Solid-State Lithium Batteries: Bipolar Design, Fabrication, and Electrochemistry

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There are increasing demands for large-scale energy storage technologies for efficient utilization of clean and sustainable energy sources. Solid-state lithium batteries (SSLBs) based on non- or less-flammable solid electrolytes (SEs) are attracting great attention, owing to their enhanced safety in comparison to conventional Li-ion batteries. Moreover, SSLBs can provide great benefits in terms of battery performance (power and energy densities) and cost when constructed using a bipolar design. In this review, we introduce the general aspects of the bipolar battery architecture and provide a brief overview of the essential components and technologies for bipolar SSLBs: Li\textsuperscript{+}-conducting SEs, composite electrodes, and bipolar plates. Furthermore, we review the recent progress in the design and construction of bipolar SSLBs with emphasis on the fabrication techniques of SEs and SSLBs and the engineering approaches to improve their electrochemical properties.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have played a central role in the successful development and rapid spread of numerous portable electronic devices. The technological advances in both materials and fabrication of LIBs have led to a remarkable improvement of their electrochemical performance in terms of power and energy densities (both gravimetric and volumetric) and cycle lifetime.\cite{1–5} As society continues to move from fossil fuels toward clean and sustainable energy sources, extensive efforts are being made for LIBs to be used in large-scale energy storage systems, for example, electric vehicles (EVs) and grid energy storage facilities.\cite{6,7} These large-scale storage systems have performance requirements that differ significantly from those for portable electronic devices.\cite{5–7}

Despite considerable enhancements in the performance of LIBs, frequent fire/explosion incidents and widespread recalls of mobile devices has caused a lot of public concerns over the safety of current LIBs. Undoubtedly, safety requirements will become more important as the LIB technology enters large-scale energy storage markets. From a fundamental point of view, safety problems are mostly associated with the flammability of the organic, liquid electrolyte solvents used in LIBs, e.g., carbonates.\cite{2,3} Under abnormal situations, LIBs can experience thermal runaway, which is an uncontrollable, rapid increase of the cell temperature. The thermal runaway process can be triggered by various unexpected events and/or abuse conditions, including overcharging, overheating, mechanical shock, and internal/external short-circuiting.\cite{2,5,6} Parasitic reactions of the active electrodes with the electrolyte as well as self-reactions in the electrolyte generate and release heat during thermal runaway. More importantly, the complete combustion of the flammable electrolyte solvents is the direct cause of a catastrophic fire and/or explosion.\cite{8–10} Thus, the main point of research has been focused on the development of functional additives and co-solvents capable of reducing the flammable nature of the liquid electrolytes.\cite{10}

Recently, the focus of interest has shifted to solid-state Li batteries (SSLBs) in which electrolytes are made up of Li\textsuperscript{+}-conducting solid materials.\cite{11–25} The use of solid electrolytes (SEs) with non- or reduced flammability can keep batteries safe even under harsh and abuse conditions. Among various types of electrochemical systems with high energy density, e.g., advanced LIBs, metal-air batteries,\cite{26,27} and fuel cells\cite{28,29} presently under development, SSLBs would provide the most promising technology for large-scale power generation and storage systems, where safety issues are crucial. Furthermore, a bipolar architecture of SSLBs can offer substantial benefits in terms of battery performance and cost compared to conventional LIBs.\cite{30–38} The bipolar design refers to the battery configuration where unit (mono) cells are in direct contact with each other and connected in series in a battery module without using external electrical connections between them. In contrast to the case of free-flowing liquid electrolytes, SEs enable the implementation of the bipolar design without concerns of electrolyte leakage.\cite{39–41} As will be detailed in the following sections, the bipolar design allows for an easy series connection of multiple cells to build up the total output voltage and shortens electronic pathways in the module, which leads to increased power capability.\cite{30,34,36–38,41} Moreover, the bipolar design can avoid the use of numerous passive components and parts required for packaging as well as external electrical connections. As these components are not used, the bipolar SSLB design leads to an improvement in the energy density of large-scale battery systems and is cost saving.\cite{30,34,36–38,41}

In this review, we first introduce the general aspects of the bipolar battery architecture along with its main advantages and the technical challenges that need to be addressed. Second, we provide a brief overview of the key components and technologies that are required to realize bipolar SSLBs: (i) Li\textsuperscript{+}-conducting SE materials, (ii) engineering strategies to make the composite electrodes electrochemically active, and (iii) bipolar plates (BPs). Third, we present the recent progress in the design and construction of bipolar SSLBs, focusing on the fabrication techniques of SEs and SSLBs and the technical approaches to enhance their electrochemical performance. Finally, future prospects of bipolar SSLBs are discussed. Several review articles on SEs and SSLBs have already been published.\cite{11–23} To our knowledge, however, a focused review summarizing the recent
advances in bipolar SSLBs, which is the main objective of this article, does not exist. We believe that this review will provide a valuable reference for developing large-scale bipolar SSLB systems to be used in efficient energy storage.

2. General Aspects of Bipolar Battery Architecture

A battery system is made of a number of modules, each of which comprises multiple unit cells connected in series and/or parallel, to meet the power and energy requirements for large-scale energy storage applications. For instance, a Tesla EV powered by a 100 kWh battery system contains ~8,000 LIB cells. Depending on how unit cells are electrically connected with each other in a single module, the battery architectures may be divided into two categories: monopolar and bipolar (Figure 1a).

The monopolar design represents a battery configuration commonly used for current LIBs with liquid electrolytes, and it consists of multiple cells connected in series using external wiring (Figure 1a). As illustrated in Figure 1a, the monopolar design has the following features:

- **Current collector**: A current collector acts as either a positive or negative pole, which is thus called a monopolar plate (MP).
- **Electrode**: A positive electrode (PE, cathode) and a negative electrode (NE, anode) are separately formed on the positive MP and the negative MP, respectively.
- **Unit cell**: A unit cell is assembled with the PE | MP, electrolyte, and NE | MP, and then, it is sealed and packaged.
- **Module**: Multiple unit cells are connected in series through external wiring. That is, a tab extending from the negative plate of one cell is connected by a conductive wire (strap) to a positive tab on the next cell.
- **Electron pathway in the module**: During discharge, an electron exiting the NE of one cell should travel (i) in the in-plane direction of the MP toward the negative tab, (ii) through the external wire toward the positive tab of the next cell, and (iii) in the in-plane direction of the MP to enter the PE.

An essential prerequisite for making series connections between liquid electrolyte-based cells is to seal and package individual cells, thereby preventing internal short-circuiting due to electrolyte leakage. The monopolar design allows for a simple assembly of unit cells with liquid electrolytes; however, it may not be suitable for high-voltage, high-power applications, such as battery systems for EVs, because the external electrical connections inevitably increase the resistive losses due to long electron pathways. Moreover, a large number of MPs, separate cell packaging, and external wiring not only reduce the volumetric/gravimetric energy densities of the battery module, but also increase the complexity and material cost of the battery.

On the other hand, the bipolar architecture (Figure 1b), in which multiple cells are connected in series via BPs without external wiring, provides an efficient way to stack and connect the cells in terms of electrical resistance, volume, weight, and cost. The idea of bipolar battery stacking originates from the voltaic pile at the advent of electrochemical science. In 1897,
Tribelhorn patented the first bipolar lead-acid battery in which a stack of cup-shaped electrodes were separated by glass balls. Kapitza then constructed a bipolar Pb-acid battery in 1923 by immersing Pb plates in a H₂SO₄ solution and achieved a maximum power density of 35 kW L⁻¹ and 6 kW kg⁻¹. However, the development of bipolar Pb-acid batteries with liquid electrolytes were plagued by short-circuit problems until advanced electrolyte technologies were devised to immobilize the acid in gels or absorptive glass mats.

In an attempt to address the safety issues of LIBs, a variety of Li⁺-conducting SE materials have been developed in recent years, including polymers, sulfides, oxides, and hybrids. Unlike liquid electrolytes, SEs have no fluidic nature, which eliminates the internal short-circuit issues of bipolar batteries caused by electrolyte leakage, and require no sealing or packaging of individual cells. As shown in Figure 1b, the main features of the bipolar design may be summarized as follows:

- **Current collector**: A current collector acts as both positive and negative poles, which is thus called bipolar.
- **Electrode**: A PE and an NE are formed on each side of the BP.
- **Unit cell**: A unit cell does not require individual sealing and packaging.
- **Module**: A module is constructed by sequential stacking or lamination of the PE | BP | NE assemblies and electrolytes. That is, multiple unit cells are connected in series through BPs without external wiring.
- **Electron pathway in the module**: Electrodes of adjoining cells are on either side of the BP, and hence, an electron exiting the NE of one cell travels in the cross-plane direction of the BP to the PE during discharge.

Moreover, the key advantages of the bipolar SSLB over the monopolar design may include:

- **Simple configuration and easy voltage build-up**: Multiple cells are stacked (laminated) and connected in series using BPs in a simple manner, which simplifies the design and enables the facile construction of high-voltage modules.
- **High power density**: The BPs provide a short electronic path between the NE of one cell and the PE of the next, resulting in reduced resistive losses of the whole cell assembly (module), and promote uniform current/potential distributions over the entire surfaces of large-scale electrodes.
- **High energy density**: There is no need to package (house) individual cells and to electrically connect them using external wires or straps. As a result, the bipolar SSLB design can eliminate a large number of unnecessary, passive parts and components, reducing the volume and weight of the battery module. Furthermore, the material cost can be greatly reduced.

The potential benefits of the bipolar battery architecture were studied by Shen and Halpert, who determined the effects of various design parameters, including the thickness and porosity of the electrode, as well as the thickness and conductivity of the BPs, on the performance of bipolar 10 Ah, 50 V Li/TiS₂ batteries using a mathematical simulation. Their calculations indicated that the bipolar battery could exhibit ~40% higher energy and power densities compared to the
monopolar battery, which was mainly due to the volume and weight saving of the passive materials.

The technical challenges facing the development of the bipolar battery architecture include (i) the possibility of internal short-circuits between unit cells, (ii) the corrosion susceptibility of BPs, and (iii) the complicated fabrication processes for precise and reliable cell stacking. For successful construction and operation of bipolar SSLBs, technological advancement is required in the design of cell configurations as well as in the manufacturing process for precise stacking without any misalignment. To prevent the internal short-circuits caused by cell misalignment, it is common to apply an insulating layer on the periphery of the BP, where the active electrode material layer is not formed.\[41,43,44\] The materials used for BPs should possess (i) high electronic conductivity, (ii) negligible Li\(^{+}\) conductivity, (iii) high thermal conductivity, (iv) chemical/electrochemical stability under both reductive and oxidative conditions, (v) good adhesion with the electrodes, (vi) light weight, (vii) high mechanical strength, and (viii) processability (manufacturability) for mass production. In particular, one of critical issues of the bipolar SSLBs is the corrosion susceptibility of the BP exposed to large potential gradients, i.e., highly reductive (\(-0\) V vs. Li/Li\(^{+}\)) and highly oxidative (\(>4.0\) V vs. Li/Li\(^{+}\)) conditions on the NE and PE, respectively.\[45-48\] To circumvent this problem, multiple cells may be stacked in a "side-by-side" design in which only the edges of the BPs touch each other, thus leading to a reduced contact area.\[42,49\] However, this configuration is not considered "true"-bipolar, but rather "pseudo"-bipolar, which is beyond the scope of this review.

3. Key Technologies for Solid-State Lithium Batteries

For realization of SSLBs, it is of great importance to develop SEs with high Li\(^{+}\) conductivity and a wide electrochemical window, and to construct stable, conformal interfaces between the SE and active electrodes (i.e., interfacial engineering).\[39\] To help understand the current status of bipolar SSLBs discussed in Section 4, we briefly introduce the fundamental aspects and recent advances of various Li\(^{+}\)-conducting SE materials along with the interfacial engineering technologies capable of improving the electrochemical performance of SSLBs.

3.1. Li\(^{+}\)-Conducting Solid Electrolyte Materials

Based on their chemical constituents, Li\(^{+}\)-conducting SE materials may be classified into four major families: (i) polymer, (ii) sulfide, (iii) oxide, and (iv) hybrid.\[39\] Each SE material has distinctive features in terms of Li\(^{+}\) conductivity (Figure 2) and structural characteristics such as mechanical strength, and chemical/electrochemical/thermal stabilities.\[50-52\] Therefore, in addition to the Li\(^{+}\) conduction mechanisms, it is necessary to understand the composition-structure-property relationships of various SEs at the material level. This will help determine the pros and cons of SEs for specific target applications.
3.1.1. Polymer-Based Solid Electrolytes

Polymeric SEs, including Li salt-containing polyethylene oxide (PEO), polyphenylene oxide, polyacrylonitrile (PAN), and their derivatives, have been successfully implemented in SSLBs, owing to their elasticity and deformability.[12,56] In general, polymer SEs consist of Li salt, polymeric or inorganic backbones, and anion acceptors, and can be synthesized in various ways, e.g., by solution casting processes and hot-press processes.[57,58] PEO with a semi-crystalline polymer structure has been extensively investigated because it offers relatively high Li$^+$ conductivity among polymer SEs, which arises from the coupling effect between Li$^+$ and the ether oxygen atoms of the PEO matrix.[59–62] Li$^+$ transport can be promoted by the segmental motion of the PEO chain above the glass-transition temperature. The Li$^+$ conduction in PEO is higher in the amorphous phase than in the crystalline phase that hardly allows the long-range displacement of Li$^+$. Therefore, suppressing the formation of the crystalline phase, for example, by structural modification with plasticizers or nano-fillers[63–67] and the design of polymer blends and block co-polymers,[68–74] is a practical approach to improve Li$^+$ conductivity. Despite extensive efforts, PEO-based SEs usually exhibit low Li$^+$ conductivities in the range of 10$^{-8}$ to 10$^{-5}$ Scm$^{-1}$ at 25 °C, which makes them unsuitable for room-temperature battery operations.[75–79]

Another critical concern is the instability of polymeric Li$^+$ conductors at high potentials; thus, most of the experimental studies on the SSLBs with polymer SEs have been carried out using low-potential PEs, typically LiFePO$_4$.[80–83]

3.1.2. Sulfide-Based Solid Electrolytes

Sulfide-based SEs, including sulfide glasses, sulfide glass-ceramics, and crystalline sulfides, exhibit promising conducting properties, in some cases, with Li$^+$ conductivity exceeding 1.0 × 10$^{-2}$ Scm$^{-1}$ at 25 °C.[84] According to recent reports, the Li$_2$S–P$_2$S$_5$ glass ceramics with different precipitates such as Li$_2$PS$_5$, Li$_2$P$_2$S$_5$, and Li$_{2.5}$P$_{0.5}$S$_4$ showed Li$^+$ conductivities higher than 1.0 × 10$^{-2}$ Scm$^{-1}$ at 25 °C.[85–87] More recently, a Li$^+$ conductivity of 1.2 × 10$^{-2}$ Scm$^{-1}$ was reported on Li$_{10}$GeP$_2$S$_{12}$ (LGPS), belonging to the thio-Li superionic conductor (LISICON) family, by Kanno et al.[88] Argyrodites with the general formula of Li$_{x}$P$_{3}$S$_{8}$X$_{y}$ (0 ≤ x ≤ 1; X=Cl, Br, or I) are also viable candidates, owing to their acceptable Li$^+$ conductivity (~1.3 × 10$^{-3}$ Scm$^{-1}$) and lower material cost than other sulfide-based SEs.[89,90] In addition, these SEs exhibit a large electrochemical window (~5 V) and high flexibility in chemical compositions by elemental doping. However, the achievable Li$^+$ conductivity of argyrodites is strongly dependent on the synthesis process; thus, it is important to develop a scalable, reliable process for highly conductive argyrodite SEs.[91–96] Unfortunately, most of sulfide-based SEs suffer from poor chemical stability against moisture, accompanied by significant performance degradation and H$_2$S release in ambient environments.[97,98] More attention should be paid to enhance the hydrolysis stability of sulfides before the practical use of sulfide-based SEs in SSLBs.[84,87] As an example, Liang and co-workers designed As-substituted Li$_3$SnS$_4$ (Li$_{1-x}$As$_x$Sn$_{3.33}$S$_{4.68}$S$_4$) based on the rules of hard and soft acids and bases and demonstrated a Li$^+$ conductivity of ~1.4 × 10$^{-3}$ Scm$^{-1}$ at 25 °C without significant structural degradation even after exposure to moisture for 48 h (80% humidity).[99]

3.1.3. Oxide-Based Solid Electrolytes

During the last decade, Na superionic conductor (NASICON)-type Li$^+$ conductors have been widely explored as promising SE materials.[100,101] They have three-dimensional Li$^+$ conduction pathways that allow fast Li$^+$ conduction in the structure.[102] In particular, Li$_{1-x}$Al$_x$M$_2$PO$_4$ (M=Ti or Ge) exhibits high bulk conductivity (~1.0 × 10$^{-3}$ Scm$^{-1}$) at 25 °C with excellent stability against moisture.[103] Technical approaches aimed at maximizing the total Li$^+$ conductivity of these materials may be divided into two categories:[104–107] (i) chemical substitution with trivalent or pentavalent ions (e.g., Al$^{3+}$ or Nb$^{5+}$) for Ti$^{4+}$ to change the bottleneck sizes for Li$^+$ transport;[108] and (ii) incorporation of secondary phases (e.g., Bi$_2$O$_3$) in the fabrication step of SE sheets to tune the microstructure and thus to enhance boundary conductivity.[109,110] Both Li$_{1-x}$Al$_x$Ti$_x$PO$_4$ (LATP) and Li$_{1-x}$Al$_x$Ga$_x$PO$_4$ (LAGP) are, however, unstable in contact with Li metal due to the reduction of Ti$^{4+}$ and Ge$^{4+}$.

To overcome this problem, West et al. deposited a protective Li phosphorus oxyxynitride (LiPON) layer on the LATP surface.[111] Interestingly, the LiPON-protected LATP exhibited an expanded electrochemical window of 0–5.0 V vs Li/Li$^+$ without undesirable side reactions with Li.

Li$_{1.9}$La$_{2/3}$Ti$_{2/3}$O$_3$ (LLTO) is a representative Li$^+$ conductor with a perovskite structure.[112,113] Despite its bulk conductivity (~1.0 × 10$^{-3}$ Scm$^{-1}$), the achievable total Li$^+$ conductivity of LLTO is limited by large resistances at grain and domain boundaries.[50,116] Kwon et al. demonstrated that the microstructure and composition of the LLTO domain boundaries play a significant role in Li$^+$ conduction.[114] A Li$^+$ conductivity as high as 4.8 × 10$^{-4}$ Scm$^{-1}$ at 25 °C was achieved by the optimization of the domain size and the Li concentration at the domain boundaries. Similarly to the LATP case, the reduction of Ti$^{4+}$ in direct contact with Li hinders the practical application of LLTO in SSLBs with Li NEs and necessitates further research into the surface stabilization with protective layers.[117,118]

Unlike NASICON and perovskite families, garnet-type Li$^+$ conductors have high chemical stability against the reduction reactions that can occur when the conductor is in direct contact with Li metal, which made them attractive for use in SSLBs.[119] Murugan et al. reported the study on the synthesis of cubic-structured Li$_3$La$_2$Zr$_2$O$_7$ (LZO) showing a Li$^+$ conductivity of 3.0 × 10$^{-4}$ Scm$^{-1}$ with a low activation energy of 0.3 eV.[120] LZO has two different, tetragonal and cubic, polymorphs: the cubic phase exhibits a Li$^+$ conductivity that is higher by two orders of magnitude than that of the tetragonal phase.[100] The substitution of Te for Zr improved the Li$^+$ conductivity to a level of 1.0 × 10$^{-3}$ Scm$^{-1}$.[121] Similar conductivity enhancements have been made by the introduction of various elements: Al, Ga, Fe,
Nb, Ta, and Sb for Zr; and Ba, Ca, Sr for La.\[122-125\] Despite the promising conducting properties of LLZO and its compatibility with Li, the dendritic growth of Li has been known to proceed easily through voids and/or impurity phases present in polycrystalline LLZO, resulting in internal short-circuits,\[126,127\] which needs to be further addressed in subsequent researches.

### 3.1.4. Hybrid Solid Electrolytes

At the early stage of SE developments, hybrid SEs were regarded as a subset of polymer SEs in which electrochemically inert fillers (e.g., AlO\(_2\), SiO\(_2\), and TiO\(_2\) nanoparticles) were dispersed in a polymer matrix.\[126-130\] In recent years, however, the concept of hybrid SEs has been extended to any combination of polymers, sulfides, oxides, and ionic liquids (ILs), with the objective of achieving the desired characteristics of (i) high Li\(^+\) conductivity, (ii) wide electrochemical window, (iii) mechanical flexibility and scalability, and (iv) high mechanical and thermal stabilities.\[131-135\] In fact, the hybridization approach is a popular choice in the fabrication of bipolar SSLBs because it allows for the easy, large-scale construction and performance improvement of SSLBs, as discussed in Section 4. Recently, Zhang et al. reported a free-standing oxide-polymer hybrid of Li\(_{6.73}\)La\(_{1.75}\)Ta\(_{0.25}\)O\(_{2}\) and polypropylene carbonate (PC) with a high Li\(^+\) conductivity of 5.2 × 10\(^{-6}\) S cm\(^{-1}\) and a wide electrochemical window of 4.6 V.\[136\] A similar hybridization was performed using Li\(_{6.73}\)La\(_{1.75}\)Ta\(_{0.25}\)O\(_{2}\) and a modified polyvinylidene fluoride (PVDF) matrix, which resulted in a high Li\(^+\) conductivity of 5.0 × 10\(^{-4}\) S cm\(^{-1}\) at 25 °C.\[137\] Another potential approach is to make an oxide-IL hybrid comprising IL incorporated into a nanostructured inorganic matrix. For example, the encapsulation of hollow silica spheres with lithium bis(trifluoromethanesulfonil)imide (LiTFSI) and ethylmethylimidazolium-TFSI led to the Li\(^+\) conductivity exceeding 1.0 × 10\(^{-3}\) S cm\(^{-1}\) as well as high structural stability.\[138\] In parallel, Tan et al. demonstrated the synthesis of a hybrid SE based on porous SiO\(_2\) and 1-butyl-3-methylimidazolium-TFSI and reported a remarkable Li\(^+\) conductivity of 1.0 × 10\(^{-5}\) S cm\(^{-1}\).\[139\]

### 3.2. Strategies to Improve Interfacial Properties of Composite Electrodes

In addition to the development of highly conductive SEs, the biggest challenge for realizing SSLBs is to form stable, conformal interfaces that can facilitate Li\(^+\) transport between the SE and active electrode materials. There are two fundamental origins of interfacial problems in SSLBs.\[140\] First, the abrupt potential changes across the interface facilitate the side reactions between the SE and the active electrode material to achieve a thermodynamically stable state. Figure 3 compares electrochemical potential windows of various SEs, indicating that SEs have different compatibilities with active electrode materials.\[141\] Thus, it is important to consider electrochemical potential windows of SEs against active materials. A common approach to overcome the chemical/electrochemical instability is to apply protective layers between active materials and SEs, thereby suppressing undesirable side reactions, e.g., the reduction of Ti\(^{4+}\) in LATP or Ge\(^{4+}\) in LAGP. This approach is also effective in minimizing the decomposition of sulfide-based SEs in moisture.\[142,143\] For example, LiNbO\(_3\), LiNb\(_{0.5}\)Ta\(_{0.25}\)O\(_{2}\), Li\(_5\)Ti\(_2\)O\(_{12}\), Ta\(_2\)O\(_5\), Al\(_2\)O\(_3\), and LiPO\(_4\) have been explored as protective layers, and their positive roles in stabilizing the interfaces have been demonstrated.\[144,145\]

Second, the interfacial resistance arises from the poor solid-solid contact induced by the different mechanical properties of SEs and active materials. Noteworthy advances have been made with regard to improving the contact between the SE and active electrode materials, and some selected approaches are summarized in Figure 4.\[146-148\] To ensure conformal solid-solid contacts, SEs could be coated on the surface of active materials via a solution-processable technique prior to electrode fabrication (Figure 4a). A one-step process was also proposed for making sheet-type, thick electrodes, which involved the mixing of SE precursors (e.g., Li\(_2\)S and P\(_2\)S\(_5\)) with active materials using nitrile butadiene rubber and tetrahydro-
furan to make the SE-electrode slurry. In addition, SE precursors could be directly infiltrated into as-prepared porous electrode (Figure 4b). In practice, a cell assembled with SE-infiltrated LiCoO$_2$ and graphite electrodes exhibited high capacities of 141 and 364 mAh g$^{-1}$, respectively, at a current density of 0.1 C. Kim et al. proposed a rational design for a composite electrode in which the internal pores were completely filled with N-butyl-N-methylpyrrolidinium (Py14)-TFSI.\cite{146} Filling the pores with an IL was effective for increasing contact areas and building robust interfaces between active materials and SEs, resulting in the formation of continuous Li$^+$ conduction pathways in the composite electrode. The LiNi$_x$Co$_{1-x}$Mn$_2$O$_4$-LGPS composite electrode delivered a high discharge capacity of 168 mAh g$^{-1}$ at a 0.1 C-rate. However, further optimization of process variables is still required to improve the cycle performance and rate capabilities of porous electrodes filled with SEs. The impregnation of SEs into porous scaffolds would provide the design flexibility of the composite electrodes for SSLBs, as demonstrated using Li$_2$PS$_4$ and LGPS.\cite{149} Similarly, a PE-supported SE membrane was proposed by Chen et al.: an SE was directly casted onto the electrode to enhance the wetting properties and to reinforce the interfacial adhesion.\cite{150}

Li metal is considered to be an ultimate anode material for SSLBs with high energy density. However, the following technical issues remain critical: uncontrollable growth of Li dendrites during cycling and high resistance at the interface between the SE and Li metal.\cite{23,151,152,153} Various approaches have been recently developed to engineer or stabilize the SE/Li interfaces.\cite{126,153,154,162} For instance, Zhou et al. demonstrated that a polymer Li$^+$-conducting layer (cross-linked poly (ethylene glycol) methyl ether acrylate) coated on LATP could effectively suppress the Li dendrite formation, due to the uniform Li$^+$ transport at the interface and improved wetting in contact with Li.\cite{155} In addition, Han et al. reported that the atomic layer deposition of Al$_2$O$_3$ on the garnet-type Li$_2$La$_{2.25}$Ca$_{0.25}$Zr$_{1.25}$Nb$_{2.25}$O$_{12}$ significantly reduces the interfacial resistances of SE/Li.\cite{156} Based on the experimental and simulation results, they suggested that the ultrathin Al$_2$O$_3$ layer improves the wettability of SE/Li by tuning the surface energy of garnet-SE, thus enabling the conformal SE/Li interface. Similar approaches have been adopted to form conformal garnet-SE/Li interfaces via coating of various elements such as ZnO, Sn, Au, Al, and Ge.\cite{126,157–159,162} In the field of sulfide-based SEs, Tatsumisago’s group reported that thin In and Au layers formed on Li$_2$S–P$_2$S$_5$ SEs via vacuum evaporation undergo the alloying reaction with Li and hence enable the conformal contact between SEs and Li metal, resulting in facile Li$^+$ transport and enhanced rate performance.\cite{153,154} The protective layers such as Li$_2$S–P$_2$S$_5$–P$_2$O$_5$ and LiH$_2$PO$_4$ were also found to inhibit the reduction reaction of LGPS SEs in contact with Li metal.\cite{156,161}

### 3.3. Bipolar Plates

A bipolar SSLB construction requires an electrically conductive BP (current collector) that works as both an electrical interconnection and partition between the adjacent cells.\cite{30,34,36,43,44} The BP may be electrically insulated around its edges to prevent possible internal short-circuiting between cells.\cite{42–44} For successful battery operations, the BP must be (i) electronically conductive for current to flow between the cells without any significant ohmic losses, (ii) chemically and electrochemically stable under the operation conditions (Figure 5), and

![Figure 4](https://www.chemelectrochem.org/article-pdf/10.1002/celc.201900367/10.1002/celc.201900367-fig4)

**Figure 4.** Applications of solution-processable SEs for SSLB electrodes: a) SE-coated active materials and b) SE-infiltrated electrodes. Adapted from Ref. [146]. Copyright (2018) WILEY-VCH Verlag GmbH & Co.

![Figure 5](https://www.chemelectrochem.org/article-pdf/10.1002/celc.201900367/10.1002/celc.201900367-fig5)

**Figure 5.** Effective potential ranges of Al and Cu and schematic illustration of Cu/Al clad metal for BPs.
(iii) capable of maintaining good adhesion to the electrodes as well as high mechanical stability against any possible expansion and contraction of the cell during repeated charge-discharge cycling. An overcharge tolerance is also required because in the presence of any performance variations in the cells of a bipolar module, relatively poor-performing cells can have higher states of charge at a given time than the other cells. A metallic current collector in LIBs in contact with the electrodes and a reactive fluorine-based non-aqueous electrolyte is considerably prone to corrosion. The corroded current collector may cause uneven power delivery and/or to complete battery failure. Even though the corrosion phenomena in SSLBs are expected to be different from those in liquid electrolyte-based LIBs, the material requirements for BPs in SSLBs are more stringent than those for current collectors in monopolar LIBs. The BP is in direct contact with both NE and PE; it should therefore remain stable in a wide potential range and show simultaneous compatibility with the two electrodes (Figure 5). Various metals, alloys, metal oxides, and carbonaceous materials are potential candidates for BPs. In terms of electronic conductivity, chemical/electrochemical stabilities, mechanical properties, cost, and abundance, however, the choice is limited to the materials implemented in LIBs, e.g., Al, Cu, Ni, and alloys, including stainless steel and Inconel.

Al is an inexpensive, highly conductive material that is readily available in the form of a thin foil with high purity, and it is most widely utilized as a current collector for PEs. Al is usually covered with thin protective films and hence exhibits high corrosion resistance at high potentials (~5.0 V vs. Li/Li+) in various electrolyte systems. Yet, the electrochemical alloying reaction between Al and Li can easily occur at <0.5 V vs. Li/Li+: Al has been only used in the BPs of SSLBs assembled with high-potential NEs, e.g., LiTi2O3 (~1.5 V vs. Li/ Li+) and 2,6-naphthalene dicarboxylate dilithium (~0.8 V vs. Li/ Li+). Although Ni is less suitable for high-potential PEs compared to Al, it is known to exhibit acceptable chemical stability in certain electrolytes (e.g., LiAlCl4 in SO2), Ni has been used as BPs for the Li NE and Ti5O12 PE and more recently, Nam et al. demonstrated the chemical stability of Ni with a LiPS4 SE and constructed a free-standing, stackable, bipolar SSLB using a Ni-coated non-woven scaffold BP. Stainless steels (referred to as SUS) are Fe-based alloys and are widely used for the components of coin-type cells. They have a high contact resistance but high chemical stability, due to the presence of passivation layers on their surfaces. Coin-type bipolar SSLBs with the Li NE and low-potential PEs (e.g., LiFePO4 and sulfur) have been constructed and demonstrated using stainless steel BPs.

Clad metal refers to a composite of two or more dissimilar metals bonded together and is considered a potential candidate for BPs. Clad metal implements the combined advantages of different metals; thus, the resulting metal can be engineered to fulfill the requirements for BPs, which is impossible using any single metal. For example, a Cu/Ni/Cu clad foil, in which a high-strength Ni alloy core was sandwiched between low-resistance Cu layers, was used as a current collector for nano-Si and SiO NEs with large volume variations. The clad foil led to more stable cycling performance compared to a conventional Cu foil, due to its combined advantages of high mechanical strength and low resistance. In the field of bipolar SSLBs, Shin et al. first demonstrated that an Al/Cu (thickness = 10 μm/10 μm) clad foil (inset in Figure 5) can be successfully utilized as BPs for the Li NE and the high-potential PE (LiNiO2CoO2MnO2O2,6). Given that the BP may make a significant contribution to the total weight and volume of the SSLB, thin-film deposition processes, such as electro/electroless plating, sputtering, and chemical vapor deposition, may be employed to fabricate bi-layered BPs with reduced thicknesses. Moreover, the use of light, thin, conductive materials, such as carbon (carbon nanofibers/tubes, graphite sheets, graphene papers, etc.) and conducting polymers (e.g., polypyrrole and poly(3,4-ethylenedioxythiophene)), can be considered to be alternatives for metallic BPs.

4. Fabrication and Electrochemical Properties of Bipolar-Type Solid-State Lithium Batteries

Although the non-fluidic properties of SEs enable a bipolar design by preventing the flow of ions between adjacent cells, the stacking of multiple cells within a single package has been found to be very challenging, and only a few reports on bipolar SSLBs, mostly proof-of-concept studies, have been published thus far. The stacking strategies for bipolar SSLBs reported in the literature may be broadly classified into (i) the lamination of free-standing SE sheets and (ii) the printing of SE slurries. The former involves the sequential lamination of free-standing SE sheets and electrode-coated BPs, both of which have sufficient mechanical stability. On the other hand, the latter employs layer-by-layer printing (coating) of SE slurries (inks) on the electrode-coated BPs serving as a mechanical support. Then, another unit cell is stacked on top of the as-printed one. In this section, we review the recent progress in the development of bipolar SSLBs, focusing on SEs, bipolar architectures, and electrochemical performance.

4.1. Bipolar-Type Solid-State Li Batteries Fabricated via Lamination of Free-Standing Solid Electrolytes

Among various SE materials, oxide-based SEs with garnet-, perovskite-, and NASICON-type structures have shown acceptable chemical/structural stabilities in dry and/or humid atmospheres and a wide operating temperature range. However, high-temperature sintering is essential to achieve low-resistance SE sheets with intimate contact between SE particles. Moreover, any poor contact between the SE sheet and the electrode leads to a high cell resistance. Thus, various engineering approaches have been explored to minimize interfacial resistances, for example, soft interlayer (buffer) and advanced co-sintering techniques to produce monolithic bi-layered electrode-SE structures. Zhang et al. reported a bipolar SSLB...
architecture with a sintered LAGP SE pellet. Because of the electrochemical instability of LAGP with metallic Li, an interlayer comprising PEO-Li$_2$S-P$_2$S$_5$-P$_2$O$_5$ was spin-coated on the NE side of the LAGP pellet (Figure 6a). Moreover, PEO-LiClO$_4$ was incorporated into the porous PE to form three-dimensional Li$^+$ conduction pathways in the composite electrode structure. A two-cell bipolar stack, [Al|(+)-LiFePO$_4$|SE|Li (−)+SUS (BP)|(+)-LiFePO$_4$|SE|Li (−)+Cu], was fabricated and sealed by an Al pouch, followed by isostatic cold-pressing. The bipolar SSLB exhibited an open circuit voltage (OCV) of 6.63 V, which was almost two times that of the unit cell, and it delivered a discharge capacity of 145 mAh g$^{-1}$ at 60°C. A series of destructive safety tests (cutting, burning in fire, and nail penetration) (Figure 6b) indicated an outstanding safety feature of the bipolar SSLB.

In spite of their chemical/structural instabilities against moisture, sulfide-based SEs attracted much attention owing to their advantages over oxide-based SEs including high Li$^+$ conductivity, in some cases even comparable to that of the liquid electrolyte, and deformability under pressure. A simple cold-pressing process can produce intimate contact between rigid electrode materials and ductile SEs, leading to the formation of densely packed interfaces. In a free-standing, sulfide-based SE sheet reinforced with a nonwoven polymer scaffold, a thin Li$_2$PS$_4$ SE sheet (thickness ~70 μm) was prepared by coating of the SE slurry onto a Ni foil and subsequent cold-pressing onto a poly(paraphenylene terephthalamide (PPTA) substrate that served as a mechanically compliant scaffold (Figure 6c). While the resulting thin SE sheet exhibited lower conductivity (2.0×10$^{-4}$ S cm$^{-1}$) at 30°C than that (7.3×10$^{-3}$ S cm$^{-1}$) of the thick (~700 μm) SE sheet, it exhibited a three-fold improvement in conductance (~3.7×10$^{-2}$ S). The free-standing, flexible feature of the SE sheet enabled easy stacking of unit cells. As a proof-of-concept study, a bipolar SSLB, [Ni–PPTA|(+)-Li$_2$Ti$_5$O$_{12}$|SE|LiCoO$_2$ (+)|Ni–PPTA (BP)|(+)-Li$_2$Ti$_5$O$_{12}$|SE|LiCoO$_2$ (+)|Ni–PPTA], was fabricated by stacking the two unit cells (Figure 6d). A Ni-coated nonwoven PPTA scaffold was employed as a flexible current collector and BP. According to the authors’ claim, the advanced designs of SEs and SSLBs with the PPTA scaffold offer the possibility to improve the energy density in comparison with that of the SSLB without the PPTA scaffold.

Wei et al. reported a bipolar SSLB with a polyethylene glycol diacrylate (PEGDA)-based co-polymer SE fabricated via a solvent-free UV-curing process. To prepare the SE, the photo-initiator and cross-linker were added into a mixed
solution of LiTFSI and PEGDA1000, followed by photo-polymerization via UV exposure (Figure 7a). To obtain a PE in which LiFePO$_4$ was fully integrated with the SE, the SE precursor was directly coated onto the as-formed LiFePO$_4$ electrode layer by tape-casting combined with UV-curing. A monopolar cell with a size of 5 cm×8 cm delivered an initial discharge capacity of ~135 mAh g$^{-1}$ at 60°C and exhibited a capacity retention of ~80% after 200 cycles. A two-cell bipolar SSLB, [SUS (−) Li | LiFePO$_4$ (+) Al | SUS (BP) (−) Li | SE | LiFePO$_4$ (+) Al], showed an OCV of 6.33 V and an initial discharge capacity of 138 mAh g$^{-1}$ (Figure 7b), proving the feasibility of the PEGDA-based SE and the integrated LiFePO$_4$-SE electrode. Various safety tests indicated that the fabricated bipolar SSLB has a high abuse tolerance. Shin et al. reported the design and construction of a multi-layered, bipolar-type SSLB based on a hybrid SE (Li$_{0.29}$La$_{0.57}$TiO$_3$–PEO) [170]. A flexible and free-standing SE sheet with a thickness of 30 μm was prepared by a simple casting method, and a bipolar SSLB consisting of the three cells, [Al (−) LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ | SE | Li (−) Cu/Al (BP) ... | Li (−) Cu], was constructed using Al/Cu-cladded bipolar plates (Figure 7c). The bipolar SSLB successfully operated in the voltage range of 9.2–12.0 V without any short-circuit or current leakage, and it showed a specific capacity of 125 mAh g$^{-1}$ at 60°C and stable cycling performance with a capacity retention of 83% over 50 cycles (Figure 7d), which suggest that the hybrid SE provides a promising approach to the fabrication of bipolar SSLBs with high energy density, reliability, and safety.

Highly conductive quasi (pseudo)-SEs containing immobilized liquids in solids can reduce electrolyte resistances and allow for the formation of conformal contact between the SE and electrodes, owing to their flexibility and softness [40,179]. The quasi-SE-based batteries may not be regarded as a "true" solid-state-system; however, they can still provide benefits in terms of safety over conventional LIBs either by reducing the amount of flammable organic solvents or by replacing flammable solvents with non-flammable ILs. Compared with true-SEs, moreover, quasi-SEs are more scalable for battery manufacturing. Recently, several classes of quasi-SEs have been proposed, which consist of oxide nanoparticles and Li$^+$-conducting liquids such as ILs and ether-type solvents capable of forming complex
with Li salts.\textsuperscript{[37,166,181,182]} These electrolytes with optimized compositions can be prepared in a quasi-solid-state via solidification of ILs resulting from the strong interaction with oxide nanoparticles, and hence they have a solid-like high mechanical strength and liquid-like high Li\textsuperscript{+} conductivity.

Gambe et al. first reported bipolar SSLBs with a quasi-SE composed of a Li-glyme complex and oxide nanoparticles (SiO\textsubscript{2}, CeO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and ZrO\textsubscript{2}).\textsuperscript{[37,166]} The quasi-SE powder was obtained by mixing a lithium bis(trifluoromethanesulfonyl)amide (LiTFSI)-tetraethylene glycol dimethyl ether (TEGDME) solution with fumed silica and then used to prepare a free-standing electrolyte sheet with a thickness of 200 \(\mu\)m with the help of polytetrafluoroethylene binder. A unit cell was fabricated via lamination of the LiFePO\textsubscript{4} composite (PE), quasi-SE sheet, and Li (NE), and coin-type bipolar SSLBs were constructed by stacking the cells with SUS BPs (Figure 8a). The two- and three-cell stacks exhibited plateau voltages of 6.8 and 10.2 V, respectively, and delivered capacities as high as \(\sim156\) mAhg\textsuperscript{-1} at 0.1 C-rate, translating to PE utilizations of \(\sim91\%\) (Figure 8b). Furthermore, the bipolar SSLBs showed high Coulombic efficiency (\(\sim99\%\)) and good cycling stability (91\% after 200 cycles), which were mainly attributed to the formation of Li\textsuperscript{+}-conductive interfaces between LiFePO\textsubscript{4} and quasi-SE in the composite PE.

In addition, an LLZO-IL hybrid was proposed as a quasi-SE for Swagelok-type bipolar batteries.\textsuperscript{[175]} For the preparation of a hybrid SE, \(\text{Li}_{7}\text{La}_{3}\text{Zr}_{2}\text{O}_{12}\) particles (80 wt\%) were uniformly wetted by Py14TFSI (19 wt\%) and LiTFSI (1 wt\%), which resulted in a reduced interfacial resistance between ceramic LLZO and LiCoO\textsubscript{2} particles in the composite PE (Figure 8c). After that, the SE mixture was pelletized for the assembly of the bipolar battery, \([\text{SUS}] (-) \text{Li} \text{ quasi-SE} \text{ LiCoO}_2 (+) \text{Al} \text{ SUS (BP)} (-) \text{Li} \text{ quasi-SE} \text{ LiCoO}_2 (+) \text{Al} \text{ SUS}\). The quasi-SE exhibited a Li\textsuperscript{+} conductivity of \(4.0\times10^{-3}\) Scm\textsuperscript{-1}, enhanced electrochemical stability (~5.5 V vs. Li/Li\textsuperscript{+}), and thermal stability over 200 \(\degree\)C due to the presence of inorganic LLZO particles. The two-cell bipolar battery delivered an initial discharge capacity of 113 mAhg\textsuperscript{-1} with an average working voltage of 8 V (Figure 8d) at 25 \(\degree\)C, which proved the stable operation with the LLZO-IL-based electrolyte.

### 4.2. Bipolar-Type Solid-State Li Batteries Fabricated via Printing of Solid Electrolytes

Printing (coating) processes of slurries (inks) are simple, low-cost, and easily scalable. SSLBs can be fabricated via the printing of SE and/or active material slurries with optimized rheological properties onto the supporting components (e.g., BP). Since the printable slurries can easily conform to the substrate shape, it is possible to realize novel battery
architectures with various shapes, form factors, and functionalities.

Yoshima et al. demonstrated a 12 V-class bipolar SSLB assembled with a thin hybrid SE composed of LLZO and GP, PAN-based gel polymer (GP). \cite{38} The LiMn$_{0.8}$Fe$_{0.2}$PO$_4$-PAN-GP (PE) and Li$_2$Ti$_3$O$_7$-PAN-GP (NE) composites were formed via slurry coating on either side of an Al BP. A thin hybrid SE layer of ~3 µm thickness was then fabricated by spray-coating a slurry of LLZO (94 wt%), PVDF binder (2 wt%), and PAN-GP (4 wt%) on the PE and NE (Figure 9a). The Li$^+$ conductivity of the hybrid SE was determined to be ~6.0 × 10$^{-3}$ cm$^2$ s$^{-1}$ at 25°C, which was comparable to those of liquid electrolytes. The fast Li$^+$ mobility was largely traced back to the increased concentration of Li$^+$ on the surface of LLZO particles. A pouch-type bipolar SSLB (12 V and 20 mA/h) was designed and constructed by stacking five bipolar, 6.8 cm × 8.8 cm electrodes. The resulting bipolar SSLB showed a Coulombic efficiency of > 99.8% and stable cycle performance of 85% over 200 cycles. It also exhibited capacity retentions of ~100% and ~50% at 80°C and -40°C, respectively, with respect to the nominal capacity at 25°C, which demonstrated successful operation in a wide temperature range (Figure 9b). More recently, the same research group reported an enlarged pouch-type bipolar SSLB made using a different PE (LiMn$_{0.8}$Fe$_{0.2}$Mg$_{0.2}$PO$_4$) with a size of 7 cm × 11 cm, and the further improved electrochemical performances in terms of nominal capacity, energy density, power density and cyclability (102 mAh, 90 Wh kg$^{-1}$, 1500 W kg$^{-1}$ and 82% after 600 cycles (2°C) at 25°C)\cite{38}. The excellent electrochemical performance could be explained by the conformal wetting of GP on LLZO and high Li$^+$ conductance of the extremely thin hybrid SE (Figure 9c).

The printed SSLBs with a bipolar configuration for integrated energy generation and storage systems were reported by Um et al.\cite{177} A bipolar SSLB with quasi-SE was directly fabricated on the Al electrode of the Si photovoltaics module via repeated stencil printing and UV-curing, as illustrated in Figure 10a. The SE ink for printing was composed of an ethoxylated trimethylolpropane triacrylate (ETPTA) monomer with a photo-initiator, 1 M LiPF$_6$ in ethylene carbonate (EC)/PC, and Al$_2$O$_3$ nanoparticles. The same monomer and liquid electrolyte were also added into the PE (LiCoO$_2$) and NE (Li$_2$Ti$_3$O$_7$) inks for the solidification of the electrodes by UV irradiation, thus forming the intimate contact between the active material and the quasi-SE. The bipolar SSLB fabricated on the photovoltaic (PV) module delivered an areal capacity of 0.5 mAh cm$^{-2}$ and exhibited almost the same charge-discharge behavior with the monopolar cell, except for a two-fold increase in voltage (Figure 10b), as well as a stable cycle performance (~95% capacity retention over 200 cycles). In particular, the monolithically integrated photovoltaic/SSLB device displayed a rapid photo-charging capability within 2 min and a high discharge capability (~28 C-rate) under the photo-charge/discharge protocol. More recently, the same research group reported the fabrication process of bipolar SSLBs with mechanical flexibility and shape versatility based on a UV-assisted multistage printing technique.\cite{163} The unit cell was fabricated by the sequential printing of NE, SE, and PE inks on the Al current collector followed by UV-induced solidification, and then, the same printing process was repeatedly conducted to fabricate the multi-layered bipolar SSLB battery without delamination and cracking. The hybrid-type quasi-SE was made of Al$_2$O$_3$ nanoparticles and 1 M LiBF$_4$ in sebacanitrile/ETPTA/poly(vinylidene-fluoride-co-hexafluoro-propylene) (PVDF-co-HFP). The authors...
suggested that the optimization and tuning of rheological properties of the electrode and electrolyte inks play a significant role in improving the printing processability and successful fabrication of seamlessly integrated bipolar SSLBs.

The printing process allows the design of novel bipolar architectures with an in-plane configuration as well as vertically stacked designs. Zheng et al. reported the design and on-chip construction of a planar integrated bipolar SSLB using a mask-assisted printing procedure. The electrode ink was prepared by mixing LiFePO$_4$ (PE) or Li$_4$Ti$_5$O$_{12}$ (NE) powders with exfoliated graphene (EG, conducting agent) in ethanol. As schematically illustrated in Figure 10c, the EG nanosheet of interdigitated patterns was printed on a nylon membrane substrate first and utilized as the conductive two-dimensional current collector. The PE and NE inks were sequentially printed on the top EG layers of each side, and then the quasi-SE (LiTFSI-P14TFSI-PVDF-co-HFP) was drop-casted onto the surface of the electrode films and solidified under vacuum. The integrated SSLB exhibited a volumetric energy density of 146 mWh cm$^{-3}$ and excellent cyclability over ~3,300 cycles as well as flexibility under various bending conditions. More importantly, the high-voltage and high-capacity planar-integrated SSLB can be easily fabricated by connecting multiple printed cell arrays in series and in parallel, respectively. In series connection, the voltage increased linearly from 1.8 V for the unit cell to 5.4 V for the three cells.

5. Summary and Outlook

In this review, we have summarized the basic aspects of the bipolar battery architecture with its advantages and the technical issues that still need to be overcome, followed by the recent progress in the design and fabrication of bipolar SSLBs. Table 1 summarizes the selected recent reports on bipolar SSLBs focusing on their architectures and electrochemical performance. The SSLBs provide a fundamental solution that can resolve the safety issues of the current LIBs. Furthermore, the bipolar SSLB design in which unit cells are series-connected via BPs within a single module has the potential to increase the energy density of the large-scale battery system and can allow current to uniformly flow through the entire surface area of the electrodes, thus leading to higher power capability.

The development activities on bipolar SSLBs are still at the early stage, and many technical challenges remain unsolved at
### Table 1. Architectures and electrochemical performance of bipolar SSLBs in the literature.

<table>
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<tr>
<td>Polymer</td>
<td>PEGDA-PEGDMA25-LITFSI</td>
<td>~20</td>
<td>LiFePO₄ (70)</td>
<td>N/A</td>
<td>2.5/6–7.6</td>
<td>~136 mAh g⁻¹</td>
<td>(0.5 C-rate)</td>
<td>~76 (40)</td>
<td>60</td>
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<td>Polymer</td>
<td>PEGDA-LITFSI</td>
<td>~130</td>
<td>LiFePO₄ (70)</td>
<td>40</td>
<td>2.5/5–7.5</td>
<td>~138 mAh g⁻¹</td>
<td>(0.05 C-rate)</td>
<td>N/A</td>
<td>174</td>
</tr>
<tr>
<td>Polymer</td>
<td>PEOLITFSI + PVDF + Al₂O₃</td>
<td>~9.5</td>
<td>LiCoO₂ (80)</td>
<td>N/A</td>
<td>3/9.12</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>150</td>
</tr>
<tr>
<td>Sulfide</td>
<td>Li₃PS₁</td>
<td>~70</td>
<td>LiCoO₂ (70)</td>
<td>N/A</td>
<td>2/2.0–6.4</td>
<td>~83 mAh g⁻¹</td>
<td>(14 mA g⁻¹)</td>
<td>N/A</td>
<td>149</td>
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<td>Oxide</td>
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<td>LiFePO₄ (N/A)</td>
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<td>(0.1 C-rate)</td>
<td>~100 (10)</td>
<td>173</td>
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<td>Hybrid</td>
<td>Lithiated Nafton + sulfonanodiglyme</td>
<td>16</td>
<td>S–C (20) [84]</td>
<td>N/A</td>
<td>3/2.3–5.6</td>
<td>~940 mAh g⁻¹</td>
<td>(167.5 mA g⁻¹)</td>
<td>~75 (80)</td>
<td>167</td>
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<tr>
<td>Hybrid</td>
<td>PSIDEME-TFSI-LITFSI</td>
<td>80</td>
<td>LiMnO₂ (84)</td>
<td>8</td>
<td>2/3.0–6.0</td>
<td>~40 mAh g⁻¹</td>
<td>(2.3 mAh)</td>
<td>N/A</td>
<td>25</td>
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<tr>
<td>Hybrid</td>
<td>PVDF-co-HFP + LiPF₆-EC-DEC25-EMC25</td>
<td>N/A</td>
<td>LiNi₀.8Mn₀.2O₄ (85)</td>
<td>N/A</td>
<td>2/5.4–8.4</td>
<td>~100 mAh g⁻¹</td>
<td>(0.02 C-rate)</td>
<td>~100 (100)</td>
<td>35</td>
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<td>Hybrid</td>
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<td>LiCoO₁ (60)</td>
<td>9</td>
<td>2/3.0–5.4</td>
<td>~115 mAh g⁻¹</td>
<td>(0.1 C)</td>
<td>~90 (50)</td>
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<td>ETPTA + PVDF-co-HFP + Al₂O₃ + LiBF₆-2MN</td>
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<td>LiCoO₁ (55)</td>
<td>N/A</td>
<td>3/4.5–8.1</td>
<td>~63 mAh cm⁻³</td>
<td>N/A</td>
<td>N/A</td>
<td>25</td>
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<tr>
<td>Hybrid</td>
<td>PVDF-co-HFP + LiTFSI</td>
<td>N/A</td>
<td>LiFePO₄ (80)</td>
<td>~1.5</td>
<td>3/3.0–7.2</td>
<td>~100 mAh g⁻¹</td>
<td>(0.02 C-rate)</td>
<td>~100 (100)</td>
<td>35</td>
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<tr>
<td>Hybrid</td>
<td>LiTFSASEGDME + Al₂O₃</td>
<td>~200</td>
<td>LiFePO₄ (34)</td>
<td>~0.39</td>
<td>2/5.0–8.0</td>
<td>~100 mAh g⁻¹</td>
<td>(0.02 C-rate)</td>
<td>~166 (100)</td>
<td>35</td>
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<td>LiFePO₄ (34)</td>
<td>~0.13</td>
<td>3/7.0–12.0</td>
<td>~156 mAh g⁻¹</td>
<td>(0.1 C-rate)</td>
<td>~98 (100)</td>
<td>37</td>
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<td>Hybrid</td>
<td>LLTO + PEO-LIClO₄</td>
<td>30</td>
<td>LiNi₀.8Co₀.2Mn₀.2O₄ (70)</td>
<td>25</td>
<td>3/9.2–12.0</td>
<td>~125 mAh g⁻¹ (4–4 mA)</td>
<td>(30 mA g⁻¹)</td>
<td>83 (50)</td>
<td>170</td>
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<tr>
<td>Hybrid</td>
<td>LLZO + Py14TFS-LITFSI</td>
<td>~150</td>
<td>LiCoO₁ (80)</td>
<td>N/A</td>
<td>2/6.0–8.4</td>
<td>~113 mAh g⁻¹</td>
<td>(0.1 C-rate)</td>
<td>~83 (10)</td>
<td>175</td>
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<tr>
<td>Hybrid</td>
<td>LLZO + PAN + LiPF₆-PC-DEC</td>
<td>~3</td>
<td>LiNi₀.8Fe₀.2PO₄ (88)</td>
<td>~60</td>
<td>5/7.5–13.5</td>
<td>~0.3 mAh cm⁻² (19 mA)</td>
<td>(2 C-rate)</td>
<td>85 (200)</td>
<td>38</td>
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<tr>
<td>Hybrid</td>
<td>LLZO + PAN + LiPF₆-PC-DEC</td>
<td>3–8</td>
<td>LiMn₀.8Fe₀.2Mg₀.2PO₄ (89)</td>
<td>~77</td>
<td>5/7.5–13.5</td>
<td>~1.3 mAh cm⁻² (102 mA)</td>
<td>(0.2 C-rate)</td>
<td>82 (600)</td>
<td>176</td>
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</tbody>
</table>

[a] The number in parentheses represents the mass fraction (wt%) of the active material. [b] Poly(ethylene glycol) methyl ether methacrylate. [c] Polymerized silica particle. [d] N, N-diethyl-N-(2-methoxyethyl)-N-methylammonium. [e] Diethyl carbonate. [f] Ethyl methyl carbonate. [g] Sebacnitrile.
total capacity to decrease during continuous operation. The performance variation of the unit cells in a bipolar module should be minimized to achieve long cycle life.

There is no doubt that bipolar SSLBs will play a critical role in the development of large-scale energy storage systems. The selected exemplary studies on the design and construction of bipolar SSLBs presented in this review will provide researchers with useful hints for developing highly reliable and high-performance SSLBs in the future.

**Abbreviations**

BP  
biopolymer plate

EC  
ethylene carbonate

EDS  
energy-dispersive X-ray spectroscopy

EG  
exfoliated graphene

ETPTA  
ethoxytetramethylenepropylene triacylate

EV  
electric vehicle

HFP  
hexafluoro-propylene

IL  
ionic liquid

LAGP  
Li1.3Al0.7Ge0.1P1.13(PO4)1.26

LATP  
Li1.3Al0.7Ti1.2P1.13(PO4)1.26

LGPS  
Li10GeP2S12

LIB  
lithium-ion battery

LIPON  
lithium phosphorus oxyinitride

LISICON  
Li superionic conductor

LLTO  
Li1.3La2/3TiO3

LLZO  
Li1/3La2/3Zr1/3O2

MP  
Monopolar plate

NASICON  
Na superionic conductor

NE  
negative electrode

OCV  
open circuit voltage

PAN  
polyacrylonitrile

PC  
polypropylene carbonate

PE  
positive electrode

PEGDA  
 polyethylene glycol diacrylate

PEO  
polyethylene oxide

PPTA  
 poly(paraphenylene terephthalamide)

PV  
photovoltaic

PVDF  
 polyvinylidene fluoride

SE  
 solid electrolyte

SEM  
 scanning electron microscopy

SSLB  
 solid-state lithium battery

TEGDME  
 tetraethylenglycol dimethyl ether

TFSA  
 bis(trifluoromethanesulfonyl)amide

TFSI  
 bis(trifluoromethanesulfonyl)imide

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** bipolar design · electrochemistry · interfaces · solid electrolytes · solid-state lithium batteries
