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Current Status of Solid-State Electrolytes: Materials, Challenges, and Development

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Abstract. The global energy transition has reached a decisive stage. Conventional liquid batteries no longer meet what practical applications demand, and building energy storage systems that are at once highly safe and highly energy-dense has become the key to commanding the global power battery industry. Because they pair a nonflammable solid electrolyte with high energy density, solid-state batteries are widely regarded as the next-generation route past the technical ceiling of liquid lithium-ion cells. The electrolyte is the component that makes this possible.This study assesses three mainstream families of solid-state electrolyte, among them sulfides, oxides and polymers, and finds that each carries its own mix of strengths and weaknesses. No single material performs well on every count, and composite systems may prove to be the principal direction of future development. Progress from here will hinge on two lines of work advancing together: "material compounding" and "interface engineering". On that basis, solid-state batteries are expected to reach large-scale commercial use in electric vehicles, the low-altitude economy and AI robotics.

Keywords: Solid-state electrolyte, sulfide solid-state electrolytes, oxide solid-state electrolytes, polymer solid-state electrolytes

1. Introduction

Driving range and safety requirements have grown steadily more demanding across application scenarios, and solid-state batteries have drawn attention as a result. They are safe, they hold out the prospect of cell-level energy densities beyond 500 Wh/kg, and they tolerate a wider range of operating temperatures. The solid electrolyte is the component that defines an all-solid-state cell. It removes the risk of electrolyte leakage and combustion at source, and its comparatively high mechanical strength suppresses lithium dendrite growth, which in turn makes lithium metal anodes of very high theoretical specific capacity usable [1]. Developing electrolyte systems that deliver high ionic conductivity, a wide electrochemical window and good interfacial compatibility at the same time is therefore seen as the key route to industrializing solid-state batteries.

Sulfide electrolytes have broken through repeatedly on room-temperature ionic conductivity, passing the 10^{-2} S/cm mark, so that their transport performance now rivals that of liquid electrolytes [2]. Oxide electrolytes, with excellent thermal stability and a broad electrochemical window, were the first to be validated at scale in solid-liquid hybrid cells. Polymers, thanks to how readily they can

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be processed, reached limited commercialization in early thin-film batteries. No single system, however, has yet satisfied every core performance requirement at once. Modification studies aimed at the intrinsic defects of each system are plentiful, as is work on interface engineering, but systematic cross-system benchmarking and a coherent logic for functional integration are still missing.

Five mainstream families are covered here: sulfides, oxides, polymers, halides, nitrides. The treatment for each is the same. Advantages and drawbacks first, then the materials in common use, then recent breakthroughs and the directions research has taken. People hope the synthesis is of some theoretical use to fundamental research, and of practical use to industry in choosing technologies and planning strategy.

2. Core material systems

2.1. Sulfide solid-state electrolytes

Two properties make sulfides attractive: room-temperature ionic conductivity that is very high, and a mechanical ductility that ceramics cannot offer. Against that stands air sensitivity, and it is a serious liability. Moisture in the surrounding air is enough to make these materials react and give off hydrogen sulfide (H_2S), a toxic gas, which pushes up production costs and puts a hazard into the plant [3]. The intrinsic electrochemical stability window is narrow as well, usually 1.6–2.3 V. Put a sulfide in direct contact with a high-voltage cathode or with lithium metal and redox decomposition follows, leaving behind an interfacial impedance that is far from negligible.

Three sulfides account for most of the work done and most of the applications: $Li_{10}GeP_2S_{12}$ (LGPS), the argyrodites, Li_6SiS_5Cl for instance, and $Li_7P_3S_{11}$ glass-ceramics. LGPS is the performance benchmark at 12 $mS \cdot cm^{-1}$ at room temperature, and its one-dimensional and three-dimensional lithium-ion transport networks are unusual; they do a great deal for the power performance of a cell. Industry has settled on the argyrodites instead, for reasons more commercial than scientific. Chemical and electrochemical stability good enough to work with, costs that are comparatively low, and anion disorder that halogen doping can be used to tune. $Li_7P_3S_{11}$ belongs to the binary systems. Control the crystallization carefully by heat treatment and conductivity reaches 1.7×10^{-2} S/cm, which makes it a strong candidate wherever high-performance composite electrodes are being built.

Work of the past few years has gone after three bottlenecks. The first is the conductivity ceiling, and dual substitution with silicon and chlorine has given $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}C_{l0.3}$ (LSPSC), whose 25 $mS \cdot cm^{-1}$ is a record for solid conductors. The second is environmental tolerance, where hard and soft acid-base (HSAB) theory supplies the design rule: replace part of the P with softer cations such as Sn or Sb, or dope with O to improve the local structure. Either route cuts H_2S generation appreciably and improves stability in humid air [4]. The third is interfacial compatibility, approached by coating cathode surfaces with nanoscale $LiNbO_3$ buffer layers deposited by atomic layer deposition (ALD), and by inserting Ag-C nanocomposite anode layers. Side reactions at the interface are suppressed, dendrites no longer penetrate the electrolyte, and cells hold up for more than 1,000 cycles at energy densities around 900 Wh/L.

That last figure comes from the best known recent case in this system, the Ag-C nanocomposite anode from Samsung Electronics. In place of a pure lithium metal anode, a silver-carbon (Ag-C) nanocomposite layer sits between the sulfide electrolyte and the current collector. Ag alloys with Li, the nucleation barrier for lithium drops, deposition during cycling becomes uniform, and dendrites never get the chance to penetrate. Ah-class pouch cells built this way reached a volumetric energy

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density of 900 Wh/L and cycled stably past 1,000 times [5]. Safety improves, which was to be expected. Less expected is that the design also disposes of the interfacial failure that volume change in a lithium metal anode normally causes in a sulfide cell.

2.2. Oxide solid-state electrolytes

The main advantages of oxide solid-state electrolytes lie in their extremely high stability and broad electrochemical window, greater than 5 V, as well as their ability to effectively suppress lithium dendrite growth. However, the difficulty with this system is that the materials are hard and highly brittle, causing the electrode and electrolyte to form only rigid "point contacts," which generates enormous interfacial contact impedance. In addition, oxides usually require very high-temperature sintering, often above 1,000°C, to achieve densification. This not only increases energy consumption, but also readily triggers side reactions at the electrode interface [6]. Nevertheless, because oxide solid-state electrolytes offer high safety and long service life, they are currently the mainstream direction for mass production of semi-solid-state batteries.

Three representative materials dominate current oxide work: garnets such as $Li_7La_3Zr_2O_{12}$ (LLZO), NASICON-type materials such as $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP), and perovskites such as $Li_{3x}La_{2/3-x}TiO_3$ (LLTO) [7]. LLZO is thermodynamically stable against lithium metal and conducts well at room temperature once doped, which is why it is treated as the electrolyte of choice on the anode side of an all-solid-state lithium metal battery. LATP and LAGP are simple to prepare, stable in air and wide in electrochemical window, and they pair well with oxide cathodes. LLTO is the awkward one. Grain-boundary resistance is large and total conductivity consequently low, yet grain conductivity is very high and the composition can be tuned freely, so it still earns a place in composite and hybrid electrolyte systems [8-10].

Attention in this system has shifted away from conductivity alone toward interfacial compatibility and scalable preparation. On the materials side, a novel NASICON-structured compound, LZSP, prepared by liquid-phase ion exchange, has exceeded 3.59 mS/cm at room temperature while remaining stable against lithium. For the contact problem, "in-situ solidification" has become the major breakthrough of the moment: polymerizing a flexible buffer layer inside the cell compensates for the rigid contact that oxides otherwise make [11]. The most visible result to date comes from companies such as WeLion New Energy, whose oxide-based semi-solid-state cells reach 360–400 Wh/kg and have already passed vehicle installation validation in models including the NIO ET7. On the oxide route, this is the first real breakthrough in market application.

2.3. Polymer solid-state electrolytes

Polymer electrolytes are formed by complexing a polymer matrix, PEO or PVDF for instance, with a lithium salt. This is the oldest line of research and the only one ever to be commercialized, if only on a small scale. The appeal is practical: good mechanical flexibility, easy processing into films, low cost, and close compatibility with existing liquid-battery production lines [12]. The fatal weakness is conductivity. At room temperature, these materials manage only 10^{-8} to 10^{-6} S/cm, so they generally have to run hot, at 60–80 °C. Their voltage tolerance is low as well, below 4 V, which makes high-voltage cathodes hard to match. And because their mechanical strength is modest, they struggle in practice to block the short-circuit risk created by lithium dendrite penetration [13].

PEO, PVDF and PAN are the three materials in common use. PEO has the longest history and was commercialized first, at Bolloré in France; its ether oxygen units dissolve lithium salts unusually well, and lithium ions move mainly by local motion of chain segments in the amorphous

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regions. PVDF and copolymers such as PVDF-HFP have a high dielectric constant, good mechanical strength and sound chemical stability, and they are the usual choice for building quasi-solid-state or composite electrolytes. PAN attracts attention for a different set of reasons: a wide electrochemical window, good compatibility with high-voltage cathodes, and polar cyano groups that help lithium salts dissociate.

Efforts to break the ceiling here follow two strategies: in-situ solidification and multicomponent compositing. In-situ polymerization is the advance on the process side. Liquid monomers soak into the pores of the electrode and are converted to solid where they sit, which wets the interface at the molecular level and cuts impedance sharply. On the design side, the mainstream trend is to bring in metal-organic frameworks (MOFs) or ceramic nanofibers and build composite polymer electrolytes (CPEs) [14].

3. Technical challenges of solid-state electrolytes

3.1. Existing systems cannot balance all aspects of performance

Ionic conductivity in sulfides matches that of liquid electrolyte. Chemical stability does not. Trace moisture in the air will set off the release of toxic H_2S, and a narrow electrochemical stability window means a high-voltage cathode cannot be given lasting protection. Oxides invert the picture: intrinsic thermal stability excellent, mechanical strength high, yet brittle enough that fracture during processing is an ordinary occurrence, and film quality usually depends on sintering above 1,000 °C, at a heavy cost in energy and in elemental loss. Polymers are flexible and easy to work with, and their room-temperature ionic conductivity is generally too low to give useful power output. Halides hold high-voltage stability and plasticity together, and are still not stable enough against reduction to sit directly against a lithium metal anode.

3.2. Lithium dendrite penetration problem

In the early stage of research, it was believed that solid-state electrolytes with high shear modulus could theoretically suppress dendrites. However, practical studies have found that lithium metal tends to penetrate and grow along grain boundaries, pores, or microcracks inside solid electrolytes, ultimately causing internal short-circuit failure in batteries. This uneven deposition also produces "dead lithium", i.e., metallic lithium fragments that can no longer directly participate in electrode reactions because they have lost electron or ion transport pathways, leading to continuous capacity fading. In addition, because some electrolyte materials have non-negligible electronic conductivity, lithium ions may directly receive electrons inside the electrolyte and then nucleate and grow there, eventually causing unpredictable internal short circuits. Interfacial voids generated during lithium stripping can also induce uneven current distribution and form hot-spot effects, further accelerating dendrite nucleation in subsequent cycles.

3.3. Interfacial compatibility and kinetic failure

Unlike liquid electrolytes, which can naturally wet porous electrodes, solid-state electrolytes can only maintain rigid point contact with active materials, resulting in enormous interfacial contact impedance. During charge-discharge cycling, the volume expansion and contraction of electrode materials caused by lithium-ion insertion and extraction accumulate substantial mechanical stress at the rigid interface, triggering interfacial delamination, microcrack evolution, and even failure of the

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electrolyte layer. At the same time, differences in chemical potential between the cathode and the electrolyte drive lithium-ion redistribution and form a high-impedance space-charge layer. Decomposition reactions of the electrolyte under extreme potentials can also generate complex inactive intermediate phases, further worsening the kinetics of ion transport across the interface.

4. Conclusion

The solid electrolyte is the core component of an all-solid-state lithium battery, and its advantages in breaking the energy density ceiling and raising the intrinsic safety of the system are clear enough. All five mainstream families, though, show the same pattern: a pronounced strength shadowed by a pronounced weakness.

Sulfides have very high ionic conductivity and good mechanical ductility, which is why they are seen as the route most likely to scale; air stability is very poor and the electrochemical window narrow. Oxides bring thermal stability and a wide window, while intrinsic brittleness gives solid-solid contact impedance and high-temperature sintering makes manufacturing harder. Polymers are easy to process and behave well at interfaces, with room-temperature conductivity so low that high-power output stays out of reach. Halides combine a high oxidation potential with useful plasticity, but reduction stability against lithium is insufficient and the raw materials are expensive. Nitrides are thermodynamically excellent against lithium metal, and their low conductivity and narrow window rule them out as a standalone solution.

Multiscale problems continue to stand between these materials and practical use. Two of them are fundamental. One is the enormous contact impedance that comes of kinetic failure at solid-solid interfaces. The other is the internal short circuit caused by lithium dendrites penetrating along grain boundaries.

Where the field goes from here depends on "material compounding" and "interface engineering" evolving together. Composite electrolytes designed around spatial functional partitioning, combined with integrated interface engineering technologies, should let all-solid-state batteries make the leap from laboratory prototype to large-scale commercial application without giving up safety.

High safety and a step change in energy density also position solid-state batteries as a core power source for emerging fields, the low-altitude economy and AI robotics in particular. Nonflammability and wide-temperature performance suit the demands of safe flight in extreme high-altitude conditions. In robotics, doing away with the separator and with liquid electrolyte packaging makes the cells light, thin and geometrically flexible, so they fit neatly into the crowded interior of a humanoid robot. Long cycle life, at the same time, will raise the service efficiency of service robots and lower their maintenance costs. Major applications look likely in both fields.

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