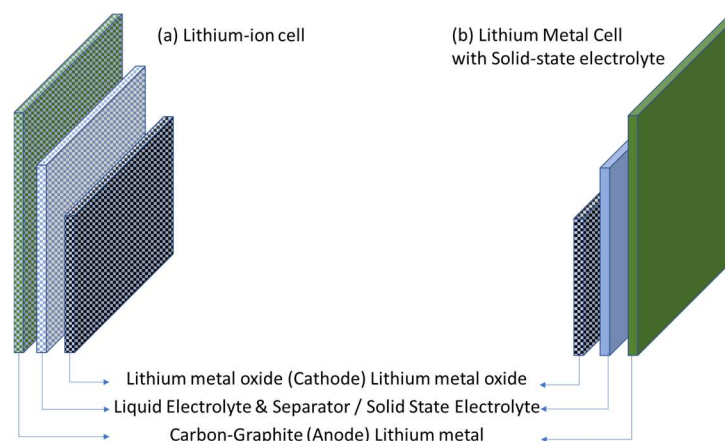


Polaris Reviews: Solid-state Electrolyte Lithium Batteries: Trends & Challenges

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Solid-state electrolytes (SSE) have been on the technology roadmap for rechargeable Lithium batteries^a for several decades now.^{1,2} The perceived benefits of these electrolytes for improving safety and for enabling the use of high energy-density Lithium metal anodes have motivated many researchers to develop novel solid-state Lithium ion conductors. **Figure 1** compares the basic construction of a Lithium-ion battery (LIB) with a Lithium-metal battery (LMB) that contains an SSE. In an LIB, ion transport between anode (Carbon -graphite) and cathode (Lithium Metal Oxide), is facilitated by solvated Lithium ions from a salt dissolved in a non-aqueous organic solvent, which forms a liquid electrolyte (LE). To prevent the anode and cathode from shorting in the tightly wound (or stacked) implementation of the cell, a microporous, electrolyte-absorbing separator-membrane (Sep) is used. In an LIB containing a gel-electrolyte, the liquid electrolyte forms a gel with a polymer. Cells containing gel-electrolytes may use separators for improved performance. While the liquid-electrolyte-separator (LE-Sep) configuration is primarily used in cells packaged in metal cans, the gel-electrolyte configuration is preferred for pouch cells, as the gel enables the desired stack pressure in a soft-package. An SSE replaces the LE-Sep (or the gel-electrolyte) with a single solid-state lithium-ion conducting layer, that performs both the electrolyte and separator functions. By eliminating the flammable non-aqueous electrolyte solvent, cell safety is significantly enhanced. Furthermore, solid electrolytes enable use of higher energy density Lithium metal electrodes, thereby paving a path to higher energy density energy storage, compared to state-of-the-art Lithium-ion.



^a The term Lithium batteries will be used here to broadly cover rechargeable Lithium-ion batteries and Lithium-metal batteries. The term batteries may also be used to refer to individual cells

Figure 1: Simplified schematics of basic construction of (a) Lithium-ion battery with a separator-liquid electrolyte combination and (b) Lithium-metal battery with solid-state electrolyte

While there have been some commercial implementations of Lithium-metal/SSE technology in niche applications, main-stream applications have largely eluded battery developers, due to performance and process limitations associated with the SSE. This white paper will review technology trends in the SSE area, key challenges that lie ahead, and our perspective on what needs to be accomplished before the technology becomes widely implemented.

1. Rationale for Solid State Electrolytes in Lithium Batteries:

After almost completely supplanting competing battery technologies in the portable electronics industry, LIBs are now making a serious push into the automotive industry to help displace the internal combustion engine. Along the way, the technology has also gained wide acceptance in other applications such as power tools and home & garden appliances. This widespread adoption of LIB is mainly attributed to the long run-times enabled by these batteries between charging events, i.e. their high energy-density. Depending on the application, these runtimes are maintained over several hundred to thousands of charge-discharge cycles, i.e. long cycle life. Furthermore, even though the LIB chemistry can be thermally unstable under certain use (or abuse) scenarios, judicious selection of chemistry, cell & pack designs, and battery management circuits & algorithms, have minimized the number of safety incidents in the field.

Even so, the quest for higher energy densities batteries continues, now spurred largely by the need for extended driving range in electric cars. New Lithium-ion anode and cathode chemistries continue to provide an incremental increase in energy density every year. However, the industry would prefer a leapfrog to LMB that could significantly increase energy densities by using Lithium metal as the anode, instead of carbon (graphite). The LE-Sep currently used in LIB are not a drop-in replacement for LMB. That is because repeated charge discharge cycling of LMB leads to the formation of dendrites on the Lithium-metal anode, which can puncture through the electrolyte-separator layer, leading to internal short circuits. At the very least, such a short-circuit issue could lead to performance issues such as poor cycle life. The more serious consequence is a potentially catastrophic failure of the battery, sometimes resulting in smoke and fire, due to the presence of the combustible LE. It is generally perceived that the dendritic growth on the Lithium anode can be thwarted by replacing the LE-Sep with an SSE. Furthermore, the combustibility of the SSE is significantly lower than the LE. Preferred characteristics in an ideal SSE include:

- *High ionic conductivity over a wide temperature range for high-rate charge-discharge*
- *Robust mechanical characteristics to withstand cycling and dendrite formation*
- *Stable electrochemical characteristics for cell integration and*
- *Scalable processing parameters for cost-effective manufacturing*

2. Compositional Classification of Solid-state Lithium Electrolytes:

Lithium-ion conducting SSEs are not a new concept. Lithium-Iodide inorganic solid electrolytes form spontaneously when a Lithium-metal anode comes into contact with an “Iodine” containing cathode during the fabrication of Lithium-Iodine batteries that are used in pacemakers.³ Polyethylene oxide (PEO), a well-known conductor of Lithium ions particularly at

temperatures above the polymer melting point ($\sim 60^\circ\text{C}$) of PEO,⁴ has seen limited application in batteries. Lithium Phosphorus Oxynitride (LiPON),⁵ another inorganic Lithium-ion conductor deposited using sputtering processes, has been used in the fabrication of thin film batteries. Indeed, the secondary-electrolyte interface (SEI) layer that is known to form in-situ in a LIB during the early formation and aging process can be considered as an SSE.⁶ Some of these solid-state electrolyte concepts still play a role in the current development of this technology.

Current Lithium SSE technologies can be classified into three major categories: (a) Solid polymer electrolytes (2) Inorganic electrolytes and (3) Composites or hybrid electrolytes. The key characteristics of these solid electrolyte classes are highlighted in **Table 1** and discussed below in further detail.

Table 1: Summary of Key Attributes of Solid-State Electrolytes

Type	Typical ionic Conductivity (S/cm) at $\sim 25^\circ\text{C}$	Typical Composition	Processing for Cell Integration	Representative candidates
Polymer SSE	$\sim 1 \times 10^{-4}$	Polymer / salt / inert filler	Extrusion / Casting	PEO – SiO ₂ – LiTFSI
Inorganic SSE(Oxides)	$\sim 5 \times 10^{-4}$	Ceramic metal oxides & phosphates (Perovskite, Garnet, NASICON)	Sintering at high temperatures & pressures	Li ₇ La ₃ Zr ₂ O ₁₂ (LLZO) LiAlTiPO ₄ (LATP)
Inorganic SSE (Sulfides)	$\sim 5 \times 10^{-3}$	Glassy Thiophosphates	Sintering at moderate temperatures & pressures	Li ₁₀ SnP ₂ S ₁₂ (LSPS)
Composite Electrolytes	$\sim 5 \times 10^{-4}$	Polymer / salt / Li-ion conducting filler	Mixing / Extrusion / Casting	PEO with LLZO / LSPS
Liquid electrolyte & Separator	$> 1 \times 10^{-3}$	Organic solvents / salt / microporous separator	Vacuum filling	$\sim 1\text{M}$ LiPF ₆ in EC/DEC/DMC in Polyolefin separator

a) **Solid polymer electrolytes:** The term solid polymer electrolyte (SPE) is generally applied to a liquid/solvent free system, that contains a Lithium salt dissolved in a polymer matrix. The key to achieving ionic conductivity in a polymer electrolyte is to ensure that the Lithium cation and corresponding anion in the salt are dissociated and that the Lithium ion is mobile to carry charge in the polymer matrix. One of the most widely studied Lithium SPE is the Polyethylene Oxide (PEO) – Lithium salt combination, wherein coulombic interactions between the oxygen on the PEO chain and Lithium cation result in dissociation of the Lithium salt, thereby freeing the Lithium cation to transport charge. Several other polymer hosts have also demonstrated the ability to conduct Lithium ions. However, for this discussion we will focus on PEO as the representative one. Plasticized polymer electrolytes, i.e. polymers with a low volume-fraction of liquid, and gel polymer electrolytes, i.e. polymers with a high-volume fraction of liquids are not classified here as SPEs. Lithium bis-trifluoromethanesulfonimide (LiTFSI) is widely used as a salt for SPE.

The ionic conductivity of a PEO electrolyte depends on the type of salt used, the molecular weight, percent crystallinity and glass transition temperatures the polymer. Only Lithium ions in the amorphous region of the polymer are typically known to carry charge, so a glass transition temperature well below ambient temperature is required. Ion transport is expected to take place via hopping from one oxygen coordination site to another, aided by segmental motion of the polymer. Conductivity can be enhanced by suppression of crystallinity, by the salt or by using

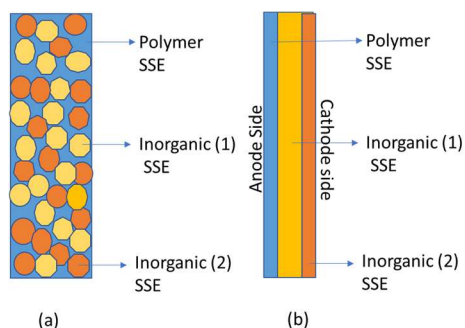
inert (non-conductive) fillers. Conductivities of around 1×10^{-4} S/cm have been achieved close to room temperature using SiO_2 (silicon dioxide) fillers and LiTFSI salt. In comparison, conventional Lithium-ion liquid electrolyte conductivity is around $\sim 1 \times 10^{-2}$ S/cm, and that for a LE-Sep combination is around $> 1 \times 10^{-3}$ S/cm.

b) **Inorganic electrolytes:** Inorganic solid-state Li-ion conducting electrolytes are usually ceramic or glassy materials that have oxide, phosphate, hydride, oxynitride, sulfide and thiophosphate compositions.² Two of the compositions that are the leading candidates in this category are the Oxides and the Sulfides.

i) **Oxides:** Typical members of this class of SSE include metal-oxides from the Perovskite (Lithium Lanthanum Titanate-LLTO), Garnet (Lithium Lanthanum Zirconate - LLZO) and LISICON (Lithium Zinc Germanium Oxide-LZGO) families. Lithium metal phosphates with NASICON structures, like LAMP (Lithium Aluminum Titanium Phosphate), may also be classified under this category. Ionic conductivities of best-in-class materials of this category are around 5×10^{-4} S/cm. In these oxides, Lithium ion transport occurs between interstitial sites and vacancies in the crystal structure. The Oxide electrolytes are ceramic materials that are synthesized by mixing the appropriate precursors in stoichiometric ratios and calcining them at relatively high temperatures, ranging from 600C-1200C. As-synthesized materials need to be subjected to high temperatures and pressures, so they can be processed into dense electrolyte layers for cell integration processes.

ii) **Sulfides:** Sulfide materials are glassy materials that are synthesized at much lower temperatures than the oxides. They are also softer and more easily processed into dense electrolyte layers than the oxide materials, thus requiring lower temperatures and pressures. Recent progress in some sulfides that belong to the Thio-LISICON class of materials like, Lithium Tin Thiophosphates (LSPS), and Halides like Argyrodite ($\text{Li}_6\text{PS}_5\text{Br}$, $\text{Li}_6\text{PS}_5\text{Cl}$), have led to the development of some materials with very high ionic conductivities in the $> 10^{-3}$ S/cm range. Some glassy electrolytes have been used to passivate Lithium-metal in non-aqueous Lithium-metal, Lithium-air and even aqueous Lithium batteries.⁷

c) **Composite electrolytes & Hybrids:**^b Composite or hybrid electrolytes refer to electrolytes that combine two or more types of electrolytes from materials sets discussed above, to achieve a synergistic optimization of the overall electrolyte performance.⁸ A schematic representation of composite and hybrid electrolytes is shown in Figure 2.



^b Combinations of polymer electrolytes with non-conductive fillers are classified as Solid Polymer Electrolytes

Figure 2: Schematic representation of (a) a composite SSE and (b) a hybrid SSE

In a typical composite electrolyte a SPE is intimately mixed with one or more of the inorganic electrolytes to achieve ionic conductivities higher than what can be achieved with the polymer electrolyte alone, while also improving the processability of the system and improving the ability of the material to inhibit Lithium dendrites in a Lithium metal battery (**Figure 2a**). Depending on the relative proportions of the polymer and inorganic electrolytes in the system, the composite may either be a polymer electrolyte reinforced with an ionically conductive filler or an inorganic electrolyte with an ionically conductive polymer electrolyte binder. In either scenario, minimizing the interfacial resistance for Lithium-ion transfer from the inorganic to the polymer medium and vice versa, are critical to achieving high overall ionic conductivities. For these composites to work, they will need to be electrochemically stable at the anode and the cathode.

The term hybrid electrolyte is used here to refer to distinct layers of different electrolyte materials sandwiched between the anode and cathode (**Figure 2b**). Each layer is selected keeping in mind its electrochemical stability with the layer next to it, with the overall construction needing to meet other performance requirements. For example, a PEO-based electrolyte may be used at the anode surface, while a metal-oxide layer is present at the cathode layer. Inorganic layers may be directly deposited on the electrodes using thin-film deposition techniques such as sputtering or atomic layer deposition (ALD). One of the layers in the hybrid electrolyte could well be a composite electrolyte. The viability of this hybrid approach would depend on the chemical and electrochemical stability of the electrolyte layers with each other. Multiple processes required for different electrolyte technologies will make this approach more expensive. That said, state-of-the-art Lithium-ion cells utilize cathode materials coated with inorganic oxides, to improve thermal stability and cycle life.

3. Key challenges for implementation in Solid-State Batteries:

Figure 3 compares the key attributes and limitations of the various SSE technologies, with cell integration and manufacturability in mind. Here we discuss these attributes and some of the challenges that need to be overcome for solid-state Lithium Metal batteries to become viable:

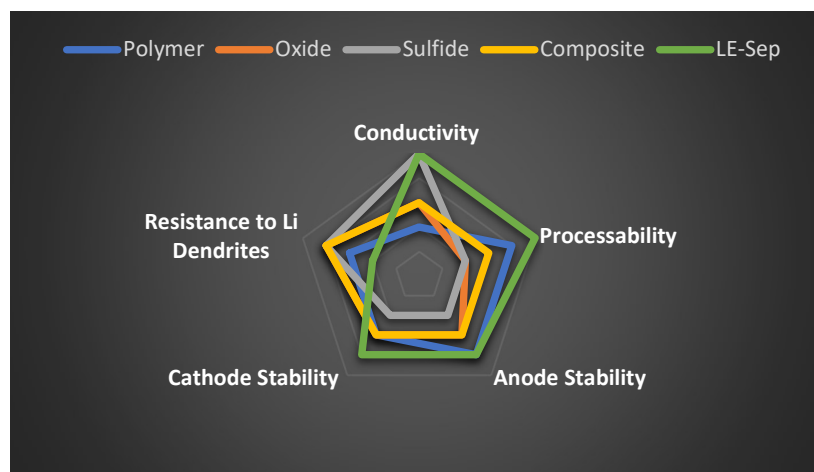


Figure 3: Qualitative comparison of key attributes and limitations of solid-state electrolytes

- a) *Ionic Conductivity:* Sulfide electrolytes come closest to meeting or even surpassing the ionic conductivities of liquid electrolytes. Inorganic oxides have reasonable ionic conductivities but are still about an order of magnitude lower. Room temperature conductivities of polymer electrolytes have improved steadily over the years. Yet, conductivity values still fall short of what is required for high rate charge and discharge. To some extent, lower conductivities in solid electrolytes could be compensated if electrolyte thickness values are reduced. The benchmark for today's separator technology in Lithium-ion batteries is 20 μ m. Achieving thickness values below 20 μ m in polymer or oxide SSEs would require a novel process that deposits the electrolyte directly on to one or both of the electrodes. Inorganic electrolytes are also expected to have density values 2-5x those of separators & electrolytes, which need to be taken into consideration for optimizing gravimetric energy densities.
- b) *Mechanical properties:* To prevent dendrite formation the SSE needs to be puncture resistant and mechanically tough for over hundreds-thousands of cycles. To this end solid oxide electrolyte are best suited, because of their hard, ceramic characteristics, if they can be fabricated into thin, dense, defect-free membranes. The ceramic characteristics may come as a disadvantage at electrolyte-electrode interfaces since the electrolyte needs to accommodate any expansion and contraction of the electrodes, to maximize cycle life. Sulfide electrolytes are softer than the oxides and may not have the same mechanical toughness as oxides. However, these softer characteristics may be beneficial at the electrode-electrolyte interface. The mechanical properties of polymers like PEO are akin to those of polyolefins that are used to make separators. Even so, polymer electrolytes will need to be made significantly tougher to withstand Lithium dendrites. Forming them into composites with inorganic fillers or utilizing multi-phase block copolymer structures are a couple of approaches being considered to address this issue.
- c) *Electrochemical stability:* Solid-state electrolytes need to be electrochemically stable at the low-voltage range at the anode as well as the high-voltage end at the cathode. PEO is known to be stable at the anode but can get oxidized at voltages >4V at the cathode. Charging to higher voltages (4.2-4.5V) is essential to achieving high energy densities. Oxide electrolytes have a relatively high oxidation voltage and have a wide-voltage stability window. Sulfide materials have low-oxidation stability and low-reduction stability at the cathode and anode, respectively. A commercially viable solid-state electrolyte may hence need to be engineered with multiple ionic-conductive materials to enable a wide electrochemical voltage stability window. Once again, a composite or hybrid structure may be better suited to optimize electrochemical stability. Alternatively, engineering anodes with artificial SEI layers and cathodes with cathode electrolyte interface (CEI) layers could address this issue. Ionic conductivity in the cathode layers also need to be addressed. In an LIB, liquid electrolytes provide this functionality in porous electrodes. In an LMB the cathode will have to be a composite layer of the cathode active material with an oxide, sulfide or polymer SSE interspersed in the layer.
- d) *Cost & Ease of Processing:* With regards to raw-materials cost, polymer electrolytes are expected to be of lowest cost. Raw materials cost for oxide materials may be a little higher than polymers because some of the precursors required for production may be expensive. The same

is the case for Sulfide electrolytes. Scalable processing parameters and cost-effective manufacturing are essential to commercialization of any mainstream battery technology. For solid state batteries, cell designs may vary from those used in Lithium-ion batteries. Spirally wound designs may be feasible for cells with flexible polymer or composite electrolytes. However, cells with inorganic electrolytes will need to use cell designs that can accommodate the inflexible nature of those solids, such as cut-and-stack designs.

Polymer electrolytes hold a distinct advantage over inorganic electrolytes in terms of manufacturability. They can be extruded or cast into membranes, to be spirally wound into cells - much like how a separator is integrated into a Lithium-ion cell. However, since Lithium salts are highly moisture sensitive, processing such membranes along with the salts at high temperatures (>100°C) could potentially lead to salt contamination or decomposition. In the process used in manufacturing Lithium-ion cells, the salt (dissolved in liquid electrolyte) is introduced into the cell at the final stage of the electrolyte assembly process, thereby preserving its integrity. Mimicking such late stage introduction of salts into the cell will require a radically different process, possibly one where the polymer is formed in situ, after cell assembly.

For the as synthesized inorganic oxides to be converted to effective electrolytes, they must be converted to dense membranes using high temperature (>1000°C) and high-pressure sintering processes. While such sintering processes may be viable for small test cells, scaling the same to achieve large areas of sintered materials required for large cells is expected to be a significant challenge.⁹ Processes like ceramic tape-casting and low-temperature cofired ceramics (LTCC) may need to be invented. Such a process may also be used to combine the inorganic SSE with cathode in “green” (non-sintered powder) form, and cofiring the combination.

With sulfide materials being softer than the oxide materials. they can be processed at lower temperatures and pressures. However, sulfides are both moisture and oxygen sensitive and can be difficult to integrate into cells during mass production. In the lab they are usually handled in oxygen-free glove box atmospheres. These conditions will be expensive to replicate in production. Oxide electrolytes may however be processed under ambient oxygen and moisture.

4. Summary & Future Perspective:

Each of the individual SSE technologies currently being developed have their unique issues related to performance, manufacturability, or cell integration. Considering this, a composite or hybrid electrolyte that utilizes more than one of the SSE technologies discussed above may be the best near-term option for a viable solid-state Lithium-metal battery. Even with this approach, the issue of Lithium ion transfer across the interface of one conductor with another still needs to be resolved and has been the focus of recent R&D efforts.⁸ Lithium-metal batteries using the composite or hybrid electrolyte concepts may be commercially viable in the 3-5 year time horizon, for applications that are less sensitive to cost, but require the performance offered.

For the longer term, improved materials with high ionic conductivities and optimum electrochemical stability, mechanical characteristics and processability are required. In addition to materials and process selection, cell design will also be a key aspect to track in solid-state battery roadmaps. Current spirally wound designs may transition to other designs, such as cut-and-stack designs used in fuel cells and capacitors, thereby enabling integration of all-inorganic

electrolytes. Such an all-inorganic solid-state battery may be at least 5-10 years away on the technology roadmap.

A recent market report¹⁰ on solid state batteries lists more than fifty companies and institutions working on solid-state electrolyte technologies. Several start-up companies have indicated that they have proprietary solid-state polymer electrolyte and inorganic electrolyte technologies that are currently viable in Lithium-metal batteries. Some large automotive manufacturers have also invested considerable internal R&D dollars for the development of new inorganic electrolytes, while simultaneously investing in the technology being developed by the start-ups. With the current push for electrification of the transportation fleet, it is safe to assume that the challenging race to develop batteries with solid state electrolytes is well underway.

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