Order-structured solid-state electrolytes

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Abstract
Solid-state electrolytes (SSEs) are recognized as attractive candidates to realize safe and high-energy-density lithium metal batteries (LMBs). However, the practical application of SSEs still faces challenges such as insufficient room-temperature ionic conductivity, unsatisfactory mechanical properties, and large internal resistance. Extensive research efforts have been made to explore new electrochemistry and technologies to address those challenges. Among them, the construction of order-structured SSEs has emerged as a promising strategy. The anisotropic behavior induced by the orientation offers SSEs with desired properties targeting specific functions, and therefore the rational design of the order-structured SSE provides an alternative solution to achieve an ideal SSE. This review discusses the structure-property correlation of SSEs, and then summarizes the design strategies to construct order-structured SSEs. Finally, the current challenges and possible future research directions for order-structured SSEs for scalable high-energy-density LMBs are presented.

KEYWORDS
alignment, ordered structure, lithium batteries, solid-state electrolytes

1 | INTRODUCTION

Rechargeable batteries are a key technology accelerating the shift toward a more sustainable and cleaner economy.1 The successful transition to a carbon-neutral society requires batteries with performance beyond their current capabilities.2 As commercial lithium-ion batteries with graphite anodes and intercalation cathodes are approaching their theoretical capacity limits, extensive efforts have been made to explore novel battery electrochemistry with higher specific capacities.3–4 Lithium (Li) metal anode with the highest specific capacity (3862 mAh g⁻¹) and the lowest redox potential (−3.04 V vs. standard hydrogen electrode) has been considered the ultimate choice for anode material.5–7 However, the side reactions between organic liquid electrolytes and Li metal anode cause uncontrollable Li dendrite growth, which leads to potential safety concerns for commercialization.8–10 Replacing the flammable liquid electrolytes with solid-state electrolytes (SSEs) is an effective way to address the safety challenges before the widespread implementation of Li metal batteries.11–15

SSEs avoid the possibility of electrolyte leakage and explosion caused by liquid organic electrolytes and are expected to suppress Li dendrite growth due to its high mechanical strength.16–19 The ideal SSE should
simultaneously have a high room temperature (RT) ionic conductivity for effective ion transport, mechanical robustness to prevent internal short circuits, and interfacial stability with electrodes to reduce internal resistance.\textsuperscript{20–22} SSEs can be generally categorized into solid polymer electrolytes (SPEs) and inorganic solid electrolytes (ISEs). SPE consists of Li salt dissolved in a polymer matrix, where ion transports through the relaxation and rearrangement of polymer chains. ISE mainly includes oxides and sulfides, and ion conduction is achieved by ion hopping through vacancies or interstitials. SPEs usually exhibit elasticity and close interfacial contact with electrodes, but insufficient RT ionic conductivity and inferior mechanical strength, whereas ISEs are the opposite. Combining SPEs with ISEs to form composite polymer electrolytes (CPEs) has been committed to taking advantage of the individual SSEs and simultaneously improving the overall performance of solid-state batteries.

Even in CPEs, RT ionic conductivity still remains a bottleneck, one to two orders of magnitude lower than the conventional liquid electrolyte ($10^{-3}$ S cm$^{-1}$). Extensive research efforts have been made to explore new electrochemistry to promote fast ion conduction. Besides the intrinsic ionic conductivity of the electrolyte components, the structure of the SSE has been recently recognized to play a crucial role in the ion transport kinetics of SSEs.\textsuperscript{23–24} In CPEs, fast ion transport is realized at the polymer/inorganic filler interphases and/or directly through the inorganic ion conductors.\textsuperscript{25–26} Conventionally, inorganic particles are randomly distributed in the polymer matrix, and ion transport may be hindered by the polymer region with low ionic conductivity. An effective design strategy to address this issue is to construct ordered pathways parallel to the ion transport direction, so that continuous and direct ion conduction in the electrolyte can be achieved. CPE composed of inorganic arrays with vertically aligned structures is reported to exhibit higher ionic conductivity compared to those with random structures.\textsuperscript{27–28} On the other hand, the mechanical properties of SSEs are equally important because they are related to the cycling stability and safety of solid-state batteries. SSEs need to be mechanically robust to prevent cell failure and internal short circuits. Meanwhile, SSE as an inactive material should be as thin as possible to maximize the attainable energy/power density on the cell level.\textsuperscript{29–30} However, the mechanical properties of SSEs would be a big issue for thin SSEs, raising concerns about battery safety and performance. In this aspect, research shows that SSEs with layered structures can strengthen the membrane in the lateral direction, providing the possibility to reduce the thickness of SSEs to <25 $\mu$m target. In particular, the nacre-mimetic structure with layered inorganic pallets connected by organic polymers enables dissipation of the mechanical shock energy by interfacial sliding and plastic deformation, which provides an enhanced toughening effect.\textsuperscript{31–32}

Order-structured SSE refers to the SSE with vertically or/and horizontally oriented channels. The anisotropic behavior induced by the orientation offers SSEs with desired properties targeting specific functions, and the rational design of the order-structured SSE provides an alternative solution to achieve an ideal SSE (Figure 1). This review first reveals the correlation between the properties and structures of SSEs and then summarizes the design strategies to construct order-structured SSEs. Finally, the current challenges and possible future research directions for order-structured SSEs are discussed based on our understanding.

2 | VERTICALLY-ORDERED SSEs

In CPE, poorly ion-conductive materials as passive fillers are introduced to the polymer matrix to reduce polymer crystallinity and increase the portion of the amorphous phase, leading to fast polymer segmental dynamics at the polymer/filler interphases.\textsuperscript{33} The surface groups of the passive filler can also act as Lewis acid centers and interact with polymer chains/Li salts, which promotes Li-ion dissolution and increases free Li-ion concentration.\textsuperscript{34–35} Unlike passive fillers, active ceramic fillers exhibit high intrinsic ionic conductivity. At a low active filler loading, ions mainly transport along the polymer/ceramic interphases.\textsuperscript{36} Ceramic active fillers construct ion hopping channels on their surfaces with low energy barriers, resulting in a significant enhancement in ion conductivity at the interphase compared to the bulk polymer electrolyte. With the addition of more active fillers in the polymer matrix, the directly-contacted fillers construct continuous transport channels and ions will conduct directly through the inorganic conductors.\textsuperscript{37–38} In CPEs with either passive or active fillers, ion conduction is highly correlated with the structure of the electrolyte, especially how fillers are distributed and oriented inside the polymer matrix. Constructing continuously aligned polymer/filler interphases or active filler arrays with fast ion transport pathways would greatly enhance the ion conductivity of CPEs.

Unlike in liquid electrolytes where ion conduction across the porous separator is much faster than the charge transfer reaction, ion migration and diffusion across the SSE film play a major role in determining the overall reaction kinetics of solid-state batteries. Ion migration and diffusion are correlated because faster ion migration results in a lower concentration gradient at a given current density.\textsuperscript{39} The effective diffusivity of the electrolyte ($D_{\text{eff}}$) is determined by both the intrinsic diffusivity of the
FIGURE 1 (A) Schematic illustration of the structure-property correlation of solid-state electrolytes (SSEs). Ionic conductivity of the SSE can be improved by constructing continuously aligned polymer/filler interphases or active filler arrays with fast ion transport pathways. On the other hand, the horizontally layered structure allows dissipation of the mechanical shock energy, providing an enhanced toughening effect. (B) Comparison of design strategies in terms of scalability, versatility, ionic conductivity, mechanical strength, and thickness.

2.1 Freeze casting method

Freeze casting is widely used in the laboratory to create ordered structures. This process usually consists of the controlled solidification of a solution, suspension, or gel, followed by sublimation of the solvent under reduced pressure. Polymeric additives as dispersants or binders are usually added to the solution/suspension to help solid particles disperse in the solution. When solvent solidifies, phase separation begins. The solidified solvent (usually ice) serves as a template that repels solid particles at the solidification front. After solvent removal by sublimation, the particle framework remains, yielding a well-structured monolith. One of the key advantages of the freeze casting method is that the macro–micro structure of the framework can be well controlled by the processing conditions, such as suspension components, solidification conditions, and posttreatment. The geometrics of the framework, such as pore structure and morphology, can be highly diversified by combining freeze casting with other processing and shaping techniques. Without the temperature gradient, the suspension is frozen in an isotropic manner, and a porous structure with randomly oriented fine pores is formed. Under temperature gradient, ordered pores can be constructed along the freezing direction. If frozen only starts from the bottom, the aligned microscale pore structure under a single vertical temperature gradient is formed after solvent removal. The freeze casting method...
has been adopted in battery research to construct oriented electrodes and SSEs.

Li-conductors such as ceramic oxides are generally in the form of micro- or nanoparticles (NPs), and they are usually randomly distributed in the polymer matrix when used as fillers. The freeze casting method can arrange those particles into a vertically oriented structure. As the dispersion of ceramic particles is freeze-dried from the bottom, ice pushes the particles together along the vertical temperature gradient and ice nucleation direction. After ice sublimation, the inorganic framework undergoes high-temperature sintering to improve crystallinity and connectivity between particles. Polymer electrolyte is then infiltrated into the framework to enhance mechanical stability and provide flexibility. For instance, Zhai et al. dispersed \( \text{Li}_{1+\text{x}}\text{Al}_{\text{x}}\text{Ti}_{2-\text{x}}(\text{PO}_4)_3 \) (LATP) NPs in water with poly(vinyl alcohol) and polyethylene glycol as binder and dispersant, respectively. The bottom of the suspension is slowly cooled at a cooling rate of 3°C min\(^{-1}\). After ice is sublimed, the vertically-aligned LATP framework undergoes high-temperature posttreatment followed by poly(ethylene oxide) (PEO)/LiClO\(_4\) polymer electrolyte infiltration (Figure 2A). The average pore size of the straight channel is 5–10 \( \mu \text{m} \), and after post-treatment, LATP NPs are sintered together, providing a more straight and direct ion transport pathway (Figure 2B). The aligned structure exhibits four-time higher ionic conductivity than the random structure, that is, 6.8 \( \times \) 10\(^{-6}\) versus 1.4 \( \times \) 10\(^{-6}\) \( \text{S cm}^{-1}\) at RT; however, it still falls short compared to the pure LATP (\( \sim \) 1.0 \( \times \) 10\(^{-4}\) \( \text{S cm}^{-1}\)) (Figure 2C). The authors attributed the discrepancy to the poor ionic conductivity at ceramic-ceramic interphases and ceramic-polymer interphases. The interphase issue can be addressed by the introduction of a plasticizer, which further improves RT ionic conductivity to 5.2 \( \times \) 10\(^{-3}\) \( \text{S cm}^{-1}\), \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) (LLZO), \( \text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3 \) (LLTO), and \( \text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3 \) (LAGP) NPs are also used to construct similar vertically aligned frameworks using the freeze-casting method. The effect of ceramic concentration in the freeze-casting slurry on the pore morphology of the as-prepared framework is investigated by Shen et al. In the range of 7.5%–12.5 vol% LLZO, higher concentration leads to smaller pore sizes (Figure 2D). As LLZO concentration exceeds 12.5 vol%, the aligned structure does not remain. This is because the decreased suspension stability at high concentration leads to nonuniform power exclusion during the ice nucleation and growth process.

2D nanosheets with a high aspect ratio can be considered a prealignment of 0D NPs. Without the particle–particle interphases, 2D nanosheets provide more continuous and efficient ion conduction channels with larger surface areas for polymer-filler interaction. However, the 2D nanostructures of ceramic Li-conductors are seldom reported, making it challenging to create continuous and aligned structures. The diverse choice of passive fillers provides the opportunity to produce 2D nanosheets and arrange them to orientated structures. Although passive fillers cannot directly participate in the ion conduction, those fillers could plasticize the polymer matrix and enhance the segmental motions at the polymer-filler interphases, which facilitates ion conduction along the continuous and oriented interphases. For instance, a vertically aligned vermiculite sheets (VSs) framework is established by freeze casting the VS dispersion (Figure 2E). After infiltrating PEO/LiTFSI into the framework, VSs exhibit close contact with the PEO matrix. The 2D sheets with a large surface area promote the dissolution of LiTFSI due to the Lewis acid-base interaction with TFSI anions (Figure 2F), which leads to a four-fold improvement in Li\(^{+}\) transference number \( (t_{\text{Li}^{+}}) \) compared to the pure PEO at RT, that is, 0.47 versus 0.125. \( t_{\text{Li}^{+}} \) is also doubled compared to the CPE filled with randomly distributed VSs, due to the direct and continuous polymer-VS interphase in the aligned framework. The large surface area of the 2D nanosheets and the aligned interphases effectively plasticize the polymer and decrease the crystallization temperature of PEO from 37 to 14°C, resulting in a two-order increase of RT ionic conductivity to 1.89 \( \times \) 10\(^{-4}\) from 7.9 \( \times \) 10\(^{-7}\) \( \text{S cm}^{-1}\) (Figure 2G). When cycled in a LiFePO\(_4\) (LFP)/Li cell at 35°C, the solid-state battery using the aligned VS-PEO CPE delivered an initial specific capacity of 167 mAh g\(^{-1}\) at 0.1 C and an 82% capacity retention after 200 cycles at 0.5 C.

The freeze casting method has emerged as a versatile and important approach in the battery research field. Utilizing solvent solidification to template suspended particles represents a distinct synthesis methodology, providing rapid transport pathways and rich reactive interphases. However, the pore structure varies along the freezing direction under a single vertical temperature gradient, which is attributed to a gradual transition from ice nucleation to cellular to columnar structures during the freeze casting process. The progressive variation of porosity and tortuosity may affect mass transport kinetics inside SSEs. Therefore, how to optimize the synthesizing parameters to construct the long-range ordered structure with homogeneous pores is worth exploring. Along with the controllable fabrication of suitable and homogeneous structures, the whole freeze casting process should be continuous and scalable to provide the possibility for industrial-level application.

### 2.2 Phase inversion method

Phase inversion is one of the most popular approaches to fabricating membranes with interconnected and hierarchical pores. Phase inversion occurs when the
equilibrium of the homogenous polymer solution breaks and phase separation occurs, where the polymer-rich phase and polymer-poor phase separate.\textsuperscript{51–52} The polymer-poor phase evolves into pores, whereas the polymer-rich phase remains as the membrane matrix. Thermodynamics equilibrium is determined by the choice of polymer and its interaction with solvent and nonsolvent, as well as reaction conditions such as temperature, pressure, and reaction time. A ternary phase diagram is generally used to determine the thermodynamic states during the phase inversion process (Figure 3A).\textsuperscript{53} In the diagram, S and B represent the slurry composition on the surface and bottom, respectively, as it immerses in the nonsolvent. The curves between S and B indicate film compositions between the surface and bottom. The membrane morphology is dictated by transport kinetics. Slow mass transport results in a delayed solvent-nonsolvent exchange. In such a process, the slurry does not enter the two-phase region, and it is still homogeneous and stable after immersion, giving rise to a homogenous sponge-like morphology. Contrarily, a fast solvent-nonsolvent transport causes rapid liquid–liquid demixing, where the single-phase solution enters the two-phase region without delay after immersion. The instantaneous demixing results in the formation of a center layer with finger-like macropores sandwiched between two dense layers. The combination of the vertically-oriented macrovoids and the dense layers provides an opportunity to integrate SSE and electrode in a single freestanding membrane, which is expected to shorten the ion transport pathway in both electrolyte and electrode.\textsuperscript{54–55}

During the phase inversion process with instantaneous demixing, the ceramic particles are affixed inside the walls of the aligned finger-like pores, forming straight microchannels terminated by dense skin layers on both sides. The upper dense layer can be removed when phase inversion completes to open up the microchannels.\textsuperscript{54–55}
After sintering in air, polymers in the framework are combusted, and ceramic particles are densified. In solid-state batteries, the microchannels can be used as the framework to hold electrode materials and provide straight, continuous ion pathways for active materials. The thin, dense layer on the bottom shortens ion transport distance between cathode and anode, reducing grain boundary resistance. An LLZO membrane with vertically aligned microchannels (VAMCs) was constructed by Jiang et al. using nylon mesh as a pore template and skin-layer remover (Figure 3B). As soon as the slurry film is immersed in water, n-methyl-2-pyrrolidone (NMP) in the slurry instantaneously diffuses to water from the surface of the slurry, forming a dense skin layer. Below the skin layer, NMP continues to diffuse to water along the mesh aperture, forming long and aligned channels. The microchannels stop growing at the bottom due to NMP depletion, and a dense bottom layer is formed. After phase inversion completes, the skin layer is peeled off by removing the nylon mesh, and the microchannels are opened up with an average diameter of 165 $\mu$m (Figure 3C–E). After sintering at 1350°C, the morphology of the aligned channels is well preserved with average pore sizes slightly reduced to 113 $\mu$m. The bottom dense layer is $\sim$200 $\mu$m thick, which is sufficient to avoid contact between cathode and Li metal anode. VAMC framework with open microchannels can host cathode materials, and the enlarged contact area reduces interfacial resistance compared to the 2D planar LLZO. The aligned LLZO inside the cathode can also offer continuous ion transport pathways. As a result, the Li/LFP solid-state batteries using VAMC LLZO deliver an initial specific capacity of 127 mAh g$^{-1}$ at 0.05 C and RT, much
higher than 87 mAh g\(^{-1}\) of the planar LLZO (Figure 3F). Ji et al. took one step further and constructed a symmetric 3D VAMC solid-state battery.\(^{57}\) Two asymmetric VAMC LLZO are glued together by casting a thin layer of LLZO slurry on the skin layer side, followed by a second solidification via the phase inversion process (Figure 3G). The symmetric VAMC LLZO was then sintered at 1350°C for 5 h to obtain the final framework. The all-ceramic solid-state batteries are fabricated by impregnating LiCoO\(_2\) cathode and Li\(_4\)Ti\(_5\)O\(_12\) (LTO) anode precursor solutions into the opposite microchannels and sequential heat treatment at 800°C (Figure 3H). As expected, the electrode/electrolyte interfacial resistance is greatly reduced, which improves the rate performance and cycling life of the solid-state battery.

Phase inversion is a facial approach to producing large-area membranes that can be used in battery applications. The freestanding inorganic membranes combining a vertical microchannel layer as electrode host and a thin, dense layer as SSE synergistically lower the internal resistance of solid-state batteries. Both electrode/electrolyte interfacial resistance and ion transport resistance inside SSE are reduced, due to the enlarged electrode/electrolyte contact area and the shortened ion transport pathway. However, the diameter and the wall thickness of the microchannels are hundreds of micrometers, which calls for a reduction to further enlarge the electrode/electrolyte contact area. Additionally, the thickness of the dense layer needs to be minimized to further shorten ion transport distance across the film. Nevertheless, the mechanical strength of the freestanding membrane should be acceptable. Optimizing phase inversion parameters to meet the above goals is critical to improving the energy/power density of solid-state batteries.

2.3 Template method

The template method has been used to create well-defined structures in wide areas. The templates can be preserved to provide mechanical support for holding electrolytes and shaping ionic transport pathways inside SSE. In this strategy, templates are usually porous sheets with good mechanical properties, and they are introduced as an additional component to form ordered ion transport pathways. The template can also be removed afterward to allow porosity for polymer infiltration, which provides abundant interphases for ion conduction.

Anodized aluminum oxide (AAO) discs with vertical nanochannels can be used as the template to construct continuous and aligned polymer-inorganic interphases after polymer electrolyte infiltration (Figure 4A). Maximized interfacial effect along the vertical interphases enhances the segment motion of PEO polymer, which lowers the crystallinity and increases the ionic conductivity of the polymer electrolyte. For instance, the crystallization temperature of PEO in the AAO template is reduced from 30 to 15°C, and the RT ionic conductivity of the CPE increases to 3.50 \(\times\) \(10^{-4}\) S cm\(^{-1}\), 20 times the pure PEO/LiTFSI.\(^{58}\) The surface properties and specific surface area can be tuned by surface chemical modification and controlling pore diameters in AAO discs. With the Al\(_2\)O\(_3\) coating on the AAO surface, the interfacial interactions with PEO are further improved. AAO templates also provide mechanical stiffness to prevent Li dendrite penetration for better SSE-Li metal anode interphase, as well as thermal stability for higher safety. Wan et al. used the polyimide film with vertical nanopores as the host of PEO/LiTFSI polymer electrolyte (Figure 4B,C) and observed anisotropic crystallinity of the polymer using two-dimensional X-ray diffraction (2D XRD).\(^{59}\) The polarized ring pattern in the 2D XRD reveals that PEO crystallites are aligned along the vertical channels, meanwhile, molecular dynamics simulations confirm that polymer-chain alignment promotes Li-ion diffusion in the alignment direction (Figure 4D). Li-ion diffusion coefficient along the vertical direction is calculated to be \(1.3 \times 10^{-5}\) cm\(^2\) s\(^{-1}\), double that in the random direction. As a result, the ionic conductivity of PEO/LiTFSI in the vertical channels is \(2.3 \times 10^{-4}\) S cm\(^{-1}\) at 30°C, one order higher than the pure PEO/LiTFSI (5.4 \(\times\) \(10^{-5}\) S cm\(^{-1}\)). The high-ionic-conductivity electrolyte together with the high-modulus framework enables stable RT cycling performance and a high energy density of 246 Wh kg\(^{-1}\).

Wood with naturally built open and aligned channels can be used as a sacrificial template to create the hierarchical aligned structure. The hydrophilic nature of wood cellulose and the capillary force of the aligned pores endow the wood template with great absorbency, which makes the precursor solution easily absorbed into the template. The pore channels in the template provide reservoirs to host the inorganic precursor, and the aligned nanofibers (NFs) serve as sacrificial pore formers to offer additional porosity for polymer infiltration. Dai et al. constructed an aligned LLZO framework using the wood template and then composed the framework with the polymer electrolyte.\(^{50}\) LLZO makes up \(~68\) vol\% in the CPE, and such a high volume of ceramics allows for direct ion conduction through LLZO particles. Unlike the conventional CPE where the random transport pathway and the insufficient particle–particle interphases obstruct the ion transport pathway, the aligned garnet with mesoporous structure offers the undisturbed ion transport along the vertical direction. This results in a high RT ionic conductivity of \(1.8 \times 10^{-4}\) S cm\(^{-1}\), close to the bulk LLZO of \(2.2 \times 10^{-4}\) S cm\(^{-1}\). The template method is attractive because it realizes well-defined and
uniform channels to hold SSEs and forms highly aligned ion conduction pathways.

2.4 Electrospinning method

Electrospinning is used to fabricate fine NFs.\textsuperscript{61-62} Electrospinning usually consists of a needle and a plastic syringe containing an electrospinning solution, a high-voltage power supply, and a grounded conducting collector. Electrospinning solution contains polymers and/or inorganic precursors, either dissolved in one or mixed solvents. During a typical electrospinning process, a liquid drop is electrified to generate a jet, which is then stretched and elongated to produce fibers. Driven by the electric field, continuous NFs are fabricated due to the electrostatic repulsive force. As the electric field is increased to the point where the repulsive force is higher than the hemispherical surface tension, a Taylor cone is formed. Immediately after the electrical field reaches the critical point, the charged jet is extended from the capillary tip to the collector. As the solvent evaporates, polymer or hybrid NFs are collected. The morphology of the as-prepared NFs is determined by solution parameters, operating parameters, and atmosphere parameters. Particularly, the rotating speed of the collector plays a vital role in determining the alignment of the fibers. By collecting NFs on the rotating drum, the NFs orient along the rotating direction of the drum due to the mechanical stretching force. The degree of alignment can be controlled by adjusting the rotation speed of the drum.

To investigate the effect of NF alignment on the ionic conductivity of SSE, Liu et al. fabricated LLTO nanowires with different degrees of orientations against electrodes (Figure 5A).\textsuperscript{23} LLZO precursor solution was collected by a 6000 rpm rotating drum, where Pt electrodes were placed at a controlled angle (Figure 5B). After calcination, polyacrylonitrile (PAN)-based polymer electrolyte was cast into the aligned ceramic NFs. At a fixed filler concentration of 3 wt\%, the RT ionic conductivities of CPEs with LLZO orientation of 0\(^\circ\) (normal direction of the electrodes), 45\(^\circ\), and 90\(^\circ\) (parallel direction of the electrodes) are 6.05 \times 10^{-5}, 2.24 \times 10^{-5} and 1.78 \times 10^{-7} S cm\(^{-1}\), respectively (Figure 5C). When LLZO nanowires are aligned parallel to the electrodes, fillers at such a low loading do not cross between electrodes, and therefore no additional ion transport pathway will be created, leading to a low ionic conductivity similar to the pure polymer electrolyte. On the contrary, the ionic conductivities of CPEs with both 45 and 0\(^\circ\) orientations are increased by two-orders compared to the pure polymer electrolyte due to the additional ion transport pathway on
F I G U R E 5  (A) Schematic showing the fabrication process of the composite polymer electrolyte (CPE) with aligned nanowires. (B) SEM image of the aligned nanowires at an orientation of 0°. (C) Ionic conductivity of CPEs with aligned nanowires at different orientation degrees. Reproduced with permission. 23 Copyright 2017, Springer Nature. (D) Schematic illustration of the solid-state battery using CPE with the electrospun nanofibers (NFs) aligned parallel to the electrodes. Reproduced with permission. 65 Copyright 2019, Elsevier.

The shorter length of the continuous nanowires across the electrodes for 0° nanowires gives rise to a higher ionic conductivity compared to that of the 45°. The above research reveals the dependency of ionic conductivity on nanowire alignment. However, how to align nanowires to the normal direction of the electrodes in a real battery setting remains challenging, as the membranes created by the electrospinning naturally align parallel to the electrodes. Although transforming the parallel to the vertical orientation can be realized by a rolling-cutting approach as reported by Wu 63 and Chen, 64 the membrane fabricated by such a strategy is quite thick, which is not suitable for SSE application. Conversely, nanowires with parallel alignment against the electrodes are also reported to enhance ionic conductivity compared to the nonordered structure, as long as nanowires make sufficient interfacial contact with the electrodes. Zhao et al. fabricated aligned LLZO NFs by controlling the composition of the electrospinning solution and the applied electric field. 65 After calcination, the aligned LLZO NFs are combined with polyvinylidene fluoride/LiClO₄ polymer electrolyte, where LLZO accounts for 75 wt% of the CPE. In such an electrolyte, LLZO NFs are aligned parallel to the electrodes, forming a planar layer at the interphase and promoting continuous planar ion conduction (Figure 5D). The ionic conductivity is measured to be 1.16 × 10⁻⁴ S cm⁻¹ at 30°C, higher than the CPE with nonordered NFs where ions need to transport along the random and disconnected pathway. The elastic surfaces of the CPE provide a close and stable interfacial contact with the electrodes, leading to smaller interfacial resistance. The high concentration of ceramics also endows the CPE with high mechanical strength, which is critical for SSE against Li dendrite growth. When assembled in the LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂/Li full cell with a high cut-off voltage of 4.6 V, the CPE exhibits a low internal resistance of 87 Ω and delivers a high initial specific capacity of 213 mAh g⁻¹ at 0.2 C and RT.

The electrospinning method can fabricate ordered 1D Li-ion conductor membranes in a scalable manner, which cannot be realized by other methods. The morphology of the NFs can be tuned by electrospinning parameters, and the orientation of the NFs can be controlled by adjusting the rotation speed of the current collector. Aligned NFs along the rotation direction of the collector can be collected on a high-speed rotating drum. Despite the great enhancement in ionic conductivity by aligning NFs along the normal direction of the electrodes, such a design is only realized using interdigital Pt electrodes. The vertical
alignment of electrospun NFs in SSE has not been reported in a practical battery setting. The challenge lies in transforming the intrinsic parallel alignment of NFs to the vertical alignment to construct SSEs at an acceptable thickness and mechanical strength. Another strategy to promote ion conduction is to enlarge the interphase contact areas between parallelly aligned NFs with electrodes by increasing NF concentration in the CPE so that continuous planar ion conduction across the interphase can be realized. Nevertheless, powering the high-speed rotating drum is costly and not applicable in industrial production. Further development of the cost-effective electrospinning techniques to construct aligned NFs is worth exploring (Table 1).

### 3.1 Traditional multilayer fabrication methods

Nacre is a layered structure that naturally exists in the shell of muscles composed of highly aligned aragonite tiles (>95 wt%) connected by the organic polymer. The elastic polymer adsorbs mechanical shock energy and undergoes interfacial sliding and plastic deformation, which prevents the cracking of ceramic pallets. Such a structure can be utilized in SSE to enhance the mechanical properties of

| Method       | Electrolyte composition | RT Ionic conductivity (S cm$^{-1}$) | Electrochemical performance | Ref. |
|--------------|-------------------------|-------------------------------------|----------------------------|------|
| Freeze casting | LATP/PEO/LiTFSI         | 0.52 × 10$^{-4}$                    | -                          | 27   |
|              | LAGP/PEO/LiTFSI         | 1.67 × 10$^{-4}$                    | 150 mAh g$^{-1}$ (LFP/Li, 0.3C, 60°C) | 46   |
|              | LLTO/PEO/LiTFSI         | 1.3 × 10$^{-4}$                     | 144.6 mAh g$^{-1}$ (LFP/Li, 1C, 60°C) | 45   |
|              | LLZO/PEO/LiTFSI         | 2.0 × 10$^{-5}$                     | -                          | 44   |
|              | LAGP/SN/LiTFSI          | 9.44 × 10$^{-4}$                    | 175 mAh g$^{-1}$ (NCM532/Li, 0.1C, 25°C) | 47   |
|              | VS/PEO/LiTFSI           | 1.89 × 10$^{-4}$                    | 167 mAh g$^{-1}$ (LFP/Li, 0.1C, 35°C) | 28   |
| Phase inversion | LLTO/PEO/LiTFSI        | -                                   | 120 mAh g$^{-1}$ (LFP/Li, 0.1C, 65°C) | 56   |
|              | LATP/PEO/LiTFSI         | 1.01 × 10$^{-4}$                    | 143.5 mAh h$^{-1}$ (LFP/Li, 1C, 60°C) | 66   |
|              | LLTO                    |                                      | 130 mAh h$^{-1}$ (LTO/LCO, 0.1C, RT) | 57   |
| Template     | AAO/PEO/LiClO$_4$       | 1.79 × 10$^{-4}$                    | 400 h (Li/Li, 0.75 mA cm$^{-2}$, RT) | 58   |
|              | LLZO/PEO/LiTFSI         | 1.8 × 10$^{-4}$                     | 175 h (Li/Li, 0.1 mA cm$^{-2}$, RT) | 60   |
|              | PI/PEO/LiTFSI           | 2.3 × 10$^{-4}$                     | 150 mAh g$^{-1}$ (LFP/Li, 0.1C, 30°C) | 59   |
| Electrospinning | LLTO/PAN/LiClO4       | 6.05 × 10$^{-5}$                    | -                          | 23   |

Abbreviations: AAO, anodized aluminum oxide; LATP, Li$_{1-x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$; LFP, LiFePO$_4$; LLTO, Li$_{0.33}$La$_{0.557}$TiO$_3$; LLZO, Li$_7$La$_3$Zr$_2$O$_{12}$; PEO, poly(ethylene oxide); RT, room temperature.

### 3. HORIZONTALLY ORDERED SSEs

Besides ionic conductivity, the mechanical strength of the SSE plays an important role in determining the performance and safety of solid-state batteries.67 SSEs need to be mechanically robust and as thin as possible to enable stable cycling and maximize the attainable energy/power density on the cell level. The thickness of SSEs needs to be greatly reduced to 25 μm to even compete with the liquid electrolyte in terms of energy density.21,68,69 However, the recent studies on the performance of ISEs are mainly based on bulky pallets with thicknesses ranging from 300 to 1000 μm.70–72 This is because brittle ceramics suffer from unfavorable mechanical properties such as low fracture toughness, and the mechanical challenge becomes more severe as thickness reduces. Fabrication strategies for ISEs with reduced thickness are highly needed. However, such techniques remain scarce, and achieving the ideal thickness of the ISE is believed to be unrealistic using the conventional sintering and densification processes. Tape casting is reported to produce thin-film ISEs, but the fracture toughness remains unsatisfactory.72,73 Although thin-film techniques such as vacuum-based deposition can produce films less than 1 μm thick, the ionic conductivity of those thin films is several orders of magnitude lower than their bulky pellet counterparts, mostly due to low crystallinity and high grain-boundary resistance.74–76 Recently, the laminar structure has been explored to enhance the mechanical robustness without comprising ionic conductivity. Specifically, the nacre-mimetic structure composed of highly aligned ceramics connected by sticky polymer electrolytes allows dissipation of the mechanical shock energy, providing an enhanced toughening effect.77–78 Other than layered ceramic pallets, the horizontally aligned 1D or 2D materials can also afford high mechanical strength and flexibility,79–80 which is beneficial for thickness reduction and Li dendrite suppression.
the membrane. For instance, Li et al. fabricated a nacre-mimetic CPE composed of ceramic ISE layers glued by soft polymers (Figure 6A). The suspension of LAGP is slurry cast on a substrate and after solvent evaporation, the films are stacked together followed by high-temperature sintering to form the multilayered ceramic film. PEO/LiTFSI polymer electrolyte is then infiltrated into the multilayer film, which is hot-pressed to break the ceramic layers into pallets and to ensure close contact between pallets and polymers. The individual LAGP layer is \( \sim 15 \) \( \mu \)m thick, and the bridging PEO layer is \( \sim 1 \) \( \mu \)m thick (Figure 6B). The total thickness of the LAGP-PEO electrolyte is 100–200 \( \mu \)m, which is expected to be further reduced to 10–20 \( \mu \)m after optimization. The nacre-mimetic structure greatly enhances the overall mechanical properties in terms of flexibility and fracture toughness. The LAGP-PEO has an ultimate flexural strength of 30.2 MPa, \( \sim 30 \) times higher than the pure PEO electrolyte, and comparable to the ceramic LAGP electrolyte (34.3 MPa) (Figure 6C). The failure strain of LAGP-PEO is 1.1%, 8 times of the pure LAGP electrolyte (0.13%). At the same time, the layered structure does not compromise the ionic conductivity. The ionic conductivity of the LAGP-PEO electrolyte is \( 1.25 \times 10^{-4} \) S cm\(^{-1}\) at 25\(^{\circ}\)C and \( 1.3 \times 10^{-3} \) S cm\(^{-1}\) at 60\(^{\circ}\)C, close to the pure LGAP, which demonstrates low interfacial resistance between the pallets and the polymer. The authors also tested the performances of pouch cells under mechanical deformation. The brittle LAGP electrolyte cannot stand a 10 N point force, leading to immediate failure of LFP/Li full cell, while the capacity of the PEO electrolyte suffers from a sudden drop followed by continuous fading. The cell using the LAGP-PEO electrolyte does not exhibit obvious capacity fading after the force is applied and maintains a 95.6% capacity retention after 100 cycles, demonstrating robustness against external impact.

For 2D nanosheets, vacuum filtration is a facile approach to creating laminar structures, and after the introduction of polymers, the nacre-mimetic structure with enhanced mechanical properties is obtained. For instance, Guo et al. prepared a freestanding LLZO laminar membrane by vacuum filtrating LLZO nanosheets followed by PEO/LiTFSI infiltration (Figure 6D,E). Due to the laminar framework of LLZO, LLZO-PEO electrolyte shows a compressive strength of 3.2 GPa, which is 10 times higher than the CPE composed of randomly orientated LLZO nanosheets (Figure 6F). The improved mechanical properties show advantages in suppressing Li dendrite penetration in Li/Li symmetric cell testing. The enhanced mechanical robustness also allows reducing the thickness of the LLZO-PEO electrolyte to only 12 \( \mu \)m. The
ionic conductivity of the electrolyte is increased to $1.04 \times 10^{-4}$ S cm$^{-1}$ at 25°C, which is due to the combined effect of the continuous ion transport pathway between adjacent LLZO layers, the decreased grain boundary of the 2D morphology, and the short ion diffusion distance by the reduced thickness. Area-specific resistance (ASR) of the composite electrolyte is 9.2 Ω cm$^2$, two orders of magnitude lower than the regular LLZO pallet. The thin laminar with significantly reduced internal resistance endows LFP/Li full cells with improved rate performance at 60 and 45°C. A similar laminar structure composed of vermiculite nanosheets is also constructed using the vacuum filtration method.

### 3.2 Layer-by-layer self-assembly method

The multilayered structure can be achieved by adsorbing the targeted components onto a substrate in a layer-by-layer (LbL) fashion.$^{82}$ In the LbL process, the driving force for assembly is usually electrostatic interaction but can be extended to other interactions such as hydrogen bonding, metal coordination, etc.$^{83-84}$ In a typical LbL process induced by the electrostatic interaction, the charge neutralization and re-adsorption of the countercharged components onto a charged surface leads to charge inversion, which allows for the alternative adsorptions of positively and negatively charged building blocks.$^{85-86}$ The thickness of a single layer is usually on the nanometer scale, and the process is repeated until the desired thickness is achieved. For certain applications, the substrate can be removed afterward, yielding freestanding membranes. Polyelectrolytes are the most common building blocks, and nanomaterials with surface charges can also be used in the LbL process, offering opportunities to further tailor the properties and applications of the LbL film. When the proper polyelectrolytes or nanomaterials are selected, the LbL process could fabricate multilayered SSE film that aligns horizontally with controllable thickness, architecture, and functions.

Immersive LbL assembly is the most widely used LbL method, which involves immersing the substrate in the solution of the desired material followed by washing to remove unbound material (Figure 7A). For SSE applications, the building blocks with specific properties are utilized to target particular functions, such as mechanical robustness and ionic conductivity. In the composite film, the building blocks can also work synergistically to improve the overall performance of the SSE. For instance, an ion-conducting membrane (ICM) composed of aramid NFs (ANFs), and PEO is fabricated by such an approach.$^{87}$ The pretreated glass substrate is alternatively immersed in 0.01% aqueous PEO solution and 0.04% ANF dispersion in dimethylformamide, separated by rinsing and air-drying, and free-standing membranes are obtained after chemical delamination (Figure 7B,C). The linear growth of ANF/PEO film by LbL cycles indicates the uniform multilayer formation after each cycle. ANF being the nanoscale version of Kevlar provides high mechanical properties and thermal stability for the LbL membranes. Young’s modulus of the ICM membrane is $\sim$5.0 GPa, 500-times higher than the PEO membrane. The crystallization of PEO in ICM is impeded due to the LbL fabrication process and the existence of ANFs. The amorphous nature of PEO results in RT ionic conductivity of $5.5 \times 10^{-5}$ S cm$^{-1}$ with the introduction of LiTFSI, higher than the pure PEO/LiTFSI electrolyte. The nanoscale controllability of the LbL process and the high mechanical strength of the ANFs provide the possibility to substantially reduce SSE thickness to 500 nm with 30 LbL cycles. The (PEO/ANF)$_{30}$ electrolyte has an internal resistance of 0.16 Ω, which is comparable to a Celgard separator filled with liquid electrolyte, and 2–3 orders of magnitude lower than the typical polymer electrolytes with thickness ranging from 100 to 400 μm. The high mechanical properties and low internal resistance enable the ICM electrolyte to physically suppress metallic dendrite growth and provide stable ion flux at the electrolyte/electrode interphases (Figure 7D). The symmetric Li/Li using a 30 μm-thick (PEO/ANF)$_{200}$ electrolyte stably cycles for 2500 cycles at 0.25 mA cm$^{-2}$, confirming the successful suppression of Li dendrites and the stable interphases.

The horizontal alignment is more obvious when 2D nanosheets are used as the building block in the LbL assembly. Wu et al. constructed a “nanobrick wall” structure by LbL assembly using MoS$_2$ nanosheets modified with positive surface charges and poly(acrylic acid) (PAA) with negative surface charges.$^{88}$ In such a structure, the horizontally oriented MoS$_2$ as bricks are uniform and densely packed in each bilayer, separated by soft polymers as mortar (Figure 7E,F). This would create a tortuous pathway to selectively impede polysulfide diffusion through the membrane while having a much smaller impeding effect on Li-ions whose diameter is significantly smaller than that of the polysulfide. The thickness and weight of membranes grow linearly with the deposition cycle, and each bilayer is $\sim$150 nm thick. The well-aligned MoS$_2$ layers with 2D structure and high modulus enhance the mechanical strength of the LbL layer, and Young’s modulus of the LbL layer is 1.93 GPa, almost three times of the Celgard separator (Figure 7G). The much improved mechanical properties can physically suppress the dendrite growth and prolong the cycle life of the Li/Li symmetric cell.

The LbL process is simple with nanoscale control, and the mild experimental conditions without complicated procedures or equipment offer a cost-effect approach to
producing thin films. The nanoscale controllability of the LbL process and a diverse selection of building blocks allow SSEs to be engineered for various functions. In the LbL process, building blocks are naturally aligned in a horizontal fashion during the repeated assemble cycles, forming a layered electrolyte membrane that is capable of synergistically combining the advantages of different multilayers. To transform LbL assembly from laboratory research to scalable application, it is crucial to automate the labor-intensive coating and rinsing steps. Increasing the reliability and reproducibility of the multilayered film, and reducing material waste during the assembly process, especially for valuable building blocks such as 2D nanosheets and customized polymers, are also important to extend the knowledge of LbL assembly to real-world applications.

### 3.3 3D printing method

3D printing (additive manufacturing) has been utilized to fabricate complex 3D objects with controllable macroscopic structures over a wide range of scales from nanometers to centimeters. The architecture and shape of SSEs can be precisely controlled by tuning the printing parameters and ink formulas. Compared to the traditional fabrication method, 3D printing makes the fabrication of uniquely structured electrolytes possible, including a wide selection of materials and geometries (e.g., morphology, porosity, and dimension) with low cost and flexible manufacturing. In 3D printing, a virtual model is first created by computer-aided design software, whose surface information is then converted to stereoLithography. Finally, a 3D printer transforms the virtual geometries and deposits the ink into a physical structure in a well-controlled layer-by-layer fashion. The width of the printed objects is usually controlled by the size of the print nozzle, while the height of the objects is determined by the number of repeated layers. The exact architecture and shape of the printed objects are strongly affected by the properties of the ink.

3D printing method can produce 3D bicontinuous ordered hybrid SSEs with ceramic channels providing continuous Li-ion pathways while polymer channels rendering resilient to fracture, resolving two key challenges in SSEs.
Zekoll et al. constructed a CPE with ordered ceramic and polymer microchannels by 3D printing (Figure 8A). Stereolithography was used to fabricate an epoxy framework, where the empty microchannels are infiltrated by LAGP powders. The epoxy template has a high porosity of 85%, allowing for high volume infiltration of ionic conductive ceramics. The LAGP-epoxy composite undergoes high-temperature sintering to remove epoxy and densify LAGP, giving rise to an ordered LAGP framework. The inorganic framework is then filled with insulating polymers to enhance mechanical strength, forming a 3D bicontinuous microchannel ceramic-polymer CPE. Various microstructures such as cube, gyroid, diamond, and bijel are printed with different tortuosity factors ranging from 1.2 to 1.6. The optimized gyroid LAGP-polymer electrolyte improves the flexural failure strain of LAGP pallets by five times (Figure 8B) and exhibits a high ionic conductivity of \(1.6 \times 10^{-4} \text{ S cm}^{-1}\). As a result, LAGP-polymer electrolytes enable a more stable cycling performance of Li/Li symmetric cells at various current densities compared to the LAGP pallets. McOwen et al. investigated the effect of ink formula on the morphology of 3D-printed SSEs. Two types of ink with different binder systems are explored, which exhibit dramatically different rheology behaviors. The conformal ink exhibits Newtonian behavior and is utilized to print thin and dense SSE <10 \(\mu\)m due to its conformity and seamless joinery with other patterns. Meanwhile, the self-supporting ink with Bingham plastic behavior is appropriate for printing complex patterns with high aspect ratios, which allows for increased surface area (Figure 8C). In an asymmetric cell composed of the stacked 3D-LLZO array sandwiched between two Li metal anodes, ASR maintains at \(\sim 20 \Omega \text{ cm}^2\) and is independent of the cycling current density (Figure 8D). The low LLZO/Li interfacial resistance is attributed to the enlarged surface area generated by the ordered and continuous electrolyte/electrode interphase and the dendrite suppression by the multilayered ordered LLZO.

3D-printing method demonstrates the advantage of structural controllability over a wide range of scales. Oriented SSEs with high structural stability can be realized with potentially low-cost and scalable operation processes.
However, the diameters of the oriented pores are usually at the micrometer scale. Since ordered pore structure at both micro- and nanoscales is important for improving ion conduction, developing advanced printing techniques with higher resolution is of tremendous interest. More importantly, the ordered SSEs produced by 3D-printing methods are over hundreds of micrometers thick, which reduces the energy density of the battery. The layer-by-layer manufacturing fashion of the 3D-printing method also leads to weakly connected interphases between layers, which may deteriorate the mechanical strength of the printed SSEs. Great efforts will be needed to reduce the thickness while improving the mechanical properties of the printed SSEs (Table 2).

| Method          | Electrolyte composition | RT Ionic conductivity (S cm⁻¹) | Mechanical properties | Thickness (µm) | Ref. |
|-----------------|-------------------------|----------------|------------------|----------------|-----|
| Electrospinning | LLZO/PVDF/LiClO₄         | 1.16 × 10⁻⁴  | -               | 73             | 65  |
| Vacuum filtration | LLZO/PEO/LiTFSI       | 1.30 × 10⁻⁴  | 3.2 GPa (compressive strength) | 12             | 81  |
|                 | VS/PEO/LiTFSI          | 1.22 × 10⁻⁵  | 131 MPa (compressive strength) | 10             | 96  |
| Slurry casting  | LAGP/PEO/LiTFSI        | 1.25 × 10⁻⁴  | 7.8 GPa (flexural modulus) 1.1% (fracture strain) | 100-200        | 31  |
| LbL             | ANF/PEO/LiTFSI         | 5.5 × 10⁻⁵   | 5.0 GPa (Young’s modulus)  | 3              | 87  |
|                 | MoS₂/PAA               | -            | 1.93 GPa (Young’s modulus) | 1.5            | 88  |
| 3D printing     | LAGP/epoxy              | 1.6 × 10⁻⁴   | ~20 MPa (flexural failure strain) | 1200           | 94  |

Abbreviations: ANFs, aramid nanofibers; LAGP, Li₁.₅Al₀.₅Ge₁.₅(PO₄)₃; LLZO, Li⁷La₃Zr₂O₁₂; PAA, poly(acrylic acid); PEO, poly(ethylene oxide); PVDF, polyvinylidene fluoride; RT, room temperature; VSs, vermiculite sheets.

**4 | SUMMARY AND PERSPECTIVE**

This review focuses on the design and development of ordered SSEs in solid-state batteries. The critical challenges of SSEs are unsatisfying RT ionic conductivity, poor interfacial stability, and insufficient mechanical properties. The ion conduction mechanism in the SSE depends on the chemistry and structure of the electrolytes. In CPE, the main diffusion path of ions is either along the polymer-filler interphases or directly through the inorganic ion conductors. Therefore, the ionic conductivity of SSEs can be greatly improved by optimizing filler structures. Constructing continuous and aligned ion pathways along the ion diffusion direction could shorten ion transport distance and promote the migration of Li-ions. The polymer-chain alignment in the ordered pores also promotes Li-ion diffusion in the alignment direction by several orders of magnitude. Besides ionic conductivity, the mechanical strength of the SSE plays an important role in determining the performance and safety of solid-state batteries. SSEs need to be mechanically strong to prevent cell failure and internal short circuits. At the same time, the thickness of the SSE needs to be greatly reduced to maximize the attainable energy/power density on the cell level. However, minimizing the thickness of SSEs will deteriorate their mechanical properties, impairing the stability and safety of solid-state batteries. Developing SSEs with horizontally layered nacre-mimetic structures allows dissipation of the mechanical shock energy in the lateral direction, which is beneficial for thickness reduction and Li dendrite suppression.

Despite the rapid progress in the research of SSEs with ordered structures, critical challenges remain, and substantial efforts are called for deeper understanding and further optimization of the fabrication process including the following (Figure 9):

1. Advanced characterization techniques. Ordered and continuous SSE design increases ionic conductivity compared to the random design, and fundamental understandings have been developed for the ion conduction in the ordered structure. Although many reports indicate a fast surface ion conduction at the interphase of the aligned fillers/polymers, the ion transport mechanisms in real-time during operation call for thorough investigations. Multidimensional or multiscale characterization techniques provide powerful tools to probe the underlying ion conduction mechanism at complicated interphases.

In situ or operando characterizations are highly useful in visualizing and unraveling ion diffusion behaviors for drawing the full picture of ion conduction in solid-state
batteries. Characterizing and understanding the processes at the SSE-electrode interphases is also important for designing safe and high-performance solid-state batteries. Advanced techniques have been developed to capture the dynamic processes. Particularly, the ultrasonic imaging as a nondestructive technique can be used to reveal the interfacial stability in solid-state batteries during long-term cycling. Optical fiber Bragg grating sensors is also a promising tool for in situ investigating the internal stress evolution in the solid-state batteries.

2. Development of SSEs with desirable mechanical properties. The mechanical properties of SSEs play a crucial role in the electrochemical performance and safety of solid-state batteries. However, it is still challenging for the brittle ceramics or soft polymers to buffer the mechanical deformation of electrodes during cycling or the external pressure during operation. The aligned CPEs exhibit anisotropic mechanical properties, providing the possibility to strengthen the membrane and resist fracture in the lateral direction. Nacre-mimetic structures can roughen the membrane by interfacial sliding and plastic deformation. The horizontal alignment also enables the planar ion conduction and sufficient electrode-electrolyte contact area. The strength and toughness of the layered SSEs can be further improved by optimizing the hierarchical structures. Developing new methodologies to construct ordered structures or new materials with diverse functionality can be useful to extend the applications of layered SSEs.

3. Thickness reduction of SSEs. Reducing the thickness of SSEs is another requirement for the practical application of solid-state batteries. The thickness of SSEs determines both the energy and power densities of solid-state batteries. The majority of the reported studies use SSEs over 100 μm thick, which not only brings redundant weight/volume but also increases ion conduction resistance inside the SSE. Reducing the thickness of the SSE would shorten the ion diffusion distance and alleviate internal resistance, leading to higher energy/power densities. However, thinner electrolyte exhibits weakened mechanical strength, which increases the risk of cell failure. Layered SSEs with nacre structures afford sufficient mechanical strength to minimize the thickness of SSEs, but it remains challenging to reduce the thickness of SSE to 25 μm to compete with polymeric separators in the liquid electrolyte. Introducing polymer frameworks with vertical channels is another effective strategy to minimize SSE thickness while providing direct ion transport expressway. Nevertheless, continuous research is needed to develop thin and robust ordered arrays for further improvement of the overall performance.

4. Scalability of ordered SSEs. Scalable and cost-effective fabrication is a prerequisite for the widespread application of SSEs with ordered structures. Although various approaches have been established to construct ordered SSEs, their effects are solely evaluated on the laboratory scale. The scalability and reproducibility of the structures produced by those approaches need to be confirmed. Also, solid-state batteries using ordered SSEs need to be assembled and tested under a condition close to real applications to provide realistic performance validation. Last but not least, cost evaluation is yet to be established on the industrial-level production. Considering that most of the fabricating approaches of ordered SSEs are not compatible with the current battery manufacturing process, great efforts are needed for process optimization and cost control of ordered SSEs.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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