Microwave assisted reactive sintering for Al doped Li7La3Zr2O12 lithium ion solid state electrolyte

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Abstract
Li6.28Al0.24La3Zr2O12 (Al-LLZO) solid electrolyte for Li-ion battery was prepared by a microwave-assisted reactive sintering (MARS) method. When sintered by the MARS method, the Al-LLZO cubic phase formed at 1000 °C, which is 100 °C lower than that in a conventional furnace sintering method. With the increase of sintering temperature and holding time in MARS, the relative density of Al-LLZO samples goes up. Also, the improved conductivity is related to the decrease of pore number between Al-LLZO grains. And the reduced grain boundary resistivity contributes the most to total reduced resistivity compared with the grain resistivity. The Li-ion conductivity of the Al-LLZO samples prepared by MARS at 1200 °C for 3 h reaches 1.06 × 10^{-4} S cm^{-1} at 25 °C and the value of conduction activation energy is 0.36 eV at 25–150 °C.

1. Introduction

Safety has been considered to be one of the most important issues for the development of next generation Li-ion batteries. As solutions to substitution for flammable, volatile and relatively unstable organic liquid-based electrolytes, solid-state Li-ion and Li-air batteries based on flame retardant and ionic conductive solid electrolyte have been extensively researched [1, 2]. Different types of solid electrolytes, including NASICON-type phosphates [3], LISICON-type sulfides [4], Li3N [5], LIPON [6], perovskite-type oxides [7], and garnet-type oxides [8] have been reported. Among these solid-state electrolytes, lithium stuffed garnets Li7La3Zr2O12 (LLZO) have drawn much concern because of their good compatibility with electrode materials, high ionic conductivity (> 10^{-4} S cm^{-1}) at room temperature and the wide electrochemical potential window [8]. It has also been reported that the ionic conductivity of cubic LLZO phase is two orders of magnitude higher than that of tetragonal phase [8, 9]. Therefore, in order to obtain cubic phase LLZO garnet with high Li+ conductivity, different synthesis methods including sol-gel method [10], combustion method [11], and the chemical co-precipitation method [12] have been tried. Janani et al. adopted the modified sol–gel technique based on citric acid as chelating agent and butan-1-ol or propan-2-ol as surface active agent and prepared cubic Li6.16Al0.28La2Zr2O12 at 1200 °C [10]. Dhivyaa et al successfully synthesized Li7La3Zr2O12 and Li6.28Al0.24La3Zr2O12 with cubic phase structure by means of solution combustion using the aqueous solution reactants and organic fuel. And it was found that the rapid synthesis can obtain high Li+ conductive cubic phase with optimization of excess lithium source, the synthesis temperature and sintering time [11–13]. For example, various researches have shown that the appropriate substitution for Li+ by Al3+ in LLZO would create Li+ vacancy and Al dopants play an important role increasing vacancies at octahedral sites [13–15]. Doping of high valance cation as well decreases lithium content in LLZO and accordingly generates more vacancy. Recent studies have also proved that doping some ions as Sr2+, or Ce4+ in La3+ site [16, 17] would facilitate the sintering and lower the sintering temperature of LLZO, and Zr4+ site doping (Nb5+ or Ta5+) [18, 19] would improve conductivity which is attributed to the decrease of lithium content in LLZO, resulting in more vacancies. Thus, it
Figure 1. XRD patterns of Al-LLZO electrolyte pellets prepared by conventional sintering method at 1000 °C and MARS at 1100, 1150 and 1200 °C.

Figure 2. Cross section SEM images for Al-LLZO pellets prepared by MARS, (a) 1000 °C for 1 h, (b) 1150 °C for 1 h, (c) 1200 °C for 1 h, (d) 1200 °C for 1.5 h, and (e) 1200 °C for 3 h.
has also been attempted to jointly improve the density and total Li$^+$ conductivity by adding appropriate dopants at La$^{3+}$ and Zr$^{4+}$ sites [20].

Another important factor affecting lithium conduction of the electrolytes is the microstructure related to grains and grain boundaries. With a dense microstructure, improvement of the conductivity would be found as a result of the decrease of porosity and the grain boundary resistance [21, 22]. Therefore, sintering aids such as Li$_4$SiO$_4$ [10] and Li$_2$O [23] were adopted to facilitate the densification of solid electrolyte. Besides, other methods like hot press sintering [24], spark plasma sintering [25], field assisted sintering [26] were also successfully applied to achieve fully dense LLZO ceramics.

In recent years, microwave heating has been well employed in the field of sintering and joining of ceramics due to its advantages against conventional sintering [27, 28]. Microwave energy is a form of electromagnetic energy in the frequency range of 300 MHz to 300 GHz [29]. And microwave heating is a process in which the materials couple with microwaves, absorb the electromagnetic energy volumetrically, and transform into heat. Leopold et al employed microwave sintering method to synthesize Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$ (PO$_4$)$_3$ ceramics with suitable properties in one single step at a relative low sintering temperature as 890 °C, which is much faster than conventional sintering method with long dwelling times (several hours) [29]. So as a flash sintering technique, microwave sintering could also be expected to lead a preparation of cubic phase LLZO and avoid the problems that exist in the conventional high temperature sintering process such as serious lithium loss and appearance of tetragonal phase [30]. Researchers such as Amores et al have successfully synthesized Al-doped LLZO garnet with the nominal composition of Li$_{6.28}$Al$_{0.24}$La$_3$Zr$_2$O$_{12}$ through microwave assisted sintering and mainly study the stoichiometry of the cubic sample, the lithium-ion diffusion behavior and diffusion efficiency by electrochemical impedance spectroscopy (EIS) and the state-of-art muon spin relaxation (MSR) spectroscopy [31].

In this work, microwave assisted reactive sintering (MARS) was employed to fabricate Li$_{6.28}$Al$_{0.24}$La$_3$Zr$_2$O$_{12}$ (Al-LLZO) in one single step. The Al-LLZO samples were characterized in terms of crystal lattice structure, pellet microstructure with grains and grain boundaries and Li ionic conductivity. The results indicate that MARS is a very promising method to achieve pure cubic phase Al-LLZO with high relative conductivity.

2. Experiment

2.1. Synthesis of Li$_{6.28}$Al$_{0.24}$La$_3$Zr$_2$O$_{12}$ electrolyte

Mixture with the nominal chemical formula Li$_{6.28}$Al$_{0.24}$La$_3$Zr$_2$O$_{12}$ (Al-LLZO) were yielded from stoichiometric amounts of Li$_2$CO$_3$, La$_2$O$_3$, ZrO$_2$ and γ-Al$_2$O$_3$ powders (All of reagents are analytically pure from Sinopharm Chemical Reagent Co. Ltd). And 10 wt% excess Li$_2$CO$_3$ was added to compensate for the evaporation loss of
lithium during sintering process. The powders were ball milled in alcohol for 24 h and then were dried in oven at 75 °C for 3 h. Then, the mixture obtained were ground and then pressed into pellets in a die with the diameter of 14 mm and thickness of 1.5 mm. Microwave sintering (HY-QS6016, Hunan Huaye Microwave Technology Co., Ltd) was carried out to fabricate the samples at 1000, 1150 and 1200 °C in N₂ atmosphere with a frequency of 2.45 GHz. The heating rate was controlled within the range of 10–35 °C min⁻¹. Al-LLZO samples were also prepared by conventional sintering for microstructure and property comparing, in which green layered compacts were sintered at the same temperature for 90 min in N₂ in a laboratory tube furnace. After sintering, all the samples are polished to the same size with the A = 1.3 cm², L = 0.13 cm, where A and L are surface area and thickness of each pellet.

2.2. Sample characterization
X-ray diffraction (XRD, SmartLab X-Ray Diffraction, Cu Kα) analysis was employed to determine the phase structure of the sintered Al-LLZO samples in the 2θ range from 10 to 60 degree with a step size of 0.02 degree. Field emission scanning electron microscope (SEM, Hitachi 8020) was used to characterize the microstructures of the sintered Al-LLZO pellets. Electrochemical impedance spectra (EIS) were measured by using an electrochemical workstation (AutoLab 86843) in the frequency range of 10 Hz to 5 MHz with Ag paste as current collector from temperature (25 °C) to 175 °C. And the electrochemical impedance spectra (EIS) was fitted by Zview software.

3. Results and discussion

3.1. Phase structural analysis
Figure 1 shows the XRD patterns of the Al-LLZO pellet prepared by conventional sintering at 1000 °C for 5 h and by MARS at 1000, 1150 and 1200 °C for 1 h respectively. It can be seen that the XRD patterns of Al-LLZO synthesized by MARS at 1000 °C reveal a highly crystalline single-phase garnet, which corresponds to the cubic LLZO garnet with Ia3d space group (PDF #45-0109) as pointed out in figure 1. But for the sample sintered at 1000 °C by conventional sintering method, the XRD pattern is indexed to a mixture of cubic and tetragonal phase indicated by the additional peaks between 30° and 32°, which is also consistent with results reported by Ezhiyl Rangasamy et al [24]. And the lattice parameter of cubic phase Al-LLZO prepared by MARS is a = 12.84214 Å, very close to the reported value, a = 12.8974 Å [32].
3.2. Microstructure of the sintered samples

Figure 2 shows the cross section SEM images of Al-LLZO pellets prepared by MARS at different conditions. The Al-LLZO samples sintered at 1000 °C have a porous structure with a relative density of 76.8% (figure 2(a)). When the sintering temperature increases to 1150 °C and 1200 °C, the relative density raises to 84.4% and 86.8%, respectively, as listed in table 1 and the grain size also becomes larger. For Al-LLZO sintered at 1200 °C, the amount of intergranular phase located out of the grains decreases. And the Al-LLZO grains still keep growing with holding time prolonged. The high magnification SEM images of cross section for Al-LLZO pellets showed in figure 3 reflect the changes of pore morphology clearly. The pores of samples sintered at 1200 °C for 1 h are almost connected. While with holding time prolonged, the amount of connected pores reduces and finally most of them become isolated and smaller when the microwave sintering time reaches 3 h.

3.3. Li ionic conductivity

In the microwave sintering process, the size of grains, length of grain boundaries and the number of pores (reflected by the density) would finally determine the ionic conductivity of Al-LLZO pellet. Figure 4(a) shows the AC impedance spectra of Al-LLZO sintered by microwave at 1150 °C for 1 h, at 1200 °C for 1 h, 1.5 h and 3 h respectively. It can be seen that with the prolonged holding time, the total resistivity of the Al-LLZO decreased greatly, which is also consistent with the increase relative density as shown in table 1. To further analyze the resistivity contribution from grains and grain boundaries, a suitable equivalent circuit $R_b(R_{gb}CPE_1)(R_{gb}CPE_2)$ based on the schematic diagram was applied for Al-LLZO electrolyte as inserted in figure 4(c). The $R_b$ and $R_{gb}$ are the grain and grain boundary resistance, and $R_q$ is the polarization resistance between Al-LLZO electrolyte and Ag current collector electrode. And figure 4(b) gives a typical EIS fitting line to separate the grain resistivity and grain boundary resistivity. It could be seen in figure 4(c), when sintered at 1150 °C, the grain boundary resistance as the value of 6.4 kOhm is the major component, and grain resistance (2.3 kOhm) is the minor component. With the increase of sintering temperature and holding time, both $R_b$ and $R_{gb}$ decrease, but it can be found that $R_b$ contributes the most to the reduction of the total resistance. Then we can find that for Al-LLZO sample sintered at 1200 °C with 3 h, the $R_b$ is 0.4 kOhm and $R_{gb}$ is 0.5 kOhm. The ever reduced CPE1 value also proves the decrease of porosity as shown in SEM images. So we can conclude that in the sintering process, the reduced

| Nominal composition | Sintering condition | Total conductivity ($S cm^{-1}$) | Relative density (%) | Activation energy (eV) |
|---------------------|---------------------|---------------------------------|----------------------|------------------------|
| Al-LLZO             | 1000 °C@1 h         | $6.21 \times 10^{-7}$          | 76.8                 | 0.47                   |
| Al-LLZO             | 1150 °C@1 h         | $1.42 \times 10^{-5}$          | 84.4                 | 0.44                   |
| Al-LLZO             | 1200 °C@1 h         | $2.19 \times 10^{-5}$          | 86.8                 | 0.44                   |
| Al-LLZO             | 1200 °C@1.5 h       | $4.64 \times 10^{-5}$          | 88.6                 | 0.36                   |
| Al-LLZO             | 1200 °C@3 h         | $1.06 \times 10^{-4}$          | 89.3                 | 0.36                   |

Figure 5. Arrhenius plots of total conductivities of Al-LLZO pellets prepared by MARS at various conditions.

Table 1. Sintering conditions, total conductivity at room temperature (25 °C), relative density and activation energy of Al-LLZO electrolyte.
Table 2. Comparison of properties of cubic LLZO ceramics fabricated by several methods from references.

| Nominal composition | Synthesis method                        | Temperature & time | Total conductivity ($S \text{ cm}^{-1}$) | Activation energy(eV) | References |
|---------------------|-----------------------------------------|--------------------|------------------------------------------|-----------------------|------------|
| LLZO                | Solid state reaction                    | 1230 °C × 36 h     | $2.44 \times 10^{-4}$                    | 0.34 (18–70 °C)       | [8]        |
| Al-LLZO             | Solid state reaction method             | 1200 °C 24 h       | $1.81 \times 10^{-4}$                    | 0.37 (25–90 °C)       | [33]       |
| Al-LLZO             | Hot pressing process                    | 1000 °C × 1 h      | $4 \times 10^{-4}$                       | 0.26                  | [24]       |
| Al-LLZO             | Microwave-assisted synthesis            | 1000 °C × 1 h      | Around $10^{-3}$                         | 0.55 ± 0.03 (50–250 °C) | [31]     |
| Al-LLZO             | Sol-gel synthesis                       | 1200 °C × 12 h     | $1.1 \times 10^{-4}$                     | 0.38 (33–240 °C)      | [10]       |
| LLZO                | Chemical co-precipitation method        | 1180 °C × 20 h     | $2 \times 10^{-4}$                       | 0.25 (15–90 °C)       | [12]       |
| Ta-LLZO             | Spark plasma sintering process          | 1000 °C × 10 min   | $1.35 \times 10^{-3}$                    | 0.41 (–10 to 80 °C)   | [25]       |
pores and increased grain size cause the reduced grain boundary length, which greatly reduces grain boundary resistivity, and finally contributes to the enhanced conductivity.

The total conductivity was obtained from the fitting plots using Zview software. Figure 5 shows the Arrhenius plots of Al-LLZO conductivity sintered at different conditions. The Li⁺ conductivity of Al-LLZO sintered at 1000 °C is very low, just about 6.21 \times 10^{-7} \text{ S cm}^{-1}. But when the sinter temperature increases to 1150 °C, the Li⁺ conductivity goes up to 1.42 \times 10^{-5} \text{ S cm}^{-1}. And when the sinter temperature reaches 1200 °C at 3 h, it is 1.06 \times 10^{-4} \text{ S cm}^{-1}. The activation energy values for Al-LLZO conductivity are listed in table 1, and they are found to be within the value range reported for LLZO garnet-type solid electrolytes. Properties of cubic LLZO based electrolyte fabricated by several methods from reference are listed in table 2. The total conductivity prepared in this work is almost at the same magnitude (10^{-4} \text{ S cm}^{-1}) compared with the hot-pressing method, sol-gel synthesis and chemical co-precipitation method. It should be noted that, the total conductivity of 1.06 \times 10^{-4} \text{ S cm}^{-1} prepared by MARS in our study is significantly higher than the value, 10^{-9} \text{ S cm}^{-1} from other work [31] also using microwave sinter.

4. Conclusions

The synthesis of Li ion conductive Al-LLZO ceramics by a fast MARS method was investigated in this work. Cubic Al-LLZO phase was successfully fabricated at 1000 °C, lower than that in a conventional sintering method. With increased sintering temperature, the Li⁺ conductivity of Al-LLZO would increases and finally arrives 1.06 \times 10^{-3} \text{ S cm}^{-1} when sintered at 1200 °C for 3 h. And the activation energy of Al-LLZO electrolyte is 0.36 eV. Within the experiment condition, the reduced electrolyte resistivity is mainly attributed to grain boundary resistivity, in which the decrease of grain resistivity is not significant. This is also consistent to the reduced capacitance caused by pores in Al-LLZO pellet. This work sheds on the fabrication of Al-LLZO solid electrolyte in a fast microwave assisted reaction method and suggests promising application potential in the Li ion solid state electrolyte.

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