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How to commercialize solid-state batteries: a perspective from solid electrolytes

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Lithium-ion batteries with flammable liquid electrolytes and graphite anodes suffer from insufficient energy density and potential safety risks. Solid electrolytes are very promising to completely address these issues [1,2], because solid electrolytes that are electrochemically stable with Li metal anodes and compatible with high-voltage cathodes can simultaneously achieve high safety and high energy density. Generally, solid electrolytes can be classified into two groups: solid polymers and inorganic solids, including oxides, sulfides and halides [3].

There have been numerous studies on solid electrolytes [4,5]; however, current lab-level processing of solid electrolytes is not suitable for massive production. Some scientific and technological issues related to solid electrolytes are illustrated in Figure 1. Rapid development of solid electrolytes does not guarantee the commercialization of solid-state batteries in a short term [6], mostly because (1) reported properties of solid-state batteries are far below the level required for practical applications, and (2) massive production of solid electrolytes is difficult and not compatible with the current battery manufacture technology.

Oxide electrolytes, including NASICONs [7], perovskites [8], and garnets [9], exhibit acceptable ionic conductivities, excellent mechanical strength, good compatibility with Li metal and oxidation stability at high voltages. However, oxides are brittle, which leads to stress concentration and cracks at electrode/electrolyte interfaces due to the volume changes of electrodes, and the contact loss at solid-to-solid interfaces seriously deteriorates the capacity and cycling lifetime as well. Insufficient interfacial contacts between oxides and electrodes are the most critical bottleneck, which causes a huge interfacial impedance, induces the dendritic growth of Li metal and deteriorates the battery performances. To achieve good interfacial contacts, high temperature treatments or co-sintering is necessary for oxide cathodes and electrolytes. Another strategy to get a good interface is to apply a stable protecting layer or buffer layer at the electrode/electrolyte interface. However, the inherent point contacts at the solid-to-solid interfaces hinder the ionic transport, making the performances of oxide-based solid-state batteries far from satisfaction, not to mention the cracking issues of ceramic pellets. In view of existing oxide electrolytes and battery configurations, the above challenges are critical but very difficult to solve simply by material and interface modifications.

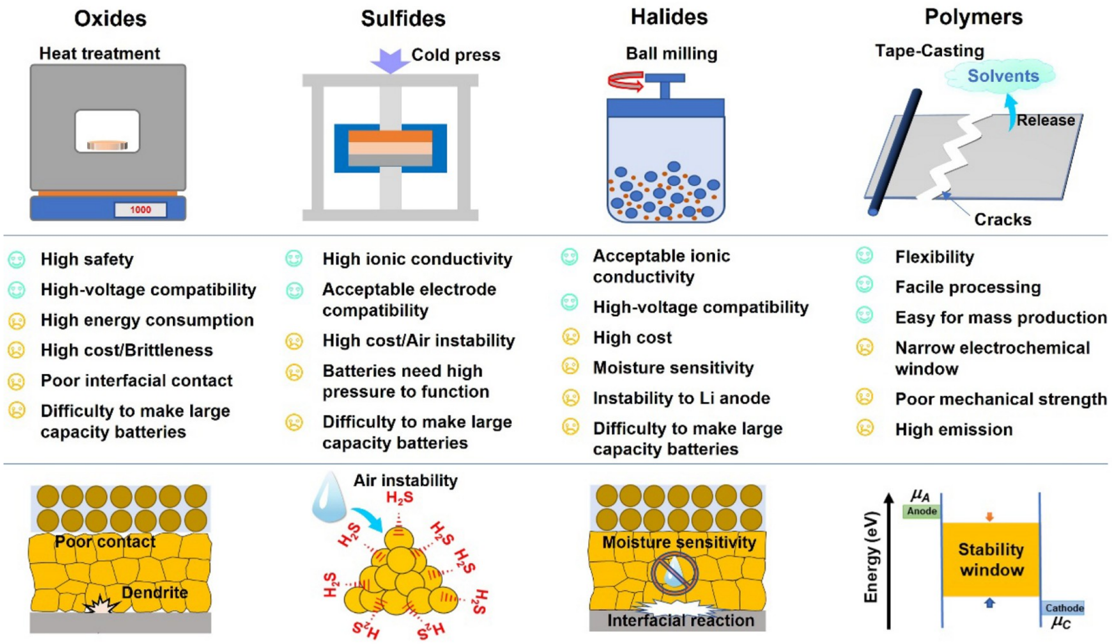

Figure 1 Different solid electrolytes, their preparation schemes and basic features. Advantages and disadvantages of each type of solid electrolytes are listed for comparison.

Sulfide electrolytes, such as $Li_{10}GeP_2S_{12}$ [10], $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ [11] and Li_6PS_5Cl [12], demonstrate high ionic conductivities of more than 10^{-2} S cm^{-1} because of the weak lithium-sulfur bonding. Although sulfides are relatively easy to synthesize at room temperature, it remains challenging to produce the electrolytes in air, because sulfides are moisture-sensitive, prone to react with H_2O to form poisonous gases and thus degrade the ionic conductivity. Integration of H_2S gas absorbing additives, such as metal oxides (e.g., Bi_2O_3, ZnO, Al_2O_3 and Fe_2O_3), sulfides (e.g., FeS), lithium halides (e.g., LiI) or Lewis acid additives, into the electrolytes can protect the sulfides from reacting with humid air and reduce the generation of H_2S gas [13], thus improving the chemical stability toward moist air. The favorable mechanical properties of sulfides do provide intimate electrode/electrolyte contacts, which allows batteries to perform reasonably well in the conventional sandwich geometry [14]. However, sulfides show an intrinsic narrow electrochemical window and poor compatibility with oxide cathodes, which limits their applications in batteries with high-voltage oxide cathodes.

Halide electrolytes, with a general formula of Li_3MX_6 (M = In, Y, Er, etc.; X = F, Br, and Cl) [15], achieve acceptable ionic conductivities because univalent halogen ions have large ionic radii and weak interaction with lithium ions. Compared with sulfides, halides show good compatibility toward oxide cathodes, thus can achieve impressive energy-density in high-voltage solid-state batteries. Compared with oxides, halides can be easily synthesized without high-temperature sintering, and deliver strong deformability and good mechanical softness. However, most halides containing non-Li metal cations are thermodynamically unstable against Li metal. Tuning the chemical composition of halides can alter the stability to some extent, especially in the case of LiF-enriched interface formation. In addition, lithium compounds that are thermodynamically stable against Li metal can be used as functional interlayers to protect halides from being reduced by Li.

Halides are also moisture-sensitive, which could significantly decrease the ionic conductivity in air as well. Developing innovative, economically feasible, and environmentally benign synthesis routes is an essential precondition for the successful commercialization of halides.

Inorganic (ceramic) solid electrolytes are much expected to inhibit the dendrite growth because of the high shear modulus. However, the dendrite penetration is rather prominent in ceramic electrolytes. Microstructure features of these electrolytes, such as grain boundaries, voids, pores, cracks and protuberance, all contribute to dendrite-induced shorting behaviors [16]. Grain boundaries exhibit relatively high electronic conductivity, which promotes the reduction of Li ions. Pre-existed/pre-generated defects, voids, pores, cracks and protrusions are also suspicious spots to aggravate the Li dendrite growth. These non-intimate sites at interfaces can easily generate a locally amplified electric field, which leads to the initial deposition of Li ions on them, inducing the inhomogeneous Li dendrite formation. Therefore, the shear modulus criterion proposed by Monroe and Newman [17] holds only for solid electrolytes without any inhomogeneity or defects. Unfortunately, it is nearly impossible to obtain a perfect inorganic solid electrolyte without surface defects, especially for the large-scale application of fragile ceramic electrolytes.

The energy density of solid-state batteries is limited by the cathode mass loading, the electrolyte thickness and the anode stability. Limited by the brittleness and synthesis/processing techniques, inorganic solid electrolytes are difficult to fabricate into thin membranes (thickness < 200 μm), which results in an energy density far below the level normally required for applications. Bulk-type solid-state batteries that are fabricated as a sandwich structure, including an anode layer, an electrolyte layer and a cathode layer, are not practical for large-scale productions and applications, since they require high pressure to function. Notably, most inorganic solid electrolytes contain rare earth elements or other expensive elements, such as La, Ge, and In. Meanwhile, their syntheses generally demand high temperatures and solid-state reactions, such as melt-quenching and ball-milling, which consume much time and energy. For sulfides and halides, the high moisture-sensitivity means that strict control of the environmental humidity is required from material synthesis, storage, and transportation to applications, which complicates the manufacture and operation of batteries and arguably not scalable [13]. In view of the above points, the massive production of inorganic solid electrolytes is not compatible with the state-of-the-art battery technology; therefore, it is unlikely that the current battery industry would welcome inorganic solid electrolytes.

Compared with inorganic solid electrolytes, polymer electrolytes demonstrate decent interface contacts, easy manufacture and economic availability [18,19]. Meanwhile, polymer electrolytes, to some extent, can overcome the safety problems of liquid electrolytes [20]. Polymer membranes can be obtained by tape-casting, the thickness of which can be easily controlled to be less than 100 μm [21]. However, most polymer electrolytes, such as polyethylene oxide, polyacrylonitrile, and poly(vinylidene fluoride) systems, demonstrate only limited ionic conductivities, and their batteries require high operating temperatures [22]. Polymer electrolytes usually have limited electrochemical stability and tend to decompose on electrodes, leading to the formation of interlayers with side products and further triggering capacity degradation or dendrite growth [23]. These issues are aggravated at elevated temperatures, and may lead to thermal runaway. Possible solutions are to combine multiple solid electrolytes compatible with respective cathodes and anodes, or to form stable interfacial layers at both cathode and anode sides to realize more electrochemically stable solid-state batteries.

Adding ceramic fillers into polymer electrolytes to form composites can modify electrolyte properties [24].

Fillers not only improve the ionic conductivity by decreasing the polymer crystallinity and/or creating extra conducting pathways at the polymer/filler interfaces, but also reinforce the mechanical strength, expand the electrochemical window and improve the thermo-stability [25,26]. However, the relatively low ionic conductivity and poor interfaces with high resistances still hinder the applications of composite polymer electrolytes in Li-based batteries working at room temperature.

As an intermediate state between liquid and solid, quasi-solid electrolytes are proposed to fabricate practical batteries [27]. Quasi-solid electrolytes combine merits of liquid electrolytes and solid electrolytes; they not only possess high ionic conductivities and superior electrode/electrolyte interface properties, but also exhibit excellent mechanical properties (solid but flexible) and good safety [28]. However, in quasi-solid electrolytes, liquid plasticizers are inevitably required to achieve satisfactory conductivity values. Although plasticizers in quasi-solid electrolytes result in poor thermal stability and safety hazards, recent researches reported non-flammable quasi-solid electrolytes, and corresponding solid-state batteries passed through the overheating and/or nail test [29,30]. In iteration, quasi-solid polymer electrolytes can overcome the problems of leakage and flammability of liquid electrolytes, satisfying the safety requirements.

Most polymer electrolytes have a narrow electrochemical stability window and cannot operate at the full voltage range of individual cathodes and anodes; they can be oxidized at high voltages or reduced at low voltages. Electrochemically decomposed electrolytes contribute to the interphase formation and increase the charge transfer resistance. Especially, plasticizers in quasi-solid polymer electrolytes greatly deteriorate the electrode/electrolyte interfaces. Unstable interfaces promote the deformation or destruction of the interface structure, and thus the morphology evolution and stress accumulation upon cycling, which results in poor electrochemical performances.

Additionally, Li dendrites can easily penetrate soft polymer electrolytes because of their relatively low moduli [31]. Impurity particles pre-located at the Li/electrolyte interface or resulting from side-reactions cause the irregular Li deposition. Electronically insulating impurity particles prevent the direct reduction of Li ions on the top of them. Instead, the nucleation and growth of Li can be preferentially concentrated at the edges of these impurities due to the increased local conductivity or electric field strength, giving rise to a globular or dendritic structure. To hinder the dendrite growth, host polymer materials, with differentiated function groups and macromolecular structures (cross-linking, copolymerization, etc.), can be employed to improve the mechanical strength. In addition, developing single Li-ion conducting polymer electrolytes can eliminate the concentration polarization and promote the uniform Li deposition.

Thin polymer electrolytes with robust mechanical strength are critical for the success of polymer-based batteries [32]. Many of the reported polymer membranes are thicker than commercial separators (e.g., Celgard), which will sacrifice the energy density. Additionally, the mass loading of active materials in commercial batteries is still too high for most of the reported solid electrolytes [33]. Therefore, most polymer-based batteries assembled in labs deliver an energy density far below the level required for practical applications, and the cycling and rate performances are quite limited as well. In addition, tape-casting of polymer membranes is complicated and always associated with the consumption of large amounts of organic solvents, which is detrimental to environments. Tape-casting of polymer membranes mainly includes casting, drying and die cutting processes. Due to the moisture-sensitivity of the used Li salts, these processes should be restricted in a drying room with a low dew point (e.g., −50 °C). Consequently, the electrolyte fabrication and the battery assembly are not compatible with the commercial roll-to-roll fabrication and electrolyte injection technologies.

Inspired by the liquid/solid interfaces in conventional Li batteries, the concept of "*in-situ* solidification" has been proposed for solid-state batteries, in which liquid precursors are *in-situ* polymerized from a liquid state to a (quasi-) solid-state inside a battery under mild thermal, light or electrical treatments [34,35]. Before solidification, liquid precursors with high mobility/wettability can adequately fill voids at the electrode/electrolyte interfaces and infiltrate porous cathodes. After solidification, the liquid is conformally solidified at filled sites, which not only guarantees continuous contacts among solid components for fast charge transport, but also maximally maintains the solid-state of batteries. Polymer electrolytes synthesized by the *in-situ* solidification can be easily controlled into a small thickness with less tendency of fracture in comparison with self-supporting electrolyte membranes [36]. Therefore, the *in-situ* solidification contributes to significantly improved interfacial contacts, and optimized thicknesses of individual layers (Figure 2A), which has significant implication in addressing the energy density and interface issues of solid-state batteries.

In terms of massive production, the *in-situ* solidification provides a simple scheme with high efficiency, low/no emission, because the preparation of electrolytes and manufacture of solid-state batteries can be completed in one step [21]. Moreover, the *in-situ* technique is highly compatible with the current manufacture technology of commercial batteries (Figure 2B). *In-situ* synthesized polymer electrolytes also show excellent thermal stability without solvent leakage/emission at high temperatures or long-term aging [37].

However, there are still several drawbacks in the *in-situ* synthesized polymer electrolytes. Unreacted residual monomers or low-molecule polymers in the electrolytes tend to decompose or deposit on electrode surfaces, which significantly increases the interfacial resistance and deteriorates the cycling performance [38]. Approaches, such as limiting the addition of active monomers, applying highly efficient initiators and appropriately increasing initiator amount, can reduce the content of residual monomers, therefore leading to enhanced electrochemical performances of polymer-based batteries. It is also convenient to add ceramic

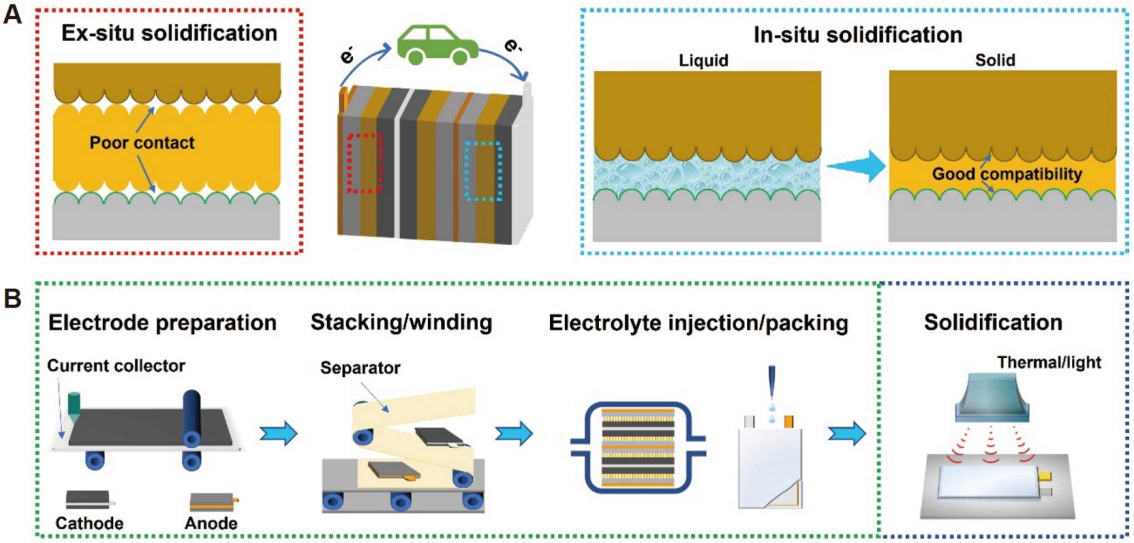

Figure 2 (A) Comparison of *ex-situ* and *in-situ* solidification of solid electrolytes. (B) Schematic illustrating the manufacture process of solid-state batteries when employing the *in-situ* solidification technique. The *in-situ* solidification is highly compatible with the state-of-the-art manufacture technology of commercial lithium-ion batteries (green area), which is then followed with an extra solidification process (blue area).

fillers, flame-retardants, functional additives, and other ingredients, which can effectively improve the ionic conductivity and the (electro)chemical stability [39]. Additionally, by employing the intermolecular chemistry, the *in-situ* solidification process leads to strong interactions among polymers, plasticizers/residual monomers/oligomers and Li salts, which help to inhibit parasitic reactions at electrode/electrolyte interfaces (e.g., the reaction between phosphate and Li metal), and accelerate the Li^+ transport.

In our opinion, the *in-situ* solidification of polymer electrolytes is the most feasible technique for the massive production of solid-state batteries. First of all, the technique is totally compatible with the state-of-the-art battery technology; secondly, the *in-situ* polymerization of liquid electrolytes inside batteries creates ultra-conformal interfaces between electrodes and electrolytes, which ensures excellent battery properties; thirdly, the residual liquid phase in quasi-solid electrolytes can accommodate the volume changes unavoidably involved in the charging/discharging of batteries; therefore, excellent cycling and rate performances are guaranteed. Although the pursuit of the all-solid-state electrolyte technology is believed to be the ultimate solution for the battery safety, respective batteries are still bound by interfacial issues and massive production technologies. These issues require much time and funding to overcome; thus the commercialization of all-solid-state batteries is not yet feasible in a short time. Since solid-state batteries with quasi-solid electrolytes can already achieve superior safety and high energy density, pursuing all-solid-state batteries is not really necessary at this stage.

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Conflict of interest

The authors declare that there is no conflict of interest.

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