

Study on LiF Assisted Firing of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

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Abstract

For a long time, safety issues have been the bottleneck restricting the development and application of lithium batteries. Replacing liquid electrolytes with solid electrolytes is one of the most effective ways to overcome this bottleneck. High ionic conductivity, low electronic conductivity, and good thermal stability are ideal properties that solid electrolytes should have. The solid electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) not only has these properties, but also has good electrochemical stability in contact with Li anode and great practical potential, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ has always been a research hotspot in the field of batteries. The effects of lithium fluoride on crystal structure, micromorphology, sintering temperature and ionic conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ceramics were studied. The XRD pattern showed that the LLZO crystal structure did not change significantly when lithium fluoride fuel was added. Sample SEM photographs show that a special microstructure was found with grain boundaries virtually removed, creating closed pores in the ceramic microstructure, which contributes to negligible grain boundaries and high total ionic conductivity. With the addition of 3% (mass fraction) of lithium fluoride to the density of LLZO ceramics, ionic conductivity can be achieved.

Keywords

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, Ionic conductivity, Lithium fluoride, Burnt aid

The solid electrolyte lithium lanthanum zirconium oxygen $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has the characteristics of high ionic conductivity, low electronic conductivity, wide electrochemical stability window, and good contact stability with Li metal anode, and has great application potential [1-2]. Among the two crystal structures of tetragonal phase and cubic phase of LLZO, the tetragonal phase LLZO has stable structure and simple preparation, but the ionic conductivity is low, which can only reach the order of 10^{-6}S/cm . The cubic phase LLZO structure is not very stable, and it is easy to decompose into $\text{La}_2\text{Zr}_2\text{O}_7$ at high temperature, but it has high ionic conductivity, which can reach the order of 10^{-4}S/cm [3-4]. In the preparation of LLZO, in order to obtain pure cubic phase LLZO, secondary sintering of LLZO precursors is often required. The sintering method used is different, and the change of process parameters such as temperature and time during sintering has a great impact on the ionic conductivity, density, impurity content, etc. of the obtained LLZO.

The burning aid can improve the sintering performance of LLZO ceramics, reduce the sintering temperature, shorten the sintering time, improve the density, and improve the ionic conductivity [5], so it has become a research topic of great significance in the direction of solid electrolyte sintering. At present, the burnt aids used in research are mainly $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ [6], $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ [7], LiBO_3 [8], Li_4SiO_4 [9], etc., glass phase materials as additives can achieve sintering and densification of ceramics at lower temperatures through liquid phase sintering, but glass burners often introduce other impurities to reduce the ionic conductivity of the electrolyte, so it is not conducive to material applications. LiF is a burning aid commonly used in traditional industries, which can be used to assist sintering without the introduction of other impurities [10]. In this work, the effects of lithium fluoride on the structure, sintering temperature and electrochemical properties of LLZO ceramic matrix were studied by adding lithium lanthanum zirconium oxide matrix during the sintering process.

1. Experimental

Lithium fluoride assisted firing LLZO was prepared and tested by liquid phase method. LiF doping amounts were 0%, 3%, 5%, and 10% (mass fraction), respectively.

1.1 Precursor preparation

In this experiment, LLZO was prepared by sol-gel method, and high-purity LiNO_3 ($\geq 99.0\%$), $\text{La}(\text{NO}_3)_3$ ($\geq 99.0\%$), $\text{Zr}(\text{NO}_3)_4$ ($\geq 99.0\%$), $\text{Ga}(\text{NO}_3)_3$ ($\geq 99.0\%$) raw materials were prepared, and a cationic concentration of 2M solution was configured according to the chemical ratio of LLZO, and then citric acid and ethylene glycol were added as chelating agents, and the water bath was heated and stirred until the solution was transparent and gel. The resulting gel was transferred to a drying oven at 150 °C and dried for 12h to obtain a reddish-brown solid, then ground to powder with an agate mortar, and then insulated at 500 degrees Celsius for 6h in a muffle furnace for degumming, after which LLZO precursors were obtained.

1.2 Sintering

In this experiment, polyvinyl alcohol (PVA) was used as a binder to improve powder plasticity. The binder was prepared according to the mass ratio of polyvinyl alcohol:water = 1:10, and the stirring was stopped after stirring in a water bath at 80 °C until the polyvinyl alcohol was completely dissolved (the solution was clear), and then cooled to room temperature and then reserved. According to the mass ratio of electrolyte powder: binder = 1:1, the binder is added to the electrolyte powder drop by drop, and it needs to be constantly ground in the process of dropwise addition until the electrolyte powder and the binder are mixed evenly, and then put into a 90 °C electric constant temperature blast drying box for drying, and after drying for 12h, take out the mixed powder for grinding and refinement. Weigh 0.5g of powder, press a 10mm diameter disc under a pressure of 10MPa, hold the pressure for 10min, and put the LLZO solid electrolyte disc formed by LLZO solid electrolyte disc into an alumina crucible and sintered at 900 °C in a muffle furnace for 6h.

1.3 Material characterization

X-ray diffractometer was used to analyze the structure of the powder, Cu-K α ray, the scanning angle was 10°~70°, and the scanning speed was 4°/min. SEM scanning electron microscopy was used to observe and analyze the topography of the powder. Ionic conductivity is measured at room temperature by AC impedance analysis (Autolab, PGSTAT302N type). Taking the potentiostat impedance model of frequency resistance analysis as the test model, the frequency range is in the range of 1 Hz~1 MHz, and the electrical disturbance is set to 20 mV. Ceramic particles are polished after the sintering process. The particle thickness is less than 1.5 mm and the diameter is about 10 mm. Before the measurement, two parallel surfaces are coated with silver paste as lithium-ion blocking electrodes.

2. Results and discussion

2.1 Effect of burning agent on LLZO sintering temperature and phase

Figure 1 shows the XRD pattern of a lithium fluoride-assisted fired LLZO solid electrolyte. It can be seen from the figure that the crystal structure of the sample after adding lithium fluoride to assist firing has not changed, and it is still a single garnet structure. LLZO solid electrolyte powder without LiF combustion is wider, which is wider in half height and width at $2\theta=31.003^\circ$, 34.048° , 38.214° , 43.234° , 51.056° , 52.101° , 53.131° , which is due to the poor spatial lattice symmetry of the tetragonal phase structure, so other characteristic diffraction peaks corresponding to the tetragonal phase structure will appear near the characteristic diffraction peaks of the cubic phase structure. LLZO solid electrolyte with 3% and 5% LiF combustion was added at $2\theta=16.835^\circ$, 27.661° , 31.003° , 34.048° , 38.214° , 43.234° , 51.056° , 52.101° , 53.131° , etc., corresponding to the characteristic diffraction peaks of (211), (400), (420), (422), (521), (521), (521), (611), (640), (633), (642) and other crystal faces, but you can see [130], which is a typical quadrilateral phase structure and cubic phase structure coexistence phenomenon, indicating that after adding LiF combustion at this time, LLZO solid electrolyte has begun to change from tetragonal phase to cubic phase, but the peak shape of 3% LiF combustion at $2\theta=16.835^\circ$ is narrower, indicating that the effect is the best at this time; The LLZO solid electrolyte with 10% LiF combustion assisted combustion had a slight LiF diffraction peak at $2\theta=16.835^\circ$, indicating that when the sintering temperature was 750 °C, 10% LiF was added as a burning aid to obtain a cubic phase garnet-type structure, but because the sintering temperature was not high enough, the raw material reaction was not sufficient, and the volatilization of Li was not serious, resulting in some LiF remaining. In addition, due to the close radius of F-ion (0.133 nm) to O²⁻-ion (0.132 nm) and similar electronegativity, it is not possible to determine whether it is replaced by

experimental means, and even if it occurs, it has little effect on the lattice constant, and will not affect the crystal structure and lattice parameters of the matrix. Therefore, the crystal structure of LLZO solid-state electrolyte with lithium fluoride combustion assisted by the addition of lithium fluoride to the XRD pattern did not change significantly, and the existence of a second phase was not observed.

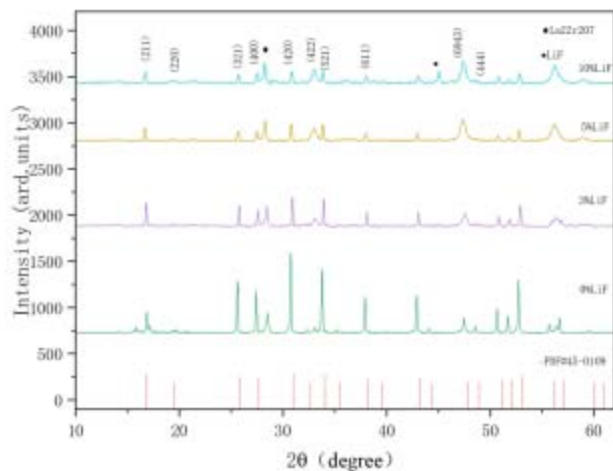


Fig. 1. XRD diffraction patterns of LLZO solid electrolytes with different initial LiF additions assisted by ignition.

Figure 2 compared with the sample without LiF, it can be seen that when 3% and 5% LiF are added, the grain size of the sample does not change significantly, and the size is relatively uniform. The grain surface is significantly smoother, and the distance between the grain particles is reduced. When 10% LiF was added, the grain diameter of the sample became significantly larger, there were still a large number of holes on the surface, and there was grain boundary fragmentation. From the results of XRD and SEM, it can be seen that LiF, as a burning agent for LLZO solid electrolyte, can promote the sintering process of materials and promote the formation of cubic phase, and a small amount of addition will not affect the crystal structure and lattice parameters of LLZO solid electrolyte.

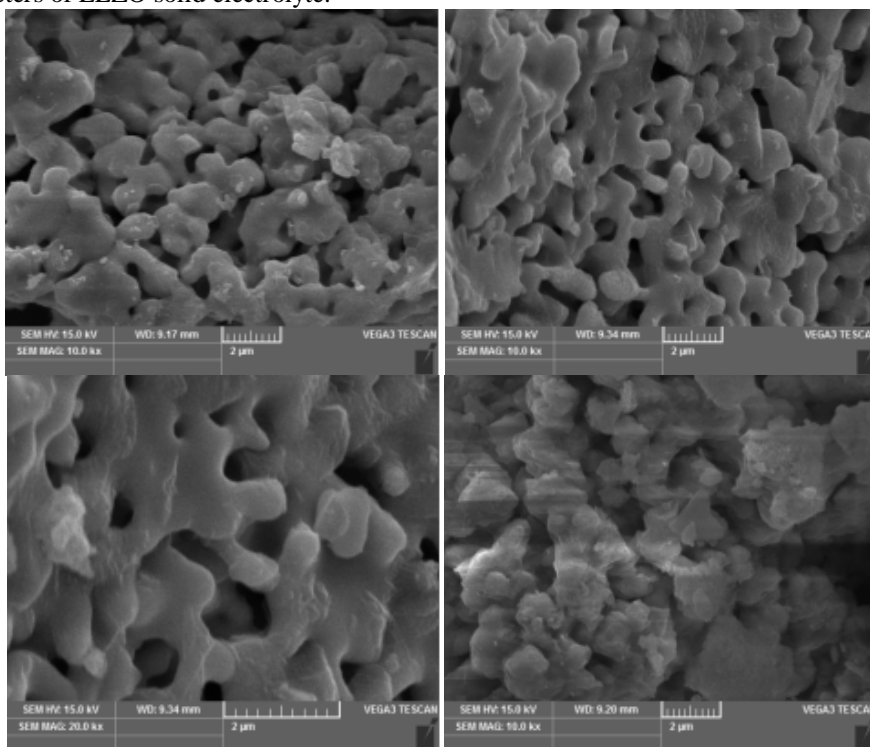


Fig. 2. SEM morphology of LLZO solid electrolyte with different initial LiF addition amounts.

2.2 Effect of sintering additive LiF on the electrochemical properties of LLZO

The AC impedance test of the electrolyte block was carried out, and the results were used to analyze the lithium ion conductivity and electronic conductivity of the corresponding electrolyte block, so as to explore the influence of LiF combustion on the electrical properties of LLZO electrolyte block. As shown in Figure 3, the EIS curve obtained when the sintering temperature is low is composed of two parts, namely the semicircle of the high-frequency region and the oblique straight line in the low-frequency region, which is inconsistent with the known high frequency region with two semicircles, it is possible that because at the low temperature, the grain of the electrolyte block has begun to contact with the grain, and the grain has begun to grow, making it difficult to clearly define the contribution value of the grain and grain boundary to the total impedance, so it is represented on the AC impedance spectrum as a semicircle coincidence representing the grain impedance and grain boundary impedance. Only one semicircle is displayed. Therefore, when calculating the ionic conductivity of the electrolyte block, the resistance value corresponding to the intersection point of the semicircle and the X-axis is selected to approximate the total impedance of the electrolyte block. However, when 0% LiF is added, the semicircle in the high-frequency region begins to gradually decrease, which means that the total impedance begins to decrease, and the total impedance becomes smaller, corresponding to an increase in lithium-ion conductivity. LLZO is an ionic conductor and requires its ionic conductivity to be as large as possible. In general, the electronic conductivity of LLZO must be relatively low. From Figure 3, it can be seen that when not added as a combustion aid, the impedance of the obtained LLZO electrolyte block is 8028Ω, and its ionic conductivity is on the order of 2.38×10^{-5} , when the tetragonal phase structure in the electrolyte block is dominant and the density is low. When 3% LiF was added as a burning agent, the impedance of the electrolyte sheet dropped rapidly to 147Ω and its lithium-ion conductivity reached a maximum of 1.29×10^{-3} S·cm⁻¹. When the amount of LiF added increases to 5% LiF, the impedance of the electrolyte sheet increases, which is 147Ω, and its lithium-ion conductivity decreases to 4.3×10^{-4} S·cm⁻¹. The reason for the rapid decrease in impedance may be that part of the tetragonal phase in the electrolyte sheet begins to transition to the cubic phase, at which time the tetragonal phase and the cubic phase in the electrolyte sheet coexist, and then the phenomenon of rising may be due to the excess of LiF, which causes the LLZO part of the cubic phase to decompose into La₂Zr₂O₇.

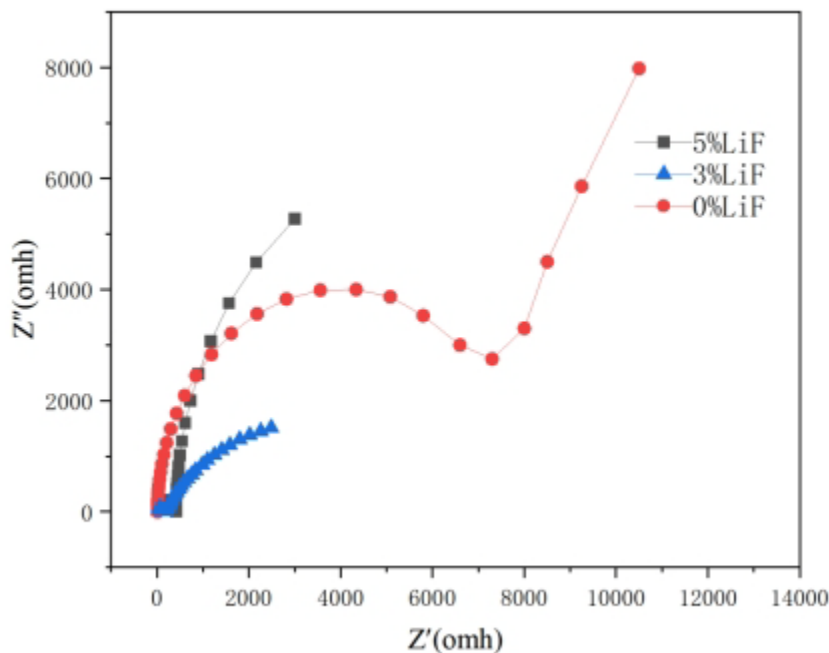


Fig. 3. AC impedance spectrum of LLZO solid electrolyte with different initial LiF addition amounts.

3. Conclusion

- (1) Incorporation of a certain amount of LiF contributes to the formation of a pure cubic garnet phase at room temperature.
- (2) The total conductivity of the prepared F-doped LLZO sample was 1.29×10^{-3} S/cm, which was much higher than the volumetric conductivity of undoped LLZO.

(3) LiF as a burning aid, which improves the sintering performance of LLZO and reduces the sintering temperature when LLZO transitions from tetragonal phase to cubic phase.

(4) LiF burner does not affect the crystal structure of the matrix, but can improve its ionic conductivity, so it can be combined with other modifiers for compound doping modification.

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