Challenges, fabrications and horizons of oxide solid electrolytes for solid-state lithium batteries

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1 | INTRODUCTION

In 1991, SONY company commercialized the first lithium-ion batteries (LIBs).

A lot of progresses have been achieved for LIBs in the past 30 years. However, with little variation from the original structure and materials, LIBs have not delivered a great leap forward energy density. Due to the use of flammable organic electrolytes, safety has always been the Damocles, sword of LIBs, although it can be relieved by adding flame retardant additives or incorporating thermal-shutdown separators. Moreover, such external and internal protection measures generally increase manufacturing costs and reduce energy density. Nowadays, the present LIBs are still limited by low energy density, and electric vehicles using LIBs have been hampered by obstacles.

All-solid-state lithium-metal batteries (ASSLMBs) are considered as one of the next generation energy storage systems with high energy density and good reliability. It is one of the directions to achieve the specific energy of 500 Wh kg$^{-1}$ for automotive power and smart grid.

Lithium metal is considered to be the most promising anode due to its extremely high theoretical specific capacity (3850 mAh g$^{-1}$), low density (0.53 g cm$^{-3}$) and the lowest theoretical electrochemical potential (-3.04 vs. SHE).

However, because the electrochemical window of liquid electrolyte is limited, and lithium metal as the anode is not compatible, which is easy to induce lithium dendrite growth, remaining serious safety risks. Meanwhile, the unstable electrolytes (mainly carbonate solvents) undergo reduction decomposition to produce solid electrolyte interphase (SEI). The fragile SEI gets out of control and breaks down, causing...
large amount of inactive Li (so-called “death Li”), which will greatly reduce Columbic efficiency of lithium and generate high cell impedance.[13] Hence, LIBs using intercalation type anode have become the mainstream power supply instead of lithium-metal batteries (LMBs) based on Li metal anode.[6] While, the implementation of solid-state electrolytes (SSEs) could provide a bright future for LMBs.

As ionic conductors, SSEs can be used for solid state batteries. On the other hand, ASSLMBs can also be used for other purposes. Electronic states and ionic defects and ionic chemistry in Li-ceramics can be modulated by Li-operation, such as through intercalation and deintercalation, conversion and alloying. This kind of SSEs can be used in sensors, neuromorphic computers, and on-chip energy storage, performing a variety of functions in chip architectures and electronic devices (Figure 1).

Solid-state batteries assembled using SSEs are expected to improve the safety and energy density of LIBs.[16,17] this is due to the good flame retardancy of SSEs and high capacity of Li metal anode. In addition, a part of the SSEs has good mechanical strength and can be used as support material, which simplifies the battery design and generally improves the battery safety performance and durability. Besides, compared with liquid organic electrolyte, SSEs has a wider electrochemical window.[18] Solid-state electrolytes are non-flammable, non-volatile and stable at high temperatures. Compared with their liquid equivalents, for some solid Li-ion conductors, they also exhibit higher transfer numbers, high elastic modulus and wide electrochemical stability without any leakage problems. However, compared with liquid electrolyte, SSE is not fluid, which cannot wet the electrode material as liquid electrolyte. Therefore, Li$^+$ migration in SSE, volume change/strain, interface mismatch, and Li|SSE interface are the main challenges in ASSLMBs (Figure 2).[19]

Hence, SSEs should meet the following characteristics:[21]

1. High ionic conductivity (required room temperature conductivity $10^{-3}$ S cm$^{-1}$).
2. Low electric conductivity (generally less than $10^{-10}$ S cm$^{-1}$ to avoid short circuit inside the battery).
3. Low interface impedance with electrodes (in many cases, interface impedance is the primary reason of cell failure).
4. Good chemical and electrochemical stability (wide electrochemical working window) to avoid electrolyte reduction and decomposition reaction.

5. Strong mechanical strength and good compatibility with electrode materials (e.g., having similar thermal expansion coefficient or compression coefficient\[22\]) to avoid physical stratification between electrode layer and SSEs when battery temperature or pressure changes frequently.

6. Easy processing and low cost.

Solid-state electrolytes include inorganic electrolytes, polymers, and composites. The performances of various SSEs materials are quite different. Solid electrolytes have high rigidity, fire resistance. However, oxide SSEs faces the problem of lithium dendrite\[23,24\] which can still grow along the grain boundary and eventually lead to short circuit. Although lithium dendrites are a problem for various electrolytes But the critical current density for short-circuiting through dendrite penetration of oxide solid electrolytes is often lower, such as for LLZO at 0.05 mA cm\(^{-2}\) and for sulfide (Li\(_2\)S-P\(_2\)S\(_5\)) at a minimum of 0.4 mA cm\(^{-2}\). And nonaqueous solvents can go up to 3 to 10 mA cm\(^{-2}\).\[25\] Polymer electrolytes have good flexibility and can be used in a variety of battery systems.\[26,27\] But the severe flammability limits the polymer electrolytes. Sulfide electrolytes have higher ionic conductivity than oxide and polymer electrolytes, reaching 10\(^{-3}\) S cm\(^{-1}\) at room temperature. But the polysulfide shuttle effect seriously affects the performance of sulfide-based batteries.
collectors, etc., to solve the interface instability between the electrode and electrolyte. The second aspect can be used to create a protective layer through ex/in situ process. Zhao et al.\textsuperscript{[41]} introduced some new strategies related to liquid phase therapy, including interfacial wetting, in situ polymerization, and interfacial reaction. By taking advantage of the high mobility of the liquid phase, a conformal interfacial layer promotes effective ion migration, usually using organic liquid electrolytes and room temperature ionic liquids. Therefore, liquid phase therapy has a good application prospect in the actual interface engineering of lithium metal battery.

2.1 Garnet type solid electrolyte

The general chemical formula of traditional garnet is $A_3B_2(XO_4)_3$. Among them, A-B-X is occupied by cations and has face-centered cubic structure. When the X position is lithium ion, garnet has the ability of lithium ion conduction. As a SSEs, garnet usually contains 5-7 lithium ions in each structure.\textsuperscript{[42]} LLZO ($Li_7La_3M_2O_12$, $M = Zr, Sn, Hf$) is called Li7 system because there are seven lithium ions in the system.

The research process of garnet is presented in Figure 4. LLZO was firstly synthesized by Meier et al. in 2007.\textsuperscript{[50]} This cubic garnet type electrolyte has high ionic conductivity, and this structure has been shown to be able to hold up seven lithium ions. In addition, the negligible electron conduction, wide potential window range, and good chemical stability to lithium metal make this electrolyte one of the most promising electrolytes. The crystal structure of LLZO is shown in the Figure 5A, which is composed of octahedral $ZrO_6$ and dodecahedral $LaO_8$.\textsuperscript{[51]} The tetrahedral and distorted octahedral networks, formed by Li and Li vacancies, are interpenetrated with the skeleton structure. As shown in Figure 5, experiment and theoretical calculation method have been used to study the lithium ion transport mechanism.\textsuperscript{[50]} In the cubic structure, the Li-ion transport path is proposed to be is $24d$ → $96$ hours → $24$ d → $96$ hours → $24$ d in the cubic structure and $24d$ is the node location of...
the conduction path in LLZO.\textsuperscript{[52]} Based on the results of high temperature neutron diffraction (HTND), Han et al. also reported a similar transmission mechanism (24 d→96 hours→48 g→96 hours→24 d).\textsuperscript{[53]}

The concentration of lithium ions will not only affect the transfer path of lithium ions in the electrolyte, but also affect the garnet-type phase. With the increase of total lithium ion concentration, the share of tetrahedral position decreases, while the share of octahedral position increases. Therefore, the conductivity of the garnet structure electrolyte is closely related to the concentration of lithium ions. In general, the ion conductivity of lithium-rich garnet increases with the increase of lithium ion concentration. For the Li7 system discussed in LLZO, the ion conductivity has a linear relationship with lithium ion concentration.\textsuperscript{[55,56]} For example, the bulk phase conductivity of Li7 system (LLZO) with high lithium concentration is much higher than that of Li3, Li5 and Li6. The increase in conductivity may be due to an increase in the cell parameters of the cubic phase structure, an increase in the concentration of lithium ions, or a higher relative density (usually more than 92\%).\textsuperscript{[57]}

In general, the cubic phase garnet has better conductivity than the tetragonal phase garnet. In the cubic phase, with the increase of lithium ion concentration and the increase of sintering temperature, the concentration of lithium ion at the octahedral position increases, and the ionic conductivity of the garnet volume phase increases. If the grain boundary impedance is smaller, the total ionic conductivity of SSEs will be better. Therefore, the promotion of the LLZO electrolyte for garnet is also focused on these three directions: (1) stabilizing cubic phase (2) increasing Li-ion concentration (3) reducing grain boundary impedance.

Even so, the ionic conductivity is lower than that of the liquid electrolyte due to the influence of crystal structure, sintering temperature and grain boundaries. A wide range researches about doping with other elements (such as Ta,\textsuperscript{[58]} Nb,\textsuperscript{[59]} Ti,\textsuperscript{[60]} Te\textsuperscript{[61]}) into LLZO to improve the
ionic conductivity have been studied. And in fact, element doping can not only improve the ionic conductivity of LLZO, but also can optimize the process of sintering, making obtaining high ionic conductivity of the cubic phase under the condition of low temperature sintering possible. Al\(^{[62]}\) W\(^{[63]}\) and the elements such as Ga\(^{[64]}\) are often used to study.

At the same time, some double ion doping can also improve the ionic conductivity. The second ion (except Al\(^{3+}\)) can change the diffusion channel of lithium ions, thus increasing the mobility of lithium ions (\(\mu\)). As previously reported, both Al\(^{3+}\) and Ta\(^{5+}\)\(^{[65]}\) and Al\(^{3+}\) and Te\(^{6+}\)\(^{[66]}\) systems have high ionic conductivity of \(10^{-3}\) Sc m\(^{-1}\) at 25°C. Recently, another two-ion doping system (i.e., Ga\(^{3+}\)&Sc\(^{3+}\) system) has been developed to enhance the ionic conductivity of the LLZO, in which Ga\(^{3+}\) is used to stabilize the cubic phase and Sc\(^{3+}\) is sequentially partially occupied to the Zr site to increase the concentration of lithium ions.\(^{[67]}\) This unique LLZO based material has a high ionic conductivity of \(1.8 \times 10^{-3}\) Sc m\(^{-1}\) at 27°C. A variety of optimization methods have been investigated to enhance the ionic conductivity of LLZO that can meet the requirements of battery applications.

In addition to ion doping, the mixing of oxides has also been proved to be effective methods to improve the performance of oxide solid electrolyte. Lin et al.\(^{[68]}\) mixed MgO and La\(_2\)Zr\(_2\)O\(_4\) into the four kinds of LLZO ceramics, and the composite electrolyte obtained has a highly dense microstructure and the most balanced performance of repeatability. Due to its compact microstructure, small amount of pores and good electrical conductivity, Li-Li symmetry and Li-Scellsshow good performance, indicating that composite ceramic micro porous ceramics have broad prospects in the application of batteries. Similar work was reported by Huang et al.\(^{[69]}\) a kind of dense Ta-LLZO/MgO composite solid electrolyte has been reported. Huang et al studied the influence of MgO on the sintering process, microstructure and properties.

While, although garnet oxide electrolytes have good stability for lithium metal compared with LLTO and LAGP,\(^{[22,70]}\) another problem that limits the application of LLZO SSEs is the instability of this electrolyte to water and carbon dioxide in the air. Exposure in the air will produce various impurities, such as Li\(_2\)CO\(_3\),\(^{[30,71]}\) resulting in a large impedance, which is mainly due to the Li\(^{+}\)/H\(^{+}\) exchange will occur in air.\(^{[72]}\)

2.2 \ NASICON type solid electrolyte

LiGe\(_x\)Ti\(_{2-x}\)(PO\(_4\))\(_3\) is a kind of NASICON type SSEs. The general formula of NASICON is AM\(_2\)X\(_4\)O\(_{12}\), in which the skeleton of [M\(_2\)X\(_3\)O\(_{12}\)] forms the basic structure of NASICON and MO\(_6\) octahedron and XO\(_4\) tetrahedron are connected in the form of common angles, forming the ion transport channel.\(^{[33,34,73,74]}\) NaM\(_2\)(PO\(_4\))\(_3\) (M = Ge, Ti, Zr), originally identified in 1992, has a NASICON structure.\(^{[75]}\) and Na\(_x\)Zr\(_2\)Si\(_3\)P\(_{3-x}\)O\(_{12}\) becomes a kind of sodium ion conductor with high ionic conductivity.\(^{[76,77]}\)

The research process of NASICON is presented in Figure 6. The NASICON type solid electrolyte in solid state lithium battery is Li system (A\(_x\)M\(_2\)X\(_4\)O\(_{12}\)), and the electrochemical properties as well as structure of the solid electrolyte change with the composition of the compound. The cellular parameters of LiM\(_2\)(PO\(_4\))\(_3\) (M = Zr Ge Ti Sn) in lithium system depend on the ionic size of the transition metal M. A common method to improve the conductivity performance is the doping of trivalent ions, such as replacing Ti\(^{4+}\) with Al\(^{3+}\) with smaller ion radius in LiTi(PO\(_4\))\(_3\), which significantly reduces the cellular size of NASICON. In the Al doped ceramic, the stoichiometric ratio of Li\(_{1.3}\)Al\(_{1.7}\)Ti\(_5\)(PO\(_4\))\(_3\) has the highest lithium ion conductivity, and at 298 K bulk phase conductivity is \(3 \times 10^{-3}\) Sc m\(^{-1}\), an increase of three orders of magnitude.\(^{[83]}\)

LAGP is a solid solution of Li\(_x\)Al\(_x\)Ge\(_{2-x}\)(PO\(_4\))\(_3\) obtained by replacing Ge\(^{4+}\) with trivalent metal in LiGe\(_x\)(PO\(_4\))\(_3\) which has the smallest cellular parameters. The ionic conductivity of the sample was greatly improved, reaching 5\(\times 10^{-3}\) Sc m\(^{-1}\). At the same time, an electrochemical window of up to 6 V gives this solid electrolyte more promising applications. Unfortunately, comparing with LLTO and LLZO, LAGP has very low stability with lithium metal, as indicated by the following equations.

\[\text{GeO}_2 + 4\text{Li} \leftrightarrow \text{Ge} + 2\text{Li}_2\text{O}, \Delta G \approx -150\text{kJ mol}^{-1} (\text{Li})\]

\[\text{GeO}_2 + 4\text{Li} \leftrightarrow \text{GeO} + \text{Li}_2\text{O}, \Delta G \approx -112\text{kJ mol}^{-1} (\text{Li})\]
2.3 | Perovskite solid electrolyte

LLTO is a solid electrolyte of type ABO$_3$ perovskite with a cubic phase structure. LLTO can be obtained by replacing La$^{3+}$ in LaTiO$_3$ with lithium ions. [86] This solid electrolyte was formed in 1987 by replacing the A position in titanate compound (ATiO$_3$) with La$^{3+}$ and Li$^+$. The research process of LLTO is shown in Figure 7.

Titanium ions and oxygen ions form the angle connection of TiO$_6$ octahedral structure, and the gap formed contains lithium ions and lanthanum ions. Therefore, like garnet electrolyte, the ionic conductivity of LLTO also depends on the concentration of lithium ions. In LLTO, lithium ions migrate through the ion-vacancy transition mechanism in the skeleton. In the transition process, lithium ions need to pass through a quadrilateral gap formed by four oxygen, and the concentration of quadrilateral gap directly affects the transition rate of lithium ions. Although the ionic conductivity of LLTO can be as high as $1.43 \times 10^{-3}$ S cm$^{-1}$ in theory, the conductivity of LLTO is obviously lower than that of single crystal material due to the barrier effect of grain boundary. The high conductivity is due to a large number of vacancies in the tetragonal phase structure, which allows the transition of lithium ions by vacancy mechanism. In addition, below 400 K, the conductivity obeys the Arrhenius relation, and the conductivity of lithium ion is excited by heat. With the increase of temperature, the activation energy and pre-exponential factor both increase to a certain extent. This suggests that as the temperature rises, the path of lithium ions will change. In addition, unlike the garnet type LLZO, rare earth elements are not required in the production process, thus providing a good cost advantage.

2.4 | Composite polymer electrolytes

Oxide solid electrolyte can also be used as inorganic filler to form composite solid electrolyte. A feasible solid-state lithium battery (SSLBs) can be constructed by combining two or more hybrid electrolytes with complementary advantages of SSE. Li et al. [94] introduced that composite electrolytes with garnet as inorganic fillers generally exhibit higher ionic conductivity than pure polymer-based electrolytes, excellent thermal and electrochemical stability, better flexibility and lower interfacial resistance than LLZO ceramics. Sun et al. [95] described the strategy for improving ionic conductivity of hybrid electrolyte, optimizing electrolyte/electrolyte and electrolyte/electrode interface through hybrid aging, and the feasibility of SSLB strategy for different hybrid electrolyte combinations. Cheng et al. [96] focused on the derivation materials of organic-inorganic composite electrolytes (O-ICSEs), including the enhancement mechanism of chemical properties, were mainly studied, and the basic characteristics of effective fillers were determined.

3 | PREPARATION METHODS OF OXIDE SOLID ELECTROLYTES

These three solid electrolytes are all inorganic oxide solid electrolytes, which share certain similarities in synthesis and preparation, and have the same goals in synthesis, such as increasing density, reducing impedance, stabilizing phase, improving ionic conductivity, and achieving...
The general preparation methods of solid oxide electrolytes with various dimensions including bulk, film, and fiber will be introduced first, and then introduce several unique or advanced preparation methods of LLZO, LLTO, LAGP.

### 3.1 Preparation methods of bulk materials

#### 3.1.1 Solid-state reaction

Solid-state reaction (SSR) method refers to the powder sintering method that does not melt in the sintering process. This method is one of the most common preparation methods of oxide solid electrolytes. This method has the advantages of simple process and low cost. Solid solutions or new compounds are formed by ion diffusion during multi-component solid phase sintering. In this method, ion diffusion plays a decisive role in the formation and homogenization of the prepared product, and the rate of ion diffusion and its homogeneity have an important effect on the quality of the product. In the actual preparation, in order to improve the purity of the product and shorten the reaction time, several methods are usually applied, such as using finer powders, improving the uniformity of powder mixing, appropriately raising the sintering temperature, and so on.

Ball milling is one of the most commonly used effective means to refine powder and improve the mixing uniformity of reactants. Ball-milling beads of different sizes and ball-milling solvents (usually alcohol solutions) must be added to the ball mill. Ball-milling solvents are thought to be beneficial for reducing particle size. Smaller particles tend to be beneficial for sintering. Compared with the larger 10 µm particles sintered at the same temperature, the smaller 1 µm particles have better densification. However, Cheng et al. found that the commonly used isopropanol solutions, although alcohols effectively reduced particle size, caused significant Li⁺ loss due to Li⁺/H⁺ exchange, which was not conducive to densification in the sintering process. They improved the solvent to acetonitrile with a small amount of surfactant, and successfully reduced the particle size to 220 nm, thus reducing the sintering temperature without affecting the concentration of Li⁺.

In the sintering process, the temperature and time will affect the grain size and grain boundary size of the solid electrolyte, and then affect the overall conductivity of the solid electrolyte. At the same time, another problem need to be considered is that in the process of high temperature sintering, lithium element will inevitably escape, so a little excess lithium source is often added in the ball milling. It was found that the cooling rate would affect the phase of the solid electrolyte, and the difference of the volume phase would lead to the change of the lithium ion transfer channel, thus affecting the ionic conductivity.

For the solid-state reaction method, it is the most common method for the preparation of solid electrolyte in the laboratory. However, ceramic particles tend to form cracks and cavities during sintering, leading to the decrease of density. In order to obtain more stable structure and better ionic conductivity, sintering research focuses on the reasonable adjustment of sintering temperature and sintering time, or the addition of sintering additives, doping ions and so on.

Take Ta doped LLZO prepared by solid state reaction as an example. With LiOH, La₂O₃, ZrO₂, Ta₂O₅ as raw material, 20% excess LiOH need to compensate the volatilization of lithium in the high temperature calcination. All the chemicals with the stoichiometric ratio are mixed in isopropyl alcohol, and after 6 hours ball milling and 6 hours calcination under 950 °C, the Ta-LLZO powders are obtained. With Al₂O₃ as sintering additive, powders are pressed into green pellets under static pressure and sintered less than 1100 °C for 12 hours. During the sintering process, in order to avoid the loss of lithium, mother powders are used to cover the pellets. LLZTO ceramic pellets are finally obtained, which are polished with sandpapers to remove impurities on the surface, and stored in an environment isolated from water and CO₂.

#### 3.1.2 Sol-gel method

Sol-gel method refers to a preparation method of uniform mixing of reactants through the process of solution-colloid-gel-solid change, which involves the preparation of inorganic salt oxide or hydrated hydroxide dispersion system, such as the hydrolysis of metal ions to prepare gel:

\[ M_n + H_2O \leftrightarrow M(OH)_n + nH^+ \]

In the process of hydrolysis, by gradually adding alkaline solution to the metal salt solution, the hydrolysis reaction can be promoted to the right, and the hydroxide sol is obtained. After dehydration, sol becomes into gel. Through drying, baking and other processes, metal oxide powders can be obtained from gel.

Adding complexing agent is an effective means to reduce the effect of metal ion difference on sol-gel process. Citrate is a common complexing agent. It makes different metal ions fully mixed through complexing, to reduce the difference of metal ions hydrolysis and precipitation, and ensure the chemical homogeneity of various metal ions mixed in the sol gel method. The characteristics of the
The relationship between the synthesis method and the thickness of solid electrolyte. [32,33,97-103]

sol-gel method are the target ions can be mixed on the ion/nanometer scale with good chemical homogeneity, which can reduce the subsequent calcination temperature. Ling et al. compared the Zr-doped LLTO prepared by the solid-state reaction method and the sol-gel method, and the results showed that the sol-gel process was more feasible in achieving chemical stoichiometry than the solid-state reaction. They found that ZrO₂ occurs at a higher X value in X-ray diffraction (XRD). Besides considering the conductivity, sol-gel process is better for the synthesis of LLTO than solid-state reaction. [109] The main factor affecting the purity of the particles prepared by sol-gel method comes from cheating additive, and the loss of ball mill beads caused by long time high-energy ball milling may affect the purity of the particles prepared by solid reaction method. So it is necessary to reasonably choose the preparation method and conditions according to the requirements (Figure 9).

The factors affecting the quality of sol-gel powders include pH value of solution and drying conditions, etc. Compared with solid-state reaction, the preparation process is complex and the yield is low. Therefore, sol-gel method is generally not the preferred method for preparing ceramic powders. It is often used as a liquid intermediate to produce thin film solid electrolyte or composite solid electrolyte. [107,108,110,111] In order to solve the energy loss and high cost of sintering for a long time at high temperature, some auxiliary methods are used to optimize the above preparation process, such as hot pressing (HP), [112] spark plasma sintering (SPS), [103] field assisted sintering (FAST), [113] cold sintering process (CSP) [114] and so on. Hu’s team produced a ceramic solid electrolyte film by sintering in 3 seconds using printing and radiation heating. [115] [116]

Distinguish from conventional solid-state reaction method and sol-gel method. There are some synthesis and preparation methods can be used to provide special forms of solid electrolyte, such as film, fiber, etc. On the one hand, it can obtain solid electrolyte which have higher electrolyte conductivity and lower interface impedance than the traditional preparation methods, or save energy and avoid sintering at high temperature for a long time. On the other hand, this kind of method can be special oxide solid electrolyte, such as thinner oxide solid electrolyte, softer oxide solid electrolyte, fiber oxide solid electrolyte, etc. [117,118]

### 3.2 Preparation methods of thin films

Although all-solid-state battery assembled from solid electrolytes have a high energy density due to the application of lithium metal anode and high capacity positive electrode. However, due to the larger size and mass of the ceramic particles the energy density of the ceramic particles in the case of the same anode material will be reduced compared to that of the liquid battery, or the solid battery using the polymer thin film solid electrolyte. [35,119] In addition, the thick solid electrolyte pellet also brings high impedance. Most of the oxide solid electrolytes have high rigidity and brittleness, which brings obstacles to the assembly of solid battery and the mass production of electrolyte sheets. The oxide solid electrolyte obtained through high temperature sintering consumes a lot of energy and is not suitable for commercial production. Therefore, Radio frequency magnetron sputtering and tape casting methods are introduced here to prepare flexible or ultra-thin solid electrolytes (0.1 to 100 µm) (Figure 8), and to meet the requirements of large-scale and low-cost production. [36,99,120] The concept of all-solid-state thin film electrolytes have been demonstrated by lithium phosphorus oxynitridide glass electrolytes (LIPON). [121] With careful adjustment, the magnetron sputtering process can result in a reduction of defects and thus a reduction of interfacial impedance. The thin film deposition of the electrolyte on the anode or cathode material can reduce the resistance by 1–2 orders of magnitude compared to the traditional preparation process.

#### 3.2.1 Radio frequency magnetron sputtering

Magnetron sputtering is a kind of physical vapor deposition, which was initially used to make metals, semiconductors, insulators and other materials, and has the advantages of simple equipment, easy control, large coating area and strong adhesion. Under the action of electric field, electrons collide with argon atoms in the process of flying to the substrate, which ionizes and generates Ar positive ions and new electrons. The new electrons fly to the substrate, and Ar ions accelerate to the cathode target under the action of electric field, and bombard the target surface with high energy, making the target sputtering. In the sputtered particles, the neutral target atoms or molecules are deposited on the substrate to form a thin
film. This technology can not only produce solid electrolyte films for solid-state lithium batteries, but also study doped thin film electrolytes. For example, Liu et al.\cite{122} reported a Sm$^{3+}$ and Nd$^{3+}$ co-doped CeO$_2$ nanocrystalline thin film electrolyte prepared by RF magnetron sputtering method.

Usually, high purity solid electrolyte is used as the target material. By adjusting the deposition temperature and sputtering power in the inert gas, the ideal electrolyte film can be obtained by depositing on a clean substrate.\cite{123} The effects of temperature and power on thin films have been studied extensively. For example, Laptev et al.\cite{123} made a research about the effect of deposition temperature on the preparation of Li$_7$La$_3$Zr$_2$O$_{12}$ thin films. It was deposited in argon atmosphere with Li$_{0.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ as the target material at 150 °C to 800 °C. And a research about the effect of Radio frequency magnetron sputtering powder was made by Yoon’s group.\cite{123} XPS analysis showed that the concentration of Li$_2$O films deposited at 40 W RF power was higher than that of 60 and 80 W samples acting as Li modifiers in oxygen electrolytes which mean the conductivity of the films increases with a lower deposition power, the best group was deposited at 40 W which up to a value of $4 \times 10^{-7}$ S cm$^{-1}$ with the lowest activation energy of 0.70 eV, better than 60 and 80 W. Figure 10 overview some methods of preparing thin films oxide solid electrolyte. The thin films oxide solid electrolyte prepared by these strategies have good properties, at the same time the reduce the Li loss during film deposition or post-annealing through magnetron sputtering or chemical vapor deposition (CVD).

3.2.2 Tape casting

The traditional solid electrolyte preparation method is not only faced with the production of electrolyte with the thickness of millimeter, but also restricted by energy consumption and cost, which makes it difficult to carry out large-scale production. The tape casting method can
Figure 10  Schematics of unique deposition technology to obtain solid oxide electrolyte thin films. A. Thin films prepared by co-sputter sputtering. B. Construction of internal lithiation sources with secondary target for vacuum-based films. C. Overlithiation of precursor solution for wet-chemical films. Copyright 2021, Springer Nature

Table 1  The preparation methods of thin film electrolytes and their ionic conductivity in the literatures

| Electrolyte materials          | Thickness [µm] | Ionic conductivity [S cm⁻¹] (RT) | Method                | Ref. |
|--------------------------------|----------------|---------------------------------|-----------------------|------|
| $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{1.6}(\text{PO}_4)_3$ | 75             | $3.3 \times 10^{-4}$             | tape casting           | [126]|
| $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ | 25             | $1.0 \times 10^{-4}$             | tape casting           | [35] |
| $\text{Li}_0.7\text{La}_0.3\text{TiO}_3$                  | 9.4            | $3.5 \times 10^{-7}$ (NM)        | spin coating           | [125]|
| $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$             | 200            | $2.4 \times 10^{-5}$             | tape casting           | [127]|
| $\text{Li}^-\text{La}^-\text{Zr}^-\text{O}$               | 9.4            | $4 \times 10^{-7}$               | RF magnetron sputtering| [99] |
| $\text{Li}_1\text{Al}_{1.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ | 1.2            | $1.3 \times 10^{-6}$             | RF magnetron sputtering| [120]|
| $\text{Li}_1\text{La}_3\text{Zr}_2\text{O}_{12}$           | 0.2            | $1.2 \times 10^{-4}$             | RF magnetron sputtering| [124]|
| $\text{Li}_1\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$     | 1              | $1.0 \times 10^{-4}$             | RF magnetron sputtering| [128]|

provide an alternative route for large-scale preparation as well as an attempt to reduce electrolyte thickness.\cite{[125], [126]}

The specific process of tape casting method is that ceramic powder is mixed with various additives in the solvent to form a uniform and stable precursor. When forming, the material flows on the baseband, and the film is formed through the relative movement of the scraper and the baseband, and the thickness is controlled by the distance between the scraper and the baseband. The diaphragm is sent into the dry chamber together with the baseband. In the process of solvent evaporation, the thin sheet with certain strength and flexibility is formed by bonding the ceramic particles together with the film forming action of the binder. The dry thin sheet is formed together with the baseband or separated from the baseband. Then it can be punched or cut according to the desired shape, and finally sintered to a finally product. Zhang et al.\cite{[126]} synthesized solid electrolyte membranes with a thickness of about 75 µm at low cost by the tape coating method. Spin coating method is similar to tape casting method.\cite{[35]} Table 1 summarizes the preparation and properties of some common thin film electrolytes.
3.3 | Preparation methods of fibers

3.3.1 | Electrospinning

Electrospinning is often used to investigate the nanostructure of solid electrolytes and their phase transitions, as it is a general method for preparing ceramic nanofibers or nanowires from sol-gel precursors. This technique has the following advantages over the other preparation methods.

1. The morphology is controllable, and the structure and composition of the electrospun material can be well realized by adjusting the parameters of electrospinning and subsequent annealing process.
2. By adjusting the precursor solution, electrospinning can produce almost all nanoscale ordinary materials including electrolytes, anode material, cathode material.
3. One-dimensional nanostructures prepared by electrospinning can be connected to each other into a three-dimensional network, which improves the electrical conductivity and structural stability.

Electrospinning is often used for the preparation of polymer electrolytes and composite electrolytes, but can also be used for the preparation of nanowire oxide solid electrolytes. In the case of LLZO, Cui's group reported a kind of LLZO nanowires. A nitrate or acetate based sol is mixed into a polyvinylpyrrolidone (PVP) solution to prepare the precursor. After electrospinning, the first spun nanowires were stripped from the collector as flexible pads and calcined in the air in an alumina crucible at 700 °C to remove PVP and crystallize the nanowires (Figure 11).

4 | THE INTEGRATION OF ALL-CERAMIC LITHIUM BATTERIES

Like common liquid-state LIBs, solid-state batteries are assembled with a positive electrode, a solid electrolyte and a negative electrode. In the process of assembly, there are many problems, for example oxide solid electrolyte in the air is unstable to CO₂ and H₂O so it is necessary to carry out strict control of the assembly environment. This makes large-scale manufacturing and assembly of solid-state batteries face challenges. This section describes some monolithic forming methods that can help reduce interface impedance by optimizing and mitigating interface problems during the cathode-solid electrolyte integrate process. The ultimate goal is to integrate the oxide solid lithium batteries, namely all ceramic lithium batteries.

4.1 | The integration of ASSLBs by co-sintering method

4.1.1 | Conventional sintering method

Liquid-state lithium battery and solid-state lithium battery have certain similarities. For example, in the choice of cathode, LiCoO₂ (LCO) and other cathode materials are also popular in solid-state battery. In order to prepare a solid-state battery, these cathode materials need to be sintered with oxide solid electrolyte at a high temperature. Whether the cathode materials and solid oxide electrolyte can be co-sintered to obtain composite cathode material has aroused people’s interest. Besides, high temperature co-sintering is able to enhance the contact of solid electrolyte and cathode material.

Unfortunately, although high temperature sintering can improve the interface contact, it may also lead to the formation of high resistance due to the chemical instability between the cathode and the SE, leading to the incompatibility between the interfaces. An example is the LCO-LLZO composite electrode prepared by sintering LCO on LLZO particles at 700 °C. Only a low capacity of 35 mAh g⁻¹ can be achieved because the cross diffusion of elements includes the partial diffusion of Co from LiCoO₂ to LLZO and the La/Zr from LLZO to LiCoO₂, thus forming the LaCoO₃ impurity intermediate layer at the interface. And at a
voltage above 3 V, the tetragonal LLZO phase is formed at the LCO/LLZO interface. The unstable impurity intermediate and the LLZO converted into tetragonal phase greatly increase the interfacial resistance between cathode material and electrolyte, so that LCO only represents 1/4 of the theoretical capacity. The chemical instability of cathode materials and solid electrolyte at high temperature sintering has been an obstacle to the integration of oxide solid electrolyte and cathode materials, but some of these problems have been solved by means of interface engineering or optimizing sintering temperature.

The temperature will affect the co-sintering process of LiCoO$_2$ and oxide solid electrolyte. Compared with the dense oxide solid electrolyte which conventional sintering at 1100°C, such a high temperature will cause the decomposition of cathode materials and adverse interface reactions. In fact, LLZO has been shown to react with LiFePO$_4$ at temperatures as low as 500°C and with LiNi$_{1-x}$Mn$_x$O$_2$ (NMC) and LiCoO$_2$ (LCO) at temperatures about 700°C. Therefore, reducing the sintering temperature and sintering time is considered to be beneficial to the overall molding. Wood et al. introduced the influence of ball milling on the sintering of solid electrolyte. The sintering temperature of solid electrolyte with finer particles is lower to form electrolyte with the same density. They also compensate for the loss of lithium ions from prolonged ball milling by adjusting the used solvents. In addition, sintering additives can also reduce the sintering temperature to a certain extent. Al$_2$O$_3$, Li$_2$O, LiCl and ZnO all can optimize the sintering process. In 2013, Ohta et al. realized the stable sintering of LCO and solid electrolyte with the help of LiBO$_3$ (LBO). LBO is a kind of lithium ion conductor, which has chemical stability with LiCoO$_2$ and LLZO. The LBO is sintered into the cathode layer by the annealing process, and sufficient interface contact between the cathode layer and the LLZO solid electrolyte can be easily achieved. At 700°C annealing and sintering, XRD characterization did not find any impurities except LLZO, LBO, LCO. Besides, Kazunori Takada et al. also studied LiBO$_3$ as a sintering aid.

In addition to optimizing the sintering process, interface engineering of electrolyte particles or cathode material particles can also contribute to the formation of an integrated all-ceramic lithium battery. Han et al. carried out an interface project between LCO and LLZO. Compared to the direct use of LBO between LCO and LLZO, they used Li$_{2.3}$C$_{0.7}B_{0.3}$O$_3$ as the welding agent and the reaction between Li$_2$CO$_3$ coating on the surface of LLZO and LCO weld LCO and LLZO together, thus forming Li$_{2.3-x}$C$_{0.7+x}$B$_{0.3-x}$O$_3$ (LCBO) intermediate phase. This process removes and the impurity phase produced by sintering LCO and LLZO at high temperature is avoided.

### 4.1.2 Spark plasma sintering method

As a synthesis technique, Spark plasma sintering method (SPS) is used to produce many kinds of functional materials, so does the oxide solid electrolytes and electrodes of ASSLBs, which is a new method of integrated molding.

Spark plasma sintering is a new effective synthesis technique which includes a high-power circuit and a mechanical loading system (Figure 13A). In this way the entire SPS system can make a low voltage, direct pulsed current and apply a mechanical stress simultaneously. The impact of the pulsed current is to discharge to create the plasma, electrical pressure and the Joule heat. Joule heat will be created at each single piece of powder when the plasma discharging and the current flowing through the sintering body (If the sample is electrical conducting. For nonconducting samples, heat will be transferred by the electrical conducting dies). Heating and mechanical press which acting at the same time accelerate the sintering together.

Benefited from the simultaneous heating and mechanical stress, SPS technology provides a possible method to integrate electrode and the solid electrolyte efficiently and tightly. In 2011, Aboulaich’s group raised the integrated molding of ASSLBs by SPS technology (Figure 13C). The three parts of the ASSLB in this experiment are Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAG, as the solid electrolyte), LiFePO$_4$ (LFP, as the cathode) and Li$_3$V$_2$(PO$_4$)$_3$ (LVP, as the anode). Firstly, they stacked three powdered components into a graphite die. After adjusting, sintered at 680°C for 10 minutes. The induced stress was absorbed by the graded composition layers, so there was no cracking or delamination in each layer. Because the environment was vacuum and hot when sintering, so the finished product can be directly placed in Swagelok cells after metallization of each side of the pellets.

Delaizir et al. also used LAG-LVP system in the experiment (Figure 13B). They made a symmetric composite-LVP/LAG/composite-LVP battery through SPS technology to explore the best electrode formulation and sintering protocol. In conclusion, the electrochemical performance showed that optimal formulation is 25LVP/60LAG/15C (wt%).

The LAGP-LFP system is proved that it has ability to become a composite electrode by SPS. In 2017, Kubanska et al. sintered LFP/LAGP composite electrode through SPS and then assembled a ASSLB of LFP/LAGP/PEO/Li (Figure 13D). PEO is a necessary solid polymer electrolyte which placed between Li metal and LAGP ceramic to avoid the reduction of LAGP. Expect the three layers ASSLBs we mentioned above (anode/SE/cathode), a new five-layered structure has been raised by Wei et al. in
The five-layered battery has higher energy and power densities than the three-layered one by building higher quality interfaces between each layers and containing more active electrode material. This experiment selected LTO (Li$_4$Ti$_5$O$_{12}$), LCP (LiCoPO$_4$) and LATP (Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$) to sinter the three and five layered batteries through SPS. This work proved that functionally graded electrodes can improve the interface quality. The theoretical and experimental advantages of this novel battery design have been verified. The results obtained are of great significance for customizing and optimizing ASSLB through SPS technology.

4.2 The integration of ASSLBs by thin film technology

ASSLBs can be divided into bulk-type all solid-state batteries and thin film all solid-state batteries. Actually, thin film ASSLBs has even much longer history than the bulk-type ASSLBs. Toshiba Corporation announced the successful development of a practical secondary thin film battery in 1983. Through the thin film technologies including magnetron sputtering, electron beam evaporation, thermal evaporation, pulsed laser deposition (PLD) technology, the components of ASSLB can be molded layer by layer to compose a battery, which are all in the form of thin film. Thin film technology provided a kind of integrated molding technology of ASSLBs since it simplifies the assemble steps of battery.

There are some main Physical Vapour Deposition (PVD) technologies: sputtering, PLD and evaporation techniques (thermal and electron beam). They are used in different situations for depositing different target thin films. A typical work is a bendable thin film ASSLB by Koo et al. in 2012. They developed a LiCoO$_2$/LiPON/Li film battery, which can work in bent condition and indicates highest specific capacity in flexible LIBs based on nano materials (Figure 14A). A few PVD technologies is used through the forming process of the battery: the LiCoO$_2$ cathode is consecutively stacked on the base material by radio magnetron sputtering (under Ar gas) with a LiCoO$_2$ sintered target, and then annealing under 700°C. Then depositing the LiPON solid-state electrolyte film by radio magnetron sputtering (under nitrogen gas) with a Li$_3$PO$_4$
FIGURE 13  A. The schematic view of the SPS apparatus and its components.\textsuperscript{[142]} Copyright 2017, Elsevier. B. Integrated molding of ASSLBs by SPS technology.\textsuperscript{[143]} Copyright 2012, Wiley. C. The SEM image of the cross section of a LFP/LAG/LVP ASSLB.\textsuperscript{[144]} Copyright 2011, Wiley. D. The schematic ASSLBs of LFP/LAGP/PEO/Li.\textsuperscript{[145]} Copyright 2017, Springer Nature
5 CONCLUSION AND PERSPECTIVE

ASSLMBs have attracted more and more attentions due to their good safety and high energy density. In conclusion, this review provides a systematic comprehension of oxide solid electrolytes, especially, (1) the research progress; (2) the preparation methods for various dimensional structures; (3) the integration of all-ceramic lithium batteries. The practical application level of solid-state batteries could be divided into short-term and long-term target. For short-term target, ASSLMBs with good cycling performance and high energy density should be expected. Firstly, we are supposed to solve the problem of low ionic conductivity of oxide solid electrolytes in the laboratory. For long-term target, the price per kWh of ASSLMBs should be reduced to be comparable with that of liquid batteries for wide applications. Then, encourage the solid state system to promotion itself from the laboratory to the industry by improving its repeatability and reducing costs, so that the oxide solid electrolyte can be used practically. Therefore, there are still several aspects need to be further improved as follows:

1. Similar with the conventional liquid electrolyte, the Li metal dendrites still form inside SEs, especially at a high current density. The possible mechanisms are still under debate.
2. The thickness of SSEs should be well controlled, which is directly related to the energy density of cells.
3. The interfaces/interphases between electrolyte and electrodes should be well investigated. Notably, the dynamic change during cycling should be monitored as well.
4. Novel solid electrolytes are still to be discovered, which have high ionic conductivity, wide potential window, high chemical stability and so on.
5. New-type synthesis methods for SSEs and integrated technologies for the whole battery are still highly required.

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