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Effect of extra Li content on the property of tetragonal $Li_7La_3Zr_2O_{12}$ solid electrolyte prepared by auto-consolidation method

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Abstract. For all-solid-state lithium ion battery, $Li_7La_3Zr_2O_{12}$ (LLZO) is a unique solid electrolyte possessing both high total ionic conductivity and stability against Li. As to conventional preparation methods, there is a stereotype that higher density always comes from higher pressure enforced upon the LLZO pellets. A different way called “auto-consolidation” was provided by us. Without the demand of pressing operations, the preparation process is greatly simplified. The surface tension of liquid Li_2O at sintering temperature is the key factor for samples to consolidate. In this paper, the effect of extra Li content (0-25%) on the property of tetragonal LLZO was studied. Results show that only when the extra Li content reaches up to 10%, can dense tetragonal LLZO be gained. The optimized extra content value is about 15% with a relative density about 93% and a total conductivity of 5.6×10^{-5} S cm^{-1} at 30 ^oC, which is the highest one for tetragonal LLZO in reported issues, about two times higher than that prepared by hot-pressing method. At 30-100 ^oC, the activation energies for total conductivity are about 0.30~0.42 eV $atom^{-1}$, decreasing with the increasing of extra Li content, which is slightly lower than the previous reported values. This work suggests a simple and reliable route for the preparation of ceramic solid electrolytes.

Introduction

Lithium ion battery (LIB) gains great success in commercial applications as the main storage device. Nevertheless, its safety issues still haven’t be resolved due to its liquid organic electrolytes which are volatile and flammable. All-solid-state LIB is viewed as a thorough solution for the safety issues[1]. Instead of liquid electrolytes, all-solid-state LIB employs solid state electrolytes as both separators and ion conductors. Among current solid electrolyte materials, LLZO has attracted ever-increasing attention over the last few years due to its great advantages, such as high chemical stability with lithium metal electrode, wide electrochemical window (0-5 V vs. Li^+/Li) and low bulk and grain boundary resistance[2-4].

LLZO has been determined to have two different structures, which are cubic and tetragonal, respectively [2-4]. At room temperature (RT), cubic structure is unstable and tends to change into tetragonal structure. With doping of alien elements, cubic structure can be stabilized at RT with a total conductivity of 10^{-6}-10^{-3} S cm^{-1}[5-11]. On the contrary, the total conductivity for tetragonal LLZO prepared is about two orders lower about 10^{-7}-10^{-6} S cm^{-1} with a relative density of 60-73%[10, 12, 13]. For solid state electrolytes, higher density always means higher ionic conductivity. In 2012, Jeff Wolfenstine promoted the relative density of tetragonal LLZO to 98% by hot isostatic pressing method and a total conductivity of 2.3×10^{-5} S cm^{-1} was gained, which is the highest reported value for tetragonal LLZO[14].

As to conventional preparation methods, there is a stereotype that higher density always comes from higher pressure enforced upon the LLZO pellets [5, 6, 8, 15-16]. But for cold isostatic pressing method, the highest reported density for tetragonal LLZO is still as low as 73%, even when the pressure was promoted to 800 MPa [12, 13]. And for both cold and hot isostatic pressing methods, the demands for preparation equipment involving high pressure are so hard to be satisfied for practical application.

A different way with an auto-consolidation mechanism was provided and discussed in our previous work[17]. No pressing operations are employed during the whole preparation process. The preparation process for dense LLZO is greatly simplified. The surface tension of liquid Li_2O at sintering temperature is the main instinct motivation for LLZO powder to consolidate. It means that the amount of Li plays a key role in the preparation of dense LLZO solid electrolytes. Base on this, the effect of extra Li content (0-25%) on the property of tetragonal LLZO was studied. The results of this work would facilitate the development of LLZO solid electrolytes technology.

Experimental

Preparation of LLZO powders.

As described in [17], LLZO powders were prepared by solid reaction and all operations were conducted in air. Stoichiometric amounts of $LiOH{\cdot}H_2O$, La_2O_3, and ZrO_2 precursor powders (All of the reagents are analytically pure from Sinopharm Chemical Reagent Co. Ltd) were ball-milled in a ZrO_2 jar with ZrO_2 balls filled with ethanol at 400 rpm min^{-1} for 10h. Extra 0, 5, 10, 15, 20, and 25% $LiOH{\cdot}H_2O$ (the samples are marked as 000Li, 005Li, 010Li, 015Li, 020Li, and 025Li subsequently) was added into the starting powders to valuate the effects of Li content. After ball-milling, the slurries were dried at 100 ^oC for 10 h and calcined at 1150 °C for 15h in Al_2O_3 crucible. The heating rate from RT to 1150 ^oC is 10 ^oC/min. The primary LLZO powder was ball-milled again in a ZrO_2 jar with ZrO_2 balls at 500 rpm min^{-1} for 10 h. After the second ball-milling, the primary powders were grinded by agate mortar and sieved by 100 meshes. Then tetragonal LLZO powders were prepared.

Preparation of LLZO pellets.

The LLZO powders were put in Al_2O_3 crucible and compacted by vibration. They were heated step by step. From RT to 900 ^oC the heating rate is 10 ^oC/min, followed by a heating rate of 1 ^oC/min from 900 ^oC to 1150 ^oC. The powders were finally sintered to be bulks at 1150 ^oC in air for 15 h. The dense LLZO bulks were sliced by a dimond saw and polished by $1000^{\#}$ diamond chip for characterization and test.

Characterization.

Malvern Mastersizer 2000 laser-diffraction particle size analyzer was employed to determine the particle size distribution of the LLZO powders before sintering. According to Archimedes principle, the densitied of LLZO bulks were determined from their weights and volumes. The volumes were determined by draining water. The relative density value was determined by dividing the bulk density by the theoretical value (~5.108 g cm^{-3})[12].

X-ray diffraction (XRD, Bruker D8 advance X-ray diffractometer, Cu Kα radiation) was used to characterize the crystalline phases of LLZO after sintering. The morphology of the cross-section of sintered samples was characterized by scanning electron microscopy (Hitach S-4800 Field Emission SEM).

Electrical conductivity measurements were performed on the LLZO pellets using two probes method. Li-ion blocking Au electrodes were sputter coated on the top and bottom surfaces of the samples (Au|LLZO|Au). Impedance spectras were collected with an electrochemical interface (Solartron 1287, Solartron Analytical) and a frequency response analyzer (Solartron 1260, Solartron Analytical) under open-circuit voltage (OCV). The frequency range was from 1 MHz to 1 Hz and the ac amplitude was 10 mV. Temperature-dependent ionic conductivities were measured from the range of 30 °C to 100 °C.

Results and discussion

Fig.1 shows the particle size distributions of LLZO powders. It indicates that the particle sizes of LLZO powders before sintering are not uniform. The average particle sizes are 11.9, 12.3, 16.7, 11.9, 10.6, and 9.7μm for samples of 000Li, 005Li, 010Li, 015Li, 020Li, and 025Li respectively, with 3 main consecutive Gaussian distributions around 0.5, 5 and 50μm. For each sample, the amount of larger particles is several times to the amount of small ones. That is in good agreement with the optimized packing theories [18]. So, the porosity of the packing powder will be minimized.

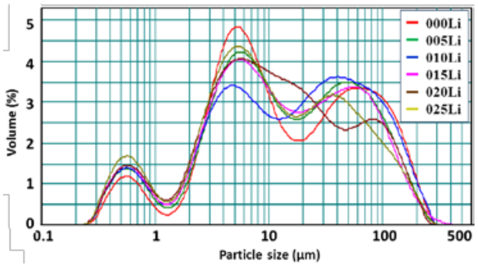

Fig.1 Particle size distribution of LLZO powders before sintering.

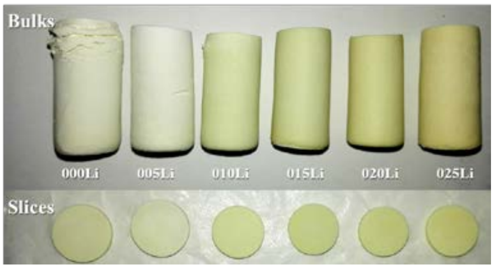

Fig.2 Picture of bulks and slices of LLZO samples.

The picture of LLZO bulks and their slices is shown in Fig.2. According to Archimedes principle, the relative density values are determine to be 86, 87, 91, 93, 92, and 91%. The relative density values of LLZO are much higher than the previous reported value (60-73%) of cold isostatic pressing method [12, 13] and just a little lower than the reported value (98%) of hot isostatic pressing method [14].

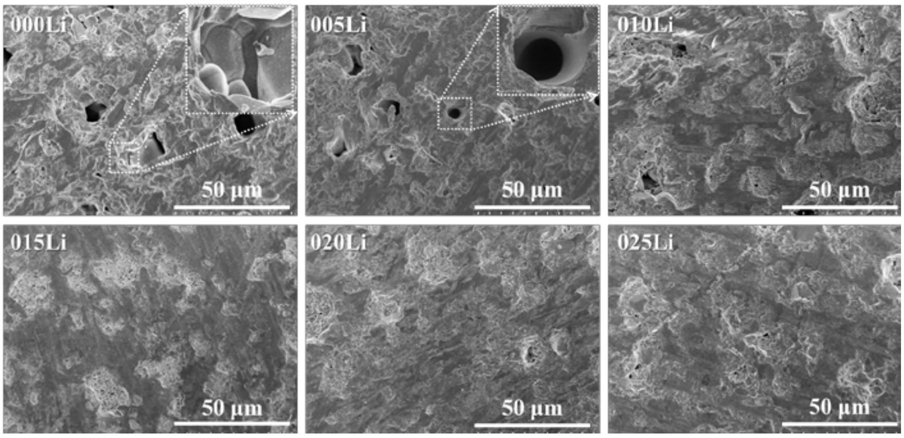

Fig.3 SEM images of dense tetragonal LLZO pellet.

The SEM images of the surface of LLZO sample are shown in Fig.3. In white dotted window of 000Li, it can be observed that the LLZO sample is built by different size particles gathering together. However, only when the extra Li content reaches up to 10%, can dense tetragonal LLZO be gained. There are apparent holes in the surface of both 000Li and 005Li. The result of SEM images is in agreement with both the picture of LLZO bulks shown in Fig.2 and the high density measured above.

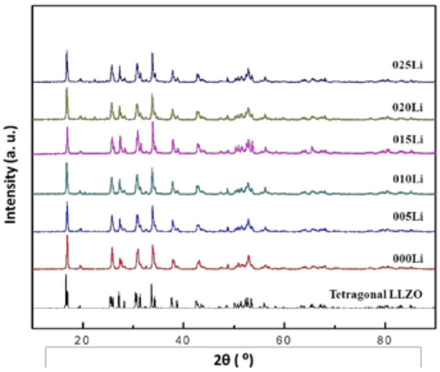

Fig.4 X-ray diffraction patterns for LLZO samples after sintering.

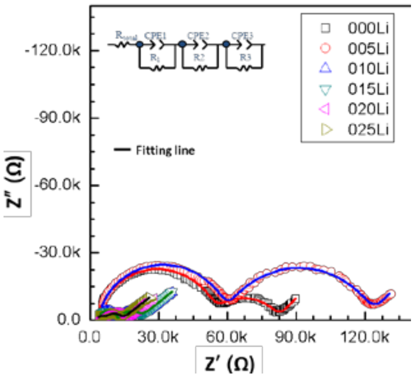

Fig.5 Nyquist plots for the total conductivities of LLZO (Au|LLZO|Au) samples at 30 °C.

The XRD patterns for LLZO samples are shown in Fig.4. The peak splitting is indicative of LLZO with a tetragonal structure (space group $I4_1/acd$ (No.142))[12]. The results of Fig.4 are in agreement with the previous reported results that, without dopants, only LLZO with tetragonal structure is stable at room temperature[2, 10, 12-14]. However, either the extra Li content is higher or lower than 15%, there are a few impurity peaks can be observed in Fig.4.

Fig.5 shows the impedance plots measured at 30 °C for Au|LLZO|Au. Each curve can be separate into a high frequency region which contains two semicircles and a low requency region which contains a spike. The semicicles are attributed to bulk resistance and grain boundary resistance seperatally and the intercept of the semicircle of higher frequency on the real Z axis gives the total ionic resistance (lattice+grain boundary) [14]. This inclined curve can be attributed to the frequency dispersion phenomenon and be described with capacitance or constant phase element (CPE)[17]. Each experimental data was fitted with an equivalent circuit consisting of R_{total} (R_1CPE_1) (R_2CPE_2) (R_3CPE_3), as shown in Fig.5. R_{total} is the total resistance of the sample. And the fitting lines are shown in solid type. Using the value of R_{total} and the sample dimensions, the total conductivity of the tetragonal LLZO sample was calculated. Fig.6a shows the Arrhenius plots of LLZO samples. From left to right of each curve, the spots refer to 100, 90, 80, 70, 60, 50, 40 and 30 °C respectively. According to Arrhenius equation[12], activation energy was determined from the slope of the ln(σT) versus 1/T plot for the total conductivity. The results of total ion conductivity at 30 °C and their activation energy for LLZO samples with different extra Li content are shown in Fig.6b. It indicates that the optimized extra content value is about 15% with a total conductivity of 5.6×10^{-5} S cm^{-1} at 30 °C, which is the highest one for tetragonal LLZO in present reported issues, about 10–500 times higher than previously reported values of cold isostatic pressing and even 2 times higher than that of hot isostatic pressing. The activation energies for total conductivity are about 0.30~0.42 eV $atom^{-1}$, decreasing with the increasing of extra Li content, slightly lower than the previous reported values.

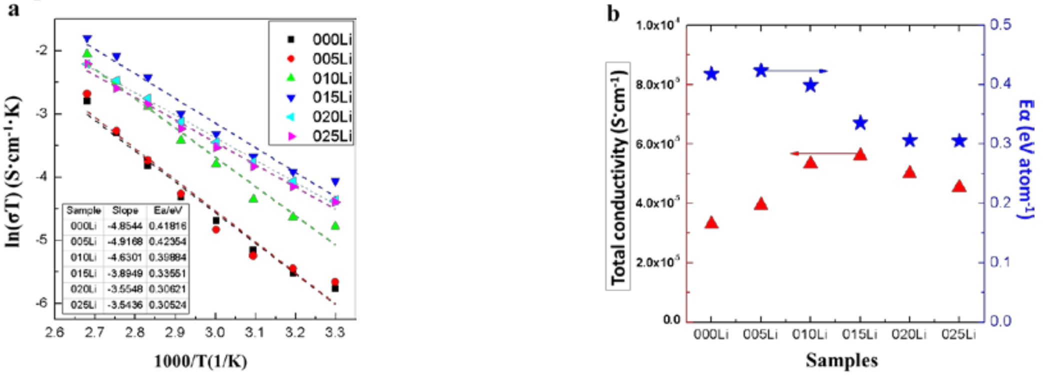

Fig.6 (a) Arrhenius plots of the total conductivities between 30 to 100 °C; (b) effect of extra Li content on total conductivity and activation energy for LLZO samples (Au|LLZO|Au).

Conclusion

All-solid-state LIB is viewed as a thorough solution for the safety issues due to the employment of solid electrolytes as both separators and ion conductors instead of liquid organic electrolytes which are volatile and flammable. LLZO is a unique solid electrolyte possessing both high total ionic conductivity and stability against Li. As to conventional preparation methods, there is a stereotype that higher density always comes from higher pressure enforced upon the LLZO pellets. A different way called “auto-consolidation” was provided by us. Without the demand of pressing operations, the preparation process is greatly simplified. The surface tension of liquid Li_2O at sintering temperature is the key factor for samples to consolidate. In this paper, the effect of extra Li content (0-25%) of the property of tetragonal LLZO was studied. According to the observation of the appearance of LLZO bulks and SEM of LLZO pellets, only when the extra Li content reaches up to 10%, can dense tetragonal LLZO be gained. The optimized extra content value is about 15%. The sample of 015Li is in a pure tetragonal structure with a relative density about 93% and a total conductivity of 5.6×10^{-5} S cm^{-1} at 30 °C, which is the highest one for tetragonal LLZO in reported issues, about 10–500 times higher than previously reported values of cold isostatic pressing and even 2 times higher than that of hot isostatic pressing. At 30-100 °C, the activation energies for total conductivity are about 0.30~0.42 eV $atom^{-1}$, decreasing with the increasing of extra Li content, which are slightly lower than the previous reported values. This work suggests a simple and reliable route for the preparation of ceramic solid electrolytes.

Acknowledgments

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