrous ethanol (EtOH), infiltrated the porous structures of the PI NWs, resulting in free-standing and thin SSE films. The excellent thermal stability of the PI NWs enabled high temperature heat treatment (400 °C), which improved the crystallinity and ionic conductivity of reprecipitated LPSClBr.^[106,107] The resultant SSE films exhibited an ionic conductance of 15 mS at 30 °C with a thickness of 40 µm. This solution process for SSE fabrication may be well-suited for applications requiring diverse dimensional needs, such as medical or wearable devices.^[16,220]

Conventional methods, including the slurry casting and solvent-free methods, face challenges in controlling SSE film thicknesses lower than sub-micrometers. In this context, spin coating has been widely adopted for fabricating thin films in various fields.^[221–225] Wu et al. utilized the spin coating method to produce thin SSE films (thickness: $0.5-1.0 \mu m$) with an ionic

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self-densification without pressure

LPS membrane

– Hydrocar binder (2	– Hydrocar binder (2
– NBR (1.5 v	– NBR (1.5 v
- SBS-COOH binder (2	- SBS-COOH binder (2
- PBMA ^b) (5 10 wt%	- PBMA ^b) (5 10 wt%
– NBR (3 wt	– NBR (3 wt
- P(MMA/nB. copolym (3 wt%	- P(MMA/nB. copolym (3 wt%
I I	I
– SEBS (5 wt	– SEBS (5 wt
– PIB (2 wt ⁶	– PIB (2 wt ⁶
– SBR (5 v	

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Table 6. Summary of SSE films with various form factors.

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Ref.	[37]	[145]	[2 00]	[138]	[202]	[לדר]	[123]	[169]	[140]	[205]	[139]	[141]	[187]	217	[206]	[182]	[142]
lonic conductivity at 25 °C [S cm ⁻¹]	1.3×10^{-3}	1.1×10^{-3}	3.8 × 10 ⁻⁴ (30 °C)	3.4 × 10 ⁻⁴ (30 °C)	1.1×10^{-4}	3.3×10^{-3} (30 °C)	2.7×10^{-3}	1.1×10^{-4}	5.8 × 10 ⁻⁵ (30 °C)	4.2 × 10 ^{−4} (20 °C)	I	6.3×10^{-3}	1.7 × 10 ⁻³ (30 °C)	3.6×10^{-4}	2.8 × 10 ⁻⁴ (40 °C)	8.4×10^{-3}	1.2×10^{-3}
Thickness [µm]	≈40	≈50	47	06		70	150	150	40	001	≈60	60	47	100	65	30	30-40
Substrate material	PET film	Silicone-coated PET film	Silicone-coated PET film	Ni foil	I	Ni foil	I	Petri dish	I	I	I	I	I	I	PTFE substrate	I	I
Scaffold material	I	I	I	PPTA NW	I	I	I	I	PI NW	I	NW fabric	Cellulose skeleton	I	Nylon mesh	I	I	P(VDF-TrFE) network skeleton
Solvent	Xylene : Isobutyl isobutyrate (50:50 w/w)	Toluene : Isobutyl isobutyrate (50:50 w/w)	Toluene	Toluene	Anisole	DBM	I	ТНЕ	Ethanol	I	Xylene and diethylbenzene	Chloroform	Toluene	I	Acetonitrile	I	Methylbenzene
Binder [wt%]	Non-aqueous acrylate-type (1 wt%)	NBR (4.8 wt%)	XNBR ^{d)} (5 wt%)	I	(PPC) (6 wt%)	NBR (1.5%)	PTFE (0.15%)	PVDF-HFP (30%)	I	I	Acrylic binder (1 wt%)	Silicone rubber (1 wt%)	Ethyl cellulose (2 wt%)	PTFE (1 wt%)	. 1	PTFE (0.2 wt%)	I
SPEs	1	I	1	1	I	I	I	1	I	Plasticized PEO (12 wt%) (PEO:LiTFSI:P _{yr1.4} TFSI = 10:1:2)	1	I	I	I	PEO (5 wt%) (PEO:LICIO ₄ :SiO ₂ = 10.5:-31	(4:5.5-	I
Sulfide SEs	Li ₆ PS ₅ Cl	Li ₆ PS ₅ Cl	Li ₆ PS ₅ Cl	Li ₃ PS ₄ , Li ₁₀ GeP ₂ S ₁₂	75Li ₂ S·25P ₂ S ₅ (mol%)	Li ₆ PS ₅ CI	Li ₆ PS ₅ Cl	Li ₇ PS ₆	Li ₆ PS ₅ Cl _{0.5} Br _{0.5}	Li _{3.25} Ce _{0.25} P _{0.75} S ₄	Li ₆ PS ₅ Cl	Li ₆ PS ₅ Cl	Li ₆ PS ₅ Cl	Li ₁₀ GeP ₂ S ₁₂	Li ₆ PS ₅ Cl	Li _{5.4} PS _{4.4} Cl _{1.6}	Li ₆ PS ₅ Cl
Fabrication method	Slurry casting	Slurry casting	Calendering	Slurry casting and transfer	Slurry casting	Slurry casting	Solvent-free	Slurry casting	Infiltration	Hot pressing	Slurry casting	Slurry casting	Vacuum filtration	Solvent-free	Slurry casting	Solvent-free	Slurry casting
Structure				Free- standing	form												

Table 6. (Continued).

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conductivity of 6.7×10^{-5} S cm⁻¹ at RT (Figure 11b).^[226] An LPS precursor solution was spin-coated onto an Au/glass substrate and subsequently sintered at 250 °C. Cao et al. demonstrated a vacuum filtration method for SSE film fabrication, using uniform LPSCl-ethyl cellulose dispersions (Figure 11c).^[187,227,228]

Depending on the fabrication method utilized, the assembly protocol for pouch-type ASSBs discussed in Section 5.1 can vary. From an industrial application perspective, considerations such as process cost and scalability are vital.^[5,19,44] While the cell assembly processes are crucial in industrial applications, the production volume and efficiency of the SSE film are also important. These aspects are dependent on the fabrication method of the SSE film, which in turn relies on the types of SSEs used, the choice of binder and solvent, and the presence or absence of solvents.^[194] In the context of selecting SSEs, considerations are guided by factors, such as price, morphology, and air stability, as previously delineated.^[42,58,59,81] Notably, the choice of binder significantly impacts the fabrication method and, consequently, the processability of the SSE film.^[121] However, as mentioned in Section 2.2, the range of binders and solvents available for SSEbased ASSBs is still limited, compared to conventional LIBs.^[58] Given the disadvantages of solvents concerning SSE degradation, the need for additional drying processes, safety, and environmental aspects, a solvent-free dry method seems to present an advantageous.^[38,123] Nevertheless, from a scalability perspective, the preference may shift.

5. ASSBs Using SSE Film

This section reviews advancements in the development of SSEbased ASSBs, with a focus on design strategies for pouch-type ASSBs that utilize SSE films.

5.1. Assembly Protocols for Pouch-Type ASSBs Based on SSE Film Form Factors

Densely stacked pouch-type cells with high energy densities that can be produced through a scalable assembly process are crucial for the practical application of ASSBs.^[6,38,42,53] In this context, the form factors of SSE films play a significant role. This section discusses various SSE film form factors and their corresponding pouch-type cell assembly processes. We categorize SSE film form factors into three types: SSE films on electrodes, SSE films on substrate materials, and SSE films in free-standing form (**Table 6**). For example, SSE films on substrate materials can include those fabricated through slurry casting, spin coating, and dip coating methods, while SSE films in free-standing form can be fabricated using slurry casting and infiltration on scaffold materials, solvent-free methods, and vacuum filtration.

Figure 12a presents a schematic of the pouch-type cell assembly process for each SSE film form factor. Prior to cell assembly, SSE films undergo densification. Depending on the form factor, densification can be conducted only on the SSE film or simultaneously during transfer of the SSE film to the electrodes by either calendering or isostatic pressing.^[6,38,43,44] In the case of SSE films on substrate materials, SSE films can be directly transferred onto electrodes using techniques such as pressurization, or can be prepared in free-standing form by peeling off from the substrate materials. Post-processing of SSE films transferred onto electrodes

Structure	Fabrication method	Sulfide SEs	SPEs	Binder [wt%]	Solvent	Scaffold material	Substrate material	Thickness [µm]	lonic conductivity at 25 °C [S cm ⁻¹]	Ref.
	Solvent-free	Li ₆ PS ₅ Cl	I	SBR (2 wt%)	I	I	I	80	2.3×10^{-3}	[2 18]
	Slurry casting	Li ₁₀ GeP ₂ S ₁₂	PEO (5 wt%) CTMS ^{a)} (5 wt%)	I	Anisole	Nylon mesh	I	60	2.4×10^{-4}	[021]
	Slurry casting	Li ₆ PS ₅ Cl _{0.5} Br _{0.5}	1	NBR and poly(1,4- butylene adipate) (3 wt%)	Benzyl acetate	1	Ni foil	80	2.2 × 10 ^{−3} (30 °C)	[[[]]

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Figure 12. Pouch-type ASSBs employing SSE films. a) Schematic of the assembly processes for pouch-type ASSBs using various forms of SSE films (SSE film on electrode, SSE film on substrate material, and free-standing SSE film). b) Schematic illustrating the stacking sequence for pouch-type ASSBs. c) Schematic of the pressurization methods (isostatic pressing and uniaxial pressing) for the assembled pouch-type ASSBs.

is similar to that of SSE films slurry-cast onto electrodes, whereas post-processing SSE films peeled off from a substrate material resembles the treatment of SSE films in free-standing form.

Following the densification, transfer, and peel-off processes, SSE films or SSE film-coated electrodes undergo a cutting process to achieve appropriate sizes and shapes for cell assembly. It is worth noting that the dimensions of SSE films on electrodes precisely match those of the adjoining electrodes, while free-standing SSE films can be larger than the electrodes. Consequently, free-standing SSE films (obtained either by peeling off from substrate materials or by densifying SSE film in freestanding form) offer flexibility in the stacking process.

ASSBs benefit from their ability to undergo bipolar stacking, which is attributed to the solid-state characteristics of SSEs that do not flow or mix.^[6,15,38,138,228,229] Bipolar stacking reduces the need for inactive components (e.g., cell housing materials) and increases cell voltages through serial stacking, resulting in high energy density at the system level. The stacking sequence, that is, parallel or series stacking (shown in Figure 12b), should be carefully considered, as it affects energy density and cell voltage.^[6,15,18,37,38] In LIB manufacturing, separators can be assembled by folding them between electrodes.^[7,14,230] However, folding-based assembly processes are not suitable for SSE films owing to their limited mechanical flexibility and the high cost of SSE materials.^[38]

After stacking, pouch-type cell assembly proceeds with welding of the current collector and packaging. The packaged cell requires pressurization under high pressures to establish intimate interfacial contact between solid components.^[16] Various methods can be used for this purpose, such as isostatic pressing (e.g., cold isostatic press (CIP) and WIP) or uniaxial pressing, depending on the cell dimensions and intended applications (Figure 12c). Most lab-scale ASSBs are pressurized using a uniaxial hydraulic press at several hundred megapascals. However, this approach has limitations in uniformly compressing largearea pouch-type cells. Uneven compression can lead to mechanical damage at edges or protrusions, resulting in failures such as ISCs.^[54] Consequently, isostatic presses are prioritized, as they allow for uniform, isotropic pressurization using a fluid, minimizing mechanical damage. However, this method has limitations for mass production, such as discontinuous processing, necessitating the development of alternative equipment or techniques.^[6]

5.2. Pouch-Type ASSBs Employing SSE Films

As mentioned earlier, different types of SSE film form factors each require specific pouch-type cell assembly methods. Herein, pouch-type ASSBs, reported in literature, demonstrated by the aforementioned assembly protocols are summarized. Nam et al. showcased pouch-type $80 \times 60 \text{ mm}^2 \text{ NCM622}$ ||Gr full-cells using slurry-cast SSE films (**Figure 13**a).^[193] LPSCI-NBR slurries were directly cast onto Gr electrodes. The resulting SSE film-coated Gr electrodes were assembled with smaller cathodes through isostatic pressing at 492 MPa.

A major hurdle in realizing practical pouch-type ASSBs is ensuring their operation at low pressures. Ensuring intimate contact between all the solid-state components despite electrode volume changes during charge and discharge is challenging for pouch-type ASSBs that must operate under low or no pressure. To address this issue, Kwon et al. recently developed 3D-network binders via vulcanization of BR and fabricated pouch-type LiNi_{0.70}Co_{0.15}Mn_{0.15}O₂||Li₄Ti₅O₁₂ ASSB fullcells (Figure 13b).^[55] They fabricated vulcanized BR via in situ crosslinking by using elemental sulfur during the wet-slurry process; vulcanized BR exhibited enhanced binding properties compared to those of the pristine binder. SSE films were coated on Ni foils, which acted as a substrate material, using the slurrycasting method. They were then transferred to Li₄Ti₅O₁₂ anodes via WIP and stacked with the cathodes. The pouch-type full cells using vulcanized BR binders outperformed those using pristine BR binder. Notably, pouch-type ASSBs performed well even without external operating pressure, emphasizing the importance of binders for low-pressure operation of pouch-type ASSBs. Lee et al. demonstrated pouch-type ASSBs based on silver-carbon composite anodes (Figure 13c).[37] They prepared SSE films coated on PET films as substrate materials and transferred them onto LiNi_{0.90}Co_{0.05}Mn_{0.05}O₂ (NCM900505) cathodes by applying an external pressure of 50 MPa using a WIP. They presented 0.6 A h-class ASSB prototypes with bi-cell structures, and the stacked pouch-type cells were pressurized at 490 MPa by WIP.

Recently, Wang et al. developed free-standing SSE films using PTFE as a binder and a solvent-free method, and demonstrated pouch-type LiCoO_2 ||Gr full cells (Figure 13d).^[231] They fabricated SSE films using 99.5 wt% LPSCl and 0.5 wt% PTFE, which exhibited a conductance of 666.7 mS at RT and a thickness of 20 µm.

Pouch-type cells were fabricated by pressurizing the cell assembly and operating them under an external pressure of \approx 50 MPa. Suzuki et al. demonstrated pouch-type ASSBs using deposition-type Li metal anodes based on thin carbon black layer with a free-standing SSE film employing an NW fabric as a scaffold material (Figure 13e).^[139] The cell assembly was pressurized at 490 MPa and 80 °C by WIP, resulting in a pouch-type full-cell.

The pouch-type ASSBs summarized in this section provided guidance not only for various assembly protocols but also key research directions for future practical ASSBs.

5.3. SSE Films for Li Metal Anode

Enabling Li metal anodes is crucial for the success of ASSBs with high energy densities.^[45,150,152,153,183] However, the poor intrinsic reduction stabilities of SSEs and the correlated electrochemomechanical issues at the interfaces remain highly challenging to overcome.^[54,57,58] Comprehensive reviews on the interfacial evolution and engineering in ASSBs employing Li metal anodes can be found in the cited references.^[17,41,53,191,192,232] In this section, we focus on the usage of SSE films for Li metal anodes. As the thicknesses of SSE films decrease, adopting Li metal anodes becomes more difficult, particularly in terms of mechanical stability. A significant decrease in the thickness of the SSE film can undermine its mechanical stability and integrity. Consequently, during Li plating and stripping processes, volume changes can impose mechanical stress, resulting in the formation of cracks or deformations.^[17,54,149,150] Such mechanical defects can increase the local current density and promote the growth of Li dendrites. Furthermore, as the SSE film becomes thinner, the propagation of mechanical defects or Li dendrites is more likely to reach the opposite electrode, thus amplifying the risk of electrical shortcircuits between the anode and cathode.^[60,150] Hence, to effectively integrate Li metal within thin SSE films, meticulous control of the interface between Li and the SSE film, as well as the properties of the SSE film, is imperative. This calls for judicious management of Li metal attachment or operating pressure.^[54,179] Additionally, potential solutions could involve compositional tuning and/or hybridization of SSEs with polymeric components.[190]

During repeated Li plating and stripping processes, there is a possibility that delamination may occur between Li metal anodes and SSE films, negatively impacting cell performance.^[54,57,94,149,179] Jiang et al. developed adhesive ethyl vinyl acetate porous (EVAP) membranes as interlayers to withstand the volume changes of Li metal anodes while providing mechanical support to SSE layers (**Figure 14**a).^[188] The sticky nature of EVAP membranes enables the handling of low-loading (35 mg) SSE layers. Li||Li symmetric cells employing SSE–EVAP exhibited stable cycling at 0.1 mA cm⁻² and 50 °C compared to those employing bare SSEs.

Despite its high ionic conductivity of $\approx 10^{-2}$ S cm⁻¹, LGPS is vulnerable to Li metal owing to its poor reduction stability and the formation of electronically conducting decomposition byproducts.^[64,83,88] Li et al. reported 100 µm-thick hybrid SSE films composed of LGPS (88 wt%) and PEO (12 wt%) with an electroconductivity of 0.42×10^{-3} S cm⁻¹ at 20 °C, prepared by hot pressing, and investigated their Li metal stability (Figure 14b).^[205] The Li||Li symmetric cells with the LGPS–PEO films exhibited





Figure 13. Electrochemical performances of pouch-type ASSBs using SSE films. a) Photograph and cross-sectional FESEM image of pouch-type NCM622||Gr full-cell. First-cycle charge–discharge voltage profiles of pelletized and pouch-type full-cells at 0.025C are shown in the inset. Reproduced with permission.^[193] Copyright 2018, Elsevier. b) Schematic of the in situ formation of vulcanized BR binders during the slurry casting process. Cycling performances of pouch-type NCM||Li₄Ti₅O₁₂ full-cells employing pristine and vulcanized BR and operated under no external pressure, with photograph of the pouch-type cell. Reproduced with permission.^[55] Copyright 2022, Elsevier. c) Schematic of pouch-type cell with bi-cell structure employing SSE films, and corresponding X-ray computerized tomography (CT) image. Cycling performance and Coulombic efficiency of Ag–C|SSE|NCM900505 prototype pouch cell (0.6 Ah) fabricated via transfer method. Reproduced with permission.^[37] Copyright 2020, Springer Nature. d) Schematic of SSE film fabricated via solvent-free method and all-solid-state pouch-type cell utilizing it. Charge–discharge curves of ASSBs with a Li₃InCl₆@LiCoO₂|LPSCl|Gr configuration and their corresponding cycling stabilities at RT. Reproduced with permission.^[231] Copyright 2022, American Chemical Society. e) Photograph and cross-sectional SEM image of pouch-type ASSB employing an SSE film fabricated using NW fabric as a scaffold material and its corresponding cycling performance. Reproduced with permission.^[139] Copyright 2021, John Wiley and Sons.

significantly more stable cycling at 0.1 mA cm⁻² and 60 °C compared to those with bare LGPS films, and no notable increase in resistance was observed even after 12 days of aging. This result was attributed to the improved wetting property of the hybrid SSE films toward the Li metal anode.

Solvent-free methods using binders such as PTFE are an alternative approach for fabricating SSE films, as discussed in Section 4.2.2.^[123] However, PTFE binders exhibit severe chemical reactivity with Li metal.^[219] To address this issue, a protective interlayer can be introduced. Zhang et al. investigated the

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Figure 14. SSE films for Li metal anodes. a) Photographs of pieces of a sticky EVAP film and an SSE–EVAP composite. Overpotential curves of Li⁺ plating/stripping in Li||Li symmetric coin cells with bare SEs and SE–EVAP composites. Reproduced with permission.^[188] Copyright 2020, American Chemical Society. b) Schematic of the fabrication process for a hybrid LGPS/PEO film and voltage profiles of the Li||Li symmetric cells using the film at 0.1 mA cm⁻² and 60 °C. Reproduced with permission.^[205] Copyright 2020, John Wiley and Sons. c) SEM image of Li metal coated with a deposited Al₂O₃ layer and EDX elemental Al map. Cycling performance of Li||Li symmetric cells with and without the interlayer. Reproduced with permission.^[182] Copyright 2021, American Chemical Society. d) Schematic of self-tightening process at the interface between a hybrid SSE film and Li metal anode (MIEC: mixed ion/electron conducting interphase) and voltage profile of pressure-controlled Li|LSnS|UPy-Li half-cells. Reproduced with permission.^[210] Copyright 2021, John Wiley and Sons.

interface between Li metal anodes and SSE films prepared via a solvent-free method using PTFE with and without an Al₂O₃ interlayer (Figure 14c).^[182] They prepared a 400 nm-thick Al₂O₃ interlayer by pretreating Li foils via radio frequency magnetron sputtering. Li||Li symmetric cells employing SSE films with an Al₂O₃ interlayer exhibited a stable cycling performance at 0.1 mA cm⁻² and 60 °C, in contrast to those without an Al₂O₃ interlayer.

For continuous cycling with Li metal anodes, addressing the electrochemical stability of SSE films toward Li metal anodes is not the only challenge, as electrochemo-mechanical issues related to defects in the SSE films and volume changes of Li metal anodes must also to be considered.^[17,57,94] Ren et al. recently investigated the use of self-healable SSE films for Li metal anodes (Figure 14d).^[210] Li half-cells with the hybrid SSE films based on self-healing units exhibited stable cycling at 1.0 mA cm⁻² and 25 °C with stack pressures of 160 kPa or 960 kPa, with the aid of a controlled amount of LE. They attributed the results to the self-tightening of the interface by the self-healing units of the SSE films. The composite electrolytes could infiltrate pores induced by Li stripping, and the adhesive properties of the binders could offer intimate contact.

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	Ref.	[176]	[182]	[200]	[143]	[169]	[201]	[712]	[206]	[185]
	Thickness of Li metal [µm]	1	80	100	I	I	I	1	I	I
	Operating pressure [MPa]	1	0	$\overline{\vee}$	I	I	I	1	I	I
	Fabricating pressure [MPa]	I	30	5	I	I	I	1	I	I
	Temperature [°C]	25	60	30	RT	RT	25	25	40	60
	Critical current density (CCD) [mA cm ⁻²]	1	I	0.3	I	I	I	1	I	I
	Cycle hour [h]	150	400	500	2000	1000 (180)	583	20	-001-001 100	600
	Duration time per cycle [h]	2	7	-	20	-	-	7	0.33	2
: films.	Areal capacity [mA h cm ⁻²]	L.0	Γ.0	0.05	L.I	0.1 (0.25)	0.15	L.O.	0.017- 0.033- 0.05	٥.٦
lls using SSE	Current density [mA cm ⁻²]	L.O	Γ.Ο	0.1	0.11	0.2 (0.5)	0.3	L.O.	0.1-0.2-0.3	٢.0
i symmetric ce	Thickness of SSE film [Jum]	35	30	<50	~50	150	12	00	65	100-150
formances of L	lonic conductivity at 25 °C [S cm ⁻¹]	2.0 × 10 ⁻⁴	8.4 × 10 ⁻³	3.8 × 10 ^{−4} (30 °C)	7.0 × 10 ⁻⁴ (RT)	1.1 × 10 ⁻⁴ (RT)	7.1 × 10 ⁻⁵ (20 °C)	3.6 × 10 ⁻⁴	2.8 × 10 ^{−4} (40 °C)	8.01 × 10 ⁻⁴ (60 °C)
ctrochemical pen	N ote	5 nm of poly- dopamine layer coated on SSE	400 nm Al ₂ O ₃ interlayer coated on Li metal	I	I	I	I	GPE (TEGDA-BA copolymer with 1 m LiTFSI in FEC) interlayer formed on Li metal	I	I
Table 7. Summary of elec	Composition of SSE film (SSE/SPE/binder/scaffold material)	Li ₆ PS ₅ Cl/-/-/-	Li _{5.4} PS _{4.4} Cl _{1.6} /-/PTFE/-	Li ₆ PS ₅ Cl/-/XNBR/-	Li ₇ P ₃ S ₁₁ /-/SEBS/-	Li ₇ PS ₆ /-/PVdF-HFP- LiTFSI/-	β-Li ₃ PS ₄ /-/-/-	Li ₁₀ GeP ₂ S ₁₂ /-/ PTFE/Nylon mesh	Li ₆ PS ₅ Cl/PEO-LiClO ₄ - SiO ₂ /-/-	Li ₃ PS ₄ /PEO/-/-

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[021] [205] Ref. [272] Thickness of Li metal [µm] 1 ī. Dperating pressure [MPa] I I. Fabricating pressure [MPa] I Temperature ⁰ 25 90 density (CCD) [mA cm⁻²] Critical current I nour [h] Cycle 700 400 400 time per cycle [h] Duration 2 2 time capacity h A m cm⁻²] Areal 0.01 0.1 0.1 mA cm⁻² Current density 0.01 0.1 0.1 **Fhickness** of SSE film [mm] 8 8 8 conductivity at 25 °C [S (22 °C) (20 °C) 2.2×10^{-4} 4.2×10^{-4} 2.4×10^{-4} cm⁻¹ (RT) lonic ormed on Li TEGDA-BA LiTFSI in interlayer copolymer with 1 m FEC) metal Note GPE (SSE/SPE/binder/scaffold Composition of SSE film -i_{3.25} Ge_{0.25} P_{0.75} S₄/ PEO-PEO-CTMS/ -/Nylon LiTFSI-P_{vrl.4}TFSI/-/-PEO-LITFSI/-/--i₁₀GeP₂S₁₂/ -i₁₀GeP₂S₁₂/ naterial) mesh

Recently, there has been an notable rise in instances of Li symmetric cells being operated using SSE films.[143,169,170,176,182,185,195,200,201,206,217] A summary of the electrochemical performances of Li symmetric cells using SSE films is provided in Table 7. However, the operation of full cells using thin SSE films remains a rarity. As the thickness of SSE films decreases, the relationship between stack pressure or fabrication pressure and the performance of Li cells become increasingly significant, considering the aforementioned mechanical properties.^[150,179] However, there is a scarcity of information in the literature concerning these experimental aspects, such as fabrication pressure and operating pressure, for Li cells using SSE films. For the successful implementation of ASSBs with Li metal anodes based on thin SSE films under low operating pressure conditions, it is vital to consider not only the composition and interfaces but also electrochemo-mechanical issues.^[17,54]

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6. Conclusion and Outlook

In this review, we have provided a comprehensive overview of design strategies for SSE films, with a focus on cell assembly and operation of high-energy-density ASSBs. We discussed the thickness requirements and challenges stemming from material and structural differences between conventional separators in LIBs and SSE films.^[6] Notably, the SSEs in SSE films inherit the ion conduction role of LEs impregnated in the separators of conventional LIBs, leading to considerable changes in the mechanical properties of the SSE films.^[54]

As illustrated in **Figure 15**, the key characteristics required for SSE films encompass not only ionic conduction properties and electrochemical stability, but also mechanical properties essential for the assembly and operation of ASSBs. Components such as binders and mechanical support materials (that is, scaffold and substrate materials) play vital roles in ensuring mechanical integrity and adaptability, particularly in ASSBs that operate under low or no external pressure.^[37,112,138] Furthermore, given that ASSBs are assembled under high pressures unlike conventional LIB systems, it is crucial to investigate the composition of SSE films (particularly the state of the binders) under varying pressure conditions to ensure practical applicability for low-pressure operation.

Throughout this review, we emphasized the importance of establishing test protocols to assess the key performances of SSE films, such as thermal and air stability and mechanical properties. The thermal and air stabilities of SSE films are directly related to the safety of ASSBs and, as such, necessitate thorough investigation. In addition, it is vital to verify that the basic characteristics, such as ionic conductivity and structural integrity, are well maintained after testing.^[138,140] Furthermore, development of advanced characterization techniques for SSE films, which can preserve the SSE film's properties during analysis, is essential. For example, considering the intrinsic instability of SSEs, it is necessary to account for protection against hydrolysis and excessive beam damage.^[199,214,216,233]

ASSBs offer the advantage of being designable with various stacking sequences, such as parallel and bipolar stacking.^[6,38] However, precise alignment and maintenance of contact between cell components, as well as successfully assembling the cells

Fable 7. (Continued).



Figure 15. Schematic illustration of SSE films with various properties required for achieving ASSBs with high energy densities and durability.

under high pressure without mechanical failure, can be highly challenging, particularly when the number of stacking layers is large. In this context, the fabrication method and corresponding form factors of SSE films are significant for the application of various electrode systems and the pressurization process for ASSBs. Effective utilization of scaffold and substrate materials is also crucial for compensating for the mechanical limitations of SSE films, particularly at ultra-low thicknesses.

To enable Li metal anodes, challenges related to the characteristics of SSE films, such as electrochemical stability, porosity, surface uniformity, and mechanical strength, must be addressed. Electrochemical instability at the interface and anisotropic stresses caused by large volume changes of electrode materials can lead to delamination and crack formation.[21,22,39,54,94] To tackle these issues, strategies such as hybridization with polymeric materials (e.g., SPEs, self-healing polymers) and designing of host structures between the SSE film and electrodes (e.g., Li metal anode), are required.^[190] Designing bilayer SSE films is a novel strategy to adopt different electrochemo-mechanical features from cathodes and anodes.^[157] Additionally, forming an interface layer between Li metal anodes and SSE films can be a promising approach for the stable operation of Li metal anodes.^[37,234-236] This interface layer can be pre-formed on the surface of either the SSE film or the Li metal anode, or can be generated in situ during battery operation. It is worth noting that ionic conduction at the interfaces should be carefully investigated. When assembling ASSBs with Li metal anodes, high pressures (e.g., \geq 70 MPa) can cause ISC and/or severe chemical reactions between the Li metal and SSEs.^[57,94,179,183] To solve this, more complicated pressurization, such as multistep pressurization, may be applied. An anodeless cell design wherein Li metal anodes are generated in situ during charging, such as ASSBs employing Ag–C anodes, offers significant advantages.^[37,139,237]

Finally, we have observed a growing number of studies on the low-pressure operation of ASSBs. Additionally, numerous previously conducted investigations on next-generation electrode applications for ASSBs (e.g., Si, Sn, Sb), which are based on testing using SE powder-based uniaxial pressurized cells, need to be re-examined for practical assessment.^[108,238,239] Throughout this review, we have extensively discussed the characteristics of various electrochemo-mechanical phenomena and engineering processes in ASSBs, emphasizing the unique mechanical properties of low-thickness SSE films. Although numerous challenges remain, it is anticipated that the gap between lab-scale research and practical goals can be narrowed through design strategies that build on the hybridization of various compositions and the immiscible nature of solid-state materials. As our understanding of these systems improves, we can further optimize the performance of ASSBs and bring their potential benefits to a wide range of applications.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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