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LLZO Solid Electrolytes in All-Solid-State Lithium Batteries

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Abstract. Because of the development of the hi-technology and improvement of AI technology, the needs of energy and the technology which can save energy are increasing continuously. But the traditional lithium-ion battery has some disadvantages and limits which can't be overcome, so researchers have explored the solid-state battery. In this field of batteries, $Li_7La_3Zr_2O_{12}$ (LLZO) has been focused because of its great mechanical properties, stability, and the compatibility of the cathodes which are made by lithium metal and some anodes which has the ability to release high voltage. LLZO is well known as one of the most valuable and potential materials which also have the best commercial prospects. Although it has a lot of benefits, it still has some core bottlenecks. For example, its ionic conductivity is lower than other solid electrolytes at room temperature. It has high solid-solid interfacial impedance, difficulties in producing and expensive cost of production. To solve the problems which are mentioned before, researchers use some elements, such as Al or Ga dropping into the original materials which can make the crystal phase more stable and improve the ionic conductivity. Using the methods which modify the surface also can make the attachment of the interface better so that it can reduce the interfacial impedance. The process also can be optimized. These methods can reduce the loss of Li which is involved in the charge and discharge chemical reaction. This paper arranges relevant researches systematically and summarizes the way of the process optimization and prospects for future research directions and supplies some reference about the research, development and industrialization of LLZO.

Keywords: garnet-type LLZO, solid-state electrolytes, all-solid-state lithium batteries, ionic conductivity, interfacial impedance

1. Introduction

The technology of saving energy which uses lithium was used widely because it has high energy density and a long cycle life. But the traditional liquid lithium battery will achieve its upper limit soon and it has a lot of drawbacks when these batteries are used. Such as expansion of the battery volume, the leakage of the electrolyte and the possibility of the short circuit which is caused by lithium dendrites. But if solid battery which uses lithium metal as the anode and solid solid-state electrolyte can be used in daily life, some traditional problems will be solved. Lithium ions in solids rely on lattice vacancies and interstitial site hopping to complete ion transitions,which happen between the anode and the cathode [1]. The charge and discharge process is the complete lithium-ion

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movement between these two place. In the same situation, solid lithium batteries will have higher content of lithium element. The battery also has different physical and chemical properties because it is solid [2]. And also it has a wider electrochemical window, higher mechanical strength so that it can ease the problems which are caused by growing of lithium dendrites. These benefits can cause lower risk of short circuit and other safety problems such as leakage [3, 4]. And its theoretical energy density is higher than any other liquid batteries' upper limit. Because of these advantages, a solid battery has received wide attention and research. There are some different kinds of solid electrolytes have already been created. Their benefits, drawbacks and using effects vary a lot. $Li_7La_3Zr_2O_{12}$ as a garnet-type inorganic solid-state oxide electrolyte, has great ionic conductivity (almost 1.42×10^{-3} S/cm) at room temperature after implementing some improvement measures. This will make the body phase become more stable and improve the electrochemical stability with lithium metal after some process optimization such as Ga element doping modification [5]. Therefore this kind of electrolyte has already been paid attention by academia and industry. But LLZO isn't perfect. It still have several challenges in three aspects: conductivity, interfacial resistance and the producing methods in the industry. And these challenges still haven't been overcome. Finally, this paper will set forth some improvement methods for solving the LLZO shortcomings in the near future and guide the development of LLZO in the future.

2. Properties and advantages of LLZO

2.1. Mechanical and thermal stability

In the field of the mechanical properties, the elasticity modulus of the LLZO reaches up to more than 50 GPa. This is much more than sulfide and polymer systems markedly. The high-rigidity ceramic framework of LLZO has a stronger capability of the structural deformation-resistant than sulfide and polymer systems. It can effectively buffer the localized stress concentration induced by electrode volume fluctuation during the charging and discharging time. It also can reduce the risk of the bulk cracking of ceramics. Great high rigidity enables LLZO to have an excellent physical ability which will defend local stress, and promote the safety of solid battery. Alsaç et al. demonstrated that LLZO's high mechanical strength will physically buffer safety hazards originating from the penetration and propagation of lithium dendrites. In addition, LLZO has great thermal stability and chemical inertness, so that it can display excellent compatibility both with ambient air and high-voltage cathodes. And it has a lower threshold of process and more appropriately compatible with the construction of high-energy-density battery systems [6].

2.2. Ionic conductivity

By using neutron diffraction and solid-state nuclear magnetic resonance two experimental methods and a way of thinking which is based on first-principles to draw a conclusion: in the garnet-type LLZO structure which is also in the cubic phase, its lithium ions can move very far by single-ion vacancy hopping. This phase also exhibits the highest ionic conductivity among the three crystalline phases, because there are a lot of vacant sites in this structure. In addition, the intrinsic ionic conductivity of LLZO is 0.3-0.5 mS/cm [6], but after the single-element or multi-element doping modification, its ionic conductivity will improve to almost 1.42 mS/cm [5].

Lithium-ion transport pathways which are interconnected in three-dimensional perspective endow the material with a low bulk migration energy barrier. Meanwhile, its electronic conductivity is

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almost 2×10^{-8} S/cm at room temperature. So at high current densities, it can restrain polarization the phenomenon effectively [7].

2.3. LLZO demonstrates favorable compatibility with lithium metal anodes

Cubic garnet-type $Li_7La_3Zr_2O_{12}$(LLZO) displays an overall performance in combination property. Its intrinsic electrochemical stability window can be expanded to almost 6V. It shows thermodynamic inertness toward lithium metal both in chemistry and electrochemistry. It also can match some high-specific-energy lithium metal anodes and high-voltage cathodes, such as the $LiCoO_2$ [8]. The Zr-O framework which belongs to LLZO also has thermodynamic stability at low potentials [9]. And it also can attach to lithium metal for a long time without any sustained interfacial side reactions. Thangadurai et al. confirmed that Garnet-type LLZO is one of the fewest oxide solid electrolyte systems which can realize thermodynamic stable compatibility with lithium metal anodes. In addition. Its interfacial chemical stability is markedly superior to sulfide and halide electrolytes [8]. This conclusion builds a core material foundation for the construction of high-energy-density lithium metal batteries.

3. Main challenges of LLZO

3.1. Low ionic conductivity

The room-temperature ionic conductivity of intrinsic cubic-phase LLZO is only 0.3×10^{-3} -0.5×10^{-3}S/cm, almost three orders of magnitude lower than conventional liquid electrolytes and sulfide-based solid electrolytes [6, 10]. LLZO will tend to change spontaneously from cubic phase to tetragonal phase transition at room temperature. In the tetragonal phase, lithium sites are fully occupied and it has zero available migration vacancy, so its room-temperature conductivity is only on the order of 10^{-6}S/cm, almost one percent of the cubic phase [6, 8]. In addition, the LLZO which has many single-crystal particle interfaces raise the migration energy barrier for lithium ions and hinders cross-boundary ion transport [6].

Its results will weaken fast-charging capability and poor high-current discharge performance, which makes LLZO batteries difficult to adapt to mainstream scenarios such as electric vehicle fast charging and high-power energy storage [6, 10].

3.2. High interfacial resistance

As a rigid ceramic, effective contact area is limited and initial interfacial impedance is up to several thousand ohms because LLZO, lithium-metal anode and cathode materials all are solid and lithium ion has to migrate among them [11]. The poor wettability of metallic lithium on the LLZO surface, and its volume will change during cycling, which causes crevices on the surface and continuously rising impedance [6].

It will generate battery polarization, reduce energy efficiency, cause rapid capacity fading and shorten cycle life. It acts as a core obstacle to the long-cycle commercialization of LLZO-based solid-state batteries [6, 11].

3.3. Challenges in LLZO processing

Existing routes have some inherent drawbacks: fabrication of pure-phase, high-conductivity cubic LLZO requires long-time sintering above 1000 ℃ . High temperature easily causes lithium

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volatilization, stoichiometric deviation and impurity phase formation, finally degrading ionic conductivity and mechanical properties and causing poor product homogeneity [12]. It also shows poor compatibility with existing lithium-battery production lines [13]. Wet-chemical routes have high raw-material costs and hazardous reagents [14]. In addition, the high brittleness of LLZO leads to extremely low yield of large-area thin films [13].

4. Common improvement methods

4.1. Element doping

Elemental doping acts as the core approach for bulk property tuning of LLZO. This method incorporates foreign metal elements into the LLZO lattice to occupy specific crystallographic sites. It also can make the crystal structure become more stable and realize the increase of the ionic conductivity and phase stability by adjusting the lithium vacancy concentration [5].

In Al dropping, Al mainly occupies lithium sublattice sites, which lowers the changing temperature between the cubic phase and the tetragonal phase. This stabilizes the high-conductivity cubic phase at room temperature. The generated lithium vacancies reduce the activation energy for lithium-ion transport and enhance the room-temperature ionic conductivity [15].

Gallium doping has a better modification effect. Ga^{3+} occupies lithium sites to suppress the ordering tendency of the lithium sublattice, which hinder the phase transformation of LLZO to the tetragonal phase in the thermodynamic field. At a doping fraction of 0.1-0.3, the lithium-ion percolation rate can be maintained at approximately 90 %, and the room-temperature ionic conductivity can reach 1.42×10^{-3} S/cm, which is remarkably superior to aluminum doping [5]. Different coulomb energy which is caused by different Ga doping concentrations can be seen in Figure 1.

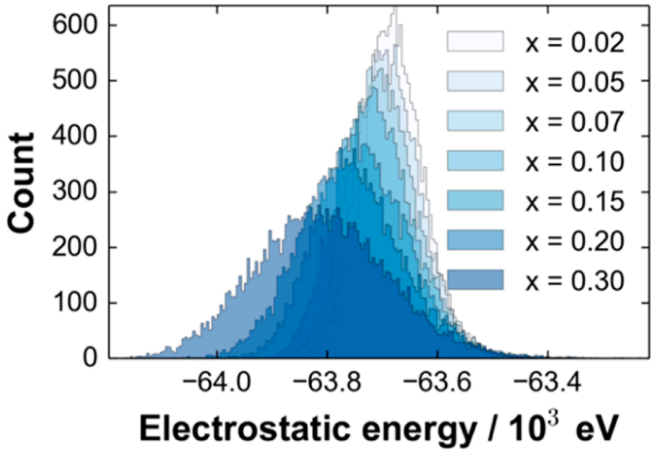


Figure 1. Different Ga concentrations show different coulomb energy [5]

The limitation of this method is that the performance improvement from single-element doping has a distinct upper limit, and excessive doping tends to a harmful effect. Furthermore, it can only optimize bulk ionic conductivity and can't solve problems such as high grain-boundary impedance and poor solid-solid interfacial contact [5, 15].

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4.2. Surface modification

Surface modification, namely solid-solid interfacial engineering design, its core changes are that contact only connects between solid and solid with lithium-metal anodes and LLZO, which lead to limited effective contact area isn't enough and initial interfacial impedance up to several thousand ohms. The objective of modification is to improve the wettability of metallic lithium against the electrolyte surface, transform the original point-to-point contact into more sufficient contact, and this can reduce interfacial impedance. The researches display that there are two mainstream methods [11, 16].

The first is self-wetting interface design. This method adds oxide nanoparticles into electrolyte surface by using one MPa pressure on the surface for 48 hours at room temperature. This way causes nanoparticles to expand along grain boundary and let metallic lithium infiltrate electrolyte holes which changes the original contact to 3D contact. By using this way will reduce to 162 $\Omega \cdot cm^2$ and solve the problem about high initial interfacial impedance [16]. But this method only can improve original interfacial contact, it can't solve interfacial cracking and continuous contact degradation these two problems which are caused by periodic stress originating from electrode volume deformation in a long cycle.

The other is molten-lithium heat-treatment which transforms lithium foil to liquid by heating to 180 ℃ , which improves the contact between LLZO and metallic lithium also can combine modification of thin-metal-layer which also can solve problem about high initial impedance. However, the process is relatively complex and may result in low product purity and deterioration of the interfacial contact [11].

4.3. Improved preparation methods

The ambition of improved preparation methods is solving the drawbacks such as severe lithium volatilization, poor product homogeneity and limited scalability when they are used in traditional process. There are two representative improved processes [13, 14].

The first is the aqueous solid-state reaction method. This way uses water as ball-milling media and adds some lithium hydroxide to participate in reactions. This method reduces the safety risk and production cost, mitigates lithium loss during reaction and reduces the sintering temperature.But it still has some limitations. For example, the purity of the product is low in mass production,and the crystallinity and density of the product is worse than product from traditional way [13].

The second is Pechini method which use inorganic metal salts as chemical precursors, deionized water as solvent, citric acid as a chelating agent and polyethylene glycol which is added into reaction as a surfactant. This method reduces the reaction time to 5 hours and decreases sintering temperature which is between 923K and 1173K significantly. Nanoparticles of the final product will be more even.But nothing is perfect, and this way is no exception. The drawbacks are that this way isn't safe and it is particularly hard to be produced in industry [17].

The Table 1 summarizes and organizes all drawbacks and benefits of the above three improvement methods in a concise way.

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Table 1. Summary of LLZO modification strategies

Modification Category	Approach	Effects	Limitations
Elemental doping	Al doping	Stabilize cubic phase and improve ionic conductivity [5, 15]	Improvement has limitation and high interfacial impedance [5]
	Ga doping	Restrain changing of phase and better ionic conductivity [5]	Improvement has limitation and high interfacial impedance [5]
Surface modification	Self-wetting interface design	Reduce initial interfacial impedance [16]	Has damage risk [16]
	Molten-lithium heat-treatment	Decrease initial impedance [11]	Process is more complex and cycling-induced interface degradation [11]
Preparation optimization	Aqueous solid-state reaction	Lower sintering temperature and production cost; safer [14]	Worth crystallinity and density [14]
	Pechini method	Faster and lower sintering temperature; purer product [17]	High cost of raw material and difficult to produce in large scale [17]

5. Conclusion

Garnet-type LLZO is an oxide-based solid-state electrolyte with great comprehensive performance. It has better room-temperature ionic conductivity than other solid electrolytes, wider electrochemical window, more excellent mechanical strength and chemical stability against lithium metal which compare with sulfide and polymer electrolytes.Because of these reasons, LLZO is regarded as one of the most safe, valuable and promising solid lithium batteries in scientific research field and commercial manufacturing field.

However, its large-scale commercial application still has many bottlenecks. For example, the ionic conductivity is lower than traditional liquid batteries and sulfide electrolytes. The interfacial impedance is very high because the contact is between solid and solid. The huge amount of lithium loss during the sintering time. The high cost of production and worth appropriateness of the manufacturing technique lead to many difficulties in the manufacturing field.

There are three main solutions from researches: elemental doping, surface modification and preparation optimization. The first method use Al or Ga doping so that can stabilize the phase structure of LLZO and adds lithium vacancies into these materials which will increase ionic conductivity. The second way changes surface contact to decrease resistance by using some processing technology methods such as self-wetting interface design and molten-lithium heat-treatment. And also use preparation optimization can solve some problems which will be faced when LLZO is produced. Based on the information and foundation, the attention and research should be paid to the methods of creating new materials which are based on LLZO and have lower resistance than any other batteries and the improvements of technological process. These are able to produce

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LLZO in a faster, safer environment and have greater output. All breakthroughs in technology will collaboratively promote the industrial development of LLZO batteries.

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