The preparation of Li$_7$La$_3$Zr$_2$O$_{12}$(LLZO) battery ceramic and its conductivity

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Abstract: For Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) solid electrolytes, higher density usually means higher ionic conductivity. Researchers tried many preparation methods to get high density samples and at same times to realize industrial production, low cost, scalable and fast synthesis techniques. In this paper, the mainstream preparation methods of LLZO was given, as polymerized complex method, sol-gel method, field assisted sintering, combustion technique, auto-consolidation method, water-based solvent method. Among these methods, the last four methods can always increase the density to more than 93%. Especially the field assisted sintering method can make the relative density to be high as 99.8%. And all of these methods can make the ion conductivity to be higher than 1.4x10$^{-4}$ S cm$^{-1}$. Also, most of these methods introduced the Al element into LLZO to realize the liquid sintering.

1. Introduction

With the rapid development in portable electronics, grid energy storage and electric vehicles, Li$^+$ batteries (LIBs) which owning high energy densities were becoming to be the dominant power supplies $^{[1-4]}$.

However, current LIBs are still sinking in safety problems, like the inherent flammability and easy leakage from liquid electrolytes $^{[3-6]}$.

So the solid electrolytes could be an inevitable selection for all-solid lithium batteries (ASSLBs) that own high conductive density, high safety $^{[7-12]}$. Composite or inorganic solid-electrolytes are the most interest owing to the high Li-ion transference number, wide operating temperature range, and safety $^{[3]}$.

In various inorganic-solid-electrolytes, garnet structure oxides are the best candidates for Li$^+$ batteries till now $^{[12-18]}$. The reason is garnet Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) is the most promising and prospective solid-electrolyte in all-solid-state Li batteries and Li-air batteries, not only for its electronic transport, and high ionic conductivity, but also for its good chemical stability and few aqueous solutions $^{[19-21]}$.

Importantly, for LLZO solid-electrolytes, higher density usually equal to higher ionic conductivity $^{[22-25]}$. To reach high density, researchers tried many preparation methods to realize industrial-production, scalable, low-cost and fast-synthesis techniques $^{[22-25]}$.

Here, an analysis about the methods for synthesis LLZO was given to make a clear comparation on
their advantages, and to make a help on the further researches of this material.

2. Preparation method

2.1 Polymerized complex method
In this method, LLZO electrolytes doped with Al of 0, 0.2, 0.7, 1.2, and 2.5 wt. % were prepared. And the preparation is the mixing of ethylene glycol (Fisher Chemical) and citric acid (99.5%, Aldrich) with 60:40 mols to nitrate-solution treated to be complexion agents. Then, the this solution was put into the nitrate-solution which had been stirred \cite{26}. The mixture was warmed at 130 °C to form a white solidified-foam \cite{27}. Then crushed this foam and followed a calcination at 900 °C for 6 h to react the precursors in an alumina crucible. It was found that just a small addition of Al added to LLZO can heavily enhance the dense process in sintering. It was found that the liquid phase with Al additions enhanced sintering rate. Also, the adding of could stabilize the higher conductivity of cubic form LLZO. With optimal additions of 1.2 wt.% Al, LLZO electrolyte showed an ionic-conductivity of 2.0 \times 10^{-4} S cm^{-1} at 30 °C which be sintered at 1200 °C for 6 h \cite{27}. The description of density was shown in Fig. 1.

![SEM microstructures of 1.2 wt.% Al-LLZO pellet which sintered at 1200 °C for 1 h. Magnification is 4k×\cite{27}.](image1.png)

Fig. 1. SEM microstructures of 1.2 wt.% Al-LLZO pellet which sintered at 1200 °C for 1 h. Magnification is 4k×\cite{27}.

![SEM images of Al_{2}O_{3}-added LLZ pellet calcinated at 1100 °C for 36 h\cite{28}.](image2.png)

Fig. 2. SEM images of Al_{2}O_{3}-added LLZ pellet calcinated at 1100 °C for 36 h\cite{28}.
Further comparison of the LLZ and LLZ-Al2O3 in stability against Li conductivity, chemical and electrochemical properties etc. showed that bulk and total were $1.4 \times 10^{-4}$ S cm$^{-1}$ and $2.4 \times 10^{-4}$ at 30 $^\circ$C, respectively$^{[28]}$.

It could be concluded by Weppner$^{[29]}$, that Al in LLZO play two important roles. One is stabilizing the cubic-structure more than the tetragonal-structure. Second is formed a liquid phase that improve densification and shorten sintering-times$^{[27]}$.

Others reported that various Al-doped garnet-like cubic-LLZO crystallizing were synthesized from Al$_2$O$_3$, Li$_2$O, La$_2$O$_3$ and ZrO$_2$ binary oxides. The synthesis was a two-step preparation route process. One step is high-energy ball milling to realize activation and the following other step is annealing process at higher temperatures$^{[30]}$. The choosing of the synthesis route will lead to a well adjustment of the cationic ratios, and gain precisely the LALZO formula. When increasing Al content, ions posited by Zr$^{4+}$ and La$^{3+}$ are replaced by Al$^{3+}$.$^{[30]}$ Finally, the replacement of Zr$^{4+}$ and La$^{3+}$ by Al$^{3+}$ ions would stabilize the cubic-garnet and heavily affects the dynamics of Li$^+$ $^{[30]}$. Its ion conductivity not only depend on the Al distribution on the different sites in LLZO but also on the chosen stoichiometry and the heat treatment conditions $^{[30]}$.

Tibet$^{[31]}$ found that the synthesis parameters of LLZO ceramic were varied from the raw materials for Li and Zr, the thermal treatments and the crucible materials $^{[32]}$. Using an alumina crucible or additional alumina will result in the successfully preparation of cubic-LLZO$^{[31]}$, and carrying out an experiment in alumina crucibles lined or in magnesia crucibles at 1000 and 1200 $^\circ$C can gain single-crystal$^{[31]}$.

Huang found usingƳ-Al$_2$O$_3$ as a content in the preparing doped-LLZO, the Al involved could improve the Nb-doped microstructure $^{[33]}$. Doping Nb and Ta can realize the conductivity at 25 $^\circ$C to be $4.10 \times 10^{-4}$ S cm$^{-1}$ and $4.50 \times 10^{-4}$ S cm$^{-1}$, respectively $^{[33]}$. When measured the Nb-doped LLZ at 50$^\circ$C in air, the conductivity was reached to be $1.23 \times 10^{-3}$ S cm$^{-1}$ $^{[33]}$.

2.2 Sol-gel method

As known from above, that preparing cubic LLZO by solid state method requires high temperature at 1,200 $^\circ$C for 36 h $^{[34]}$. By wet chemical methods, cubic-LLZO can get at lower temperatures, however decompose will occur at high temperature around 850 $^\circ$C$^{[34]}$. Anyway, synthesis of garnet-structure-electrolytes by sol-gel method with Li$^+$ and Y$^{3+}$ for Zr$^{4+}$ of formulae LLZO ($x = 0, 0.1, 0.2, 0.3$ and $0.4)$ can avoid such phenomena$^{[34]}$.

Furthermore, gaining high Li$^+$ conductive Al-LLZO by modified sol-gel technique can reach the relative density to be 96% $^{[35]}$. The study reveals that among Li$_3$BO$_3$, Li$_3$PO$_4$ and Li$_3$SiO$_4$, Li$_3$SiO$_4$, such chosen sintering additives appears to be enhancement of density and total Li$^+$ conductivity of Al-LLZO$^{[35]}$. 

![Fracture surface of Al–LLZO with 1 wt% of Li$_4$SiO$_4$](S-340ON 20.0kV 10.1mm x 5.0kW SE 10.0um)

Fig.3 Fracture surface of Al–LLZO with 1 wt% of Li$_4$SiO$_4$ $^{[35]}$
To improve the lithium conductivity, Ca-Incorporation is developed in garnet-type Li7-xLa3Zr2-xTaxO12 [36]. A new sol-gel strategy was showed in Fig. 4 [36]. It was found that the ionic conductivity of LLZTO can be increased by an adding Ca [36] in which Ca is located at the La’s sites [37].

Anyway, the others reported a low temperature, fast synthesis of cubic Li6MLa2Nb2O12 (M = Ca, Sr, Ba) also in sol-gel method [36]. The optimistically synthesis condition is 775 ℃ holding 6 h [36]. The calcination temperature is lower than that of solid-state reaction nearly 125 ℃, and the calcination time (6 h) is shorter [36] with major phases to be garnet [36]. The density will increase with increasing ionic radius. Among these compounds, the Li6BaLa2Nb2O12 exhibits the highest conductivity [36].

Fig.4 A schematic of the sol–gel process used to Ca-containing Li6.4La3Zr1.4Ta0.6O12.

2.3 Field assisted sintering [38]
Zhang etc. [38] had prepared higher quality LLZO solid-electrolytes in field assisted sintering technology (FAST). In this method, powders will be loosely filled into the die and then FAST consolidation was conducted with plasma activated [38].

In this way, cubic-LLZO can be obtained at a temperature from 1100 to 1180 ℃ for no more than 10 min [38]. And a maximum density of 99.8% and conductivity as 5.7 x 10⁻⁴ S cm⁻¹ can be gotten (the morphology is shown in Fig.5) [38]. This FAST technology can obtain higher performance LLZO in very short sintering time, one step and lower sintering temperature [38].

Fig. 5. Micrographs of the samples sintered at 1150 ℃
2.4 Combustion technique

When using a solid-state synthesis method to prepare cubic-LLZO always requires several heat treatments process and grinding and long time sintering. By combustion technique, Dhivya etc. had prepared LLZO and Al-LLZO in shorter times, in which the metal nitrates to glycine was 1:1 (in mol). And the metal-nitrates and glycine were mixed and dissolved to get a transparent solution in water, and continuously it was stirred at 90°C for 30 min. After evaporation, brown gel was formed. Removed all water from the mixture and rise to 250°C, then the viscous gel began frothing. The gel would automatically ignite and burn to gain voluminous powder. After the powder were sintered at 750°C for 6 h, it was grounded and pressed into pellets. Then it was sintered at 950°C for 24 h and 1200°C for 6 h in a Al₂O₃ crucible.

The powder burned above sintered at 950°C, and it was found to be a tetragonal LLZO and some is a high conductive cubic Al-LLZO. When it was with 10 wt% excess lithium and sintered at 1200°C for just 6 h find to have relative density of 95% and conductivity of 5.1 x 10⁻⁴ S cm⁻¹ with a particle size of about 613 nm.

2.5 Auto-consolidation method

Researchers usually tend to choose high-pressure method as (CIP) cold or (HIP) hot isostatic pressing methods for high density. In Zhao’s work, the powder of LLZO was just vibrantly compacted for sintering. No pressing were employed, that is an auto consolidation method was applied. The surface tension of liquid Li₂O is key point for dense at sintering temperature. So the dense LLZO’s sintering procedure is very simple. A density of this kind tetragonal LLZO is about 93% using this auto-consolidation method. And no voids were observed.

So, such dense cubic Al-LLZO made in self-consolidation needing no pressure was excited. The relative density reach to be about 93-96%, and the Al-LLZO with a small amount of additives reach the highest conductivity to be 1.41 x 10⁻⁴ S cm⁻¹ at room temperature compared with the samples made by traditional high-pressure methods. In this method, the molten Li deduced surface tension acts as intrinsic power.

2.6 Water-Based Solvent method

However, because of garnet-LLZO is much reactively to water, the gaining of LLZO powders and ceramics with large-scale amounts is difficult. So, a water-based solvent method is a more possible solution. LLZTO, that is, Ta-doped LLZO, and composite ceramics as LLZTO/MgO are firstly made with such method, the relative density can reach 95%, and conductivity was 3.5 X 10⁻⁴ S/cm, and grain size is uniformly obtained from a slurry of attrition-milled LLZTO/MgO which contains 2 wt % polyvinyl alcohol binder and 40 wt % solids.

2.7 Solution-based method

In Liu’s work, another battery ceramic, like LATSPO ceramic-electrolyte had been prepared by solution-based method at 650°C which is a low calcining temperature. And this LATSPO powders have rhombohedral NASICON-type structure, and the sintering temperature of it is 1000°C for 6 h which exhibits best conductivity as 1.33 x 10⁻³ S cm⁻¹. So, the solution-based method for LATSPO would be a industrialization preparation route.

3. Discussion

All solid-state batteries can take us closer to a none-emission society. Such battery system, however, requires good stability and Li⁺ conductivity. So, cubic-LLZO is attractively combining excellent thermal ionic conductivity and electrochemical stability. Al³⁺ ions etc. are usually used to stabilize the highly conductive phase, to overcome the weak stability of cubic-LLZO in room temperature. However, it was reported that even very small Al additives critical for future battery applications. Studies showed that the effective conductivities of LLZO will vary between 1 x 10⁻⁵ and 8 x 10⁻⁴ S cm⁻¹, which do not show obvious differences in sample preparation. Furthermore, the reduction of the
volume of sample and conductivity vary even within one sample. Finally, preliminary chemical analysis to identify Al is homogeneities in LLZO, which may be responsible for conductivity variations in equal samples\cite{42}.

Also, from above, the most popular additive element added in LLZO was still Al, and the main reason of its adding in this solid-state battery ceramic is to realize the liquid sintering process to improve its total density \cite{41}.

Beside Al element, others like Ta, Nb and Ca were also added to the Li-battery ceramic.

4. Conclusions

Much of efforts had been made to gain the high density LLZO battery ceramic. Besides the high-pressure technology such as CIP or HIP methods, in this paper, other mainstream preparation methods, like polymerized complex method, sol-gel method, field assisted sintering, combustion technique, auto-consolidation method, water-based solvent method, etc. were introduced. And in these methods, the last four method can always make the density improved to more than 93%. Especially the field assisted sintering method can make the relative density to be high as 99.8%. And all of these methods can make the ion conductivity to be higher than \(1.4 \times 10^{-4}\) S cm\(^{-1}\).

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