Fabrication of single-grain-layered garnet-type electrolyte sheets by a precursor method

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ABSTRACT

Thin and dense solid electrolytes are required to improve the performance of oxide-based all-solid-state batteries. We investigated the effect of the uniformity of dopant diffusion on the sinterability of the electrolyte, fabricated a garnet-type electrolyte sheet composed with a single grain along with thickness direction using the tape casting method. The electrolyte sheet using raw powder prepared by the precursor method exhibits a relatively high Li-ion conductivity of \(6.7 \times 10^{-6} \text{ S-cm}^{-1}\) at \(25^\circ\text{C}\) and low activation energy of 0.33 eV. We then investigated the factors responsible for the densification of the obtained sheets by cross-sectional morphological observation and compositional analysis.

1. Introduction

Lithium garnet-type oxides, \(\text{Li}_2\text{La}_{2}\text{Zr}_2\text{O}_{12}\) (LLZ), have attracted much attention as the solid electrolyte for all-solid-state batteries due to their high ionic conductivity, high stability toward Li metal, and wide potential window \([1–4]\). However, lithium garnet oxides have been reported to have poor sintering properties \([5–8]\), requiring long sintering times at high temperatures of around 1100°C to produce a dense LLZ sintered body. The impurities produced during the high temperature sintering have a negative effect on the densification of LLZ electrolytes. To improve the sinterability of garnet-type solid electrolytes, many previous studies have reported on the pressurization process, such as hot pressing, the investigation of dopants and a sintering additive, and the material synthesis process \([9–11]\). In this study, we focused on improving the sintering properties of electrolytes using dopants and a sintering additive. It has been reported that the sinterability and conductivity can be improved by replacing a portion of the \(\text{Zr}^{4+}\) sites with \(\text{Ta}^{5+}\) and a portion of the \(\text{Li}^+\) sites with \(\text{Al}^{3+}\) or \(\text{Ga}^{3+}\) \([12]\). Allen et al. have reported that the effect of this partial substitution of \(\text{Ta}, \text{Al}, \text{and Ga}\) on the conductivity of garnet-type electrolytes. Their paper showed that the \(\text{Ta}\) substitution for LLZ significantly increased the conductivity, but the addition of \(\text{Al}\) and \(\text{Ga}\) to \(\text{Ta}\) substituted LLZ reduced it and increased the activation energy. They concluded that the substitution of \(\text{Al}\) and \(\text{Ga}\) in the conductive pathway of the \(\text{Li}\) site inhibits the conduction of Li ions. It was also noted that the excessive amount of \(\text{Al}\) substitution resulted in a high grain boundary resistance. According to SEM-EDS analysis, \(\text{Ga}\) and \(\text{Al}\) substituted garnet-type electrolytes show a non-uniform distribution of \(\text{Ga}\) and \(\text{Al}\) elements in the sintered bulk, and an increased concentration of \(\text{Al}\) and \(\text{Ga}\) was observed at the grain boundaries \([12–14]\).

It was considered that the impurity phase was generated due to the segregation of the dopants at the grain boundaries with large resistances.

Based on these reports, we surmised that the uniform diffusion of the dopants is important to improve the sintering properties of garnet-type electrolytes. Previously, we have reported the synthesis process of \(\text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}\) (LLZT) using the precursor method \([15]\). The results of compositional analysis showed that the elemental distribution of the solid electrolytes prepared by the precursor method was more uniform than that of the solid electrolytes prepared by the conventional solid-state reaction. The feature of this synthesis method is that garnet-type oxides are synthesized below 600°C to obtain powders with sub-micron diameters particle sizes. Therefore, the precursor method is considered to be one of the useful methods to obtain fine particles to produce high-density electrolytes. In this study, we attempted to fabricate thin and dense LLZT electrolyte sheets that are sensitive to compositional changes during high temperature sintering. First, garnet-type LLZT fine powder co-doped with \(\text{Al}\) and \(\text{Ga}\) was prepared by the precursor method. This powder was then used to prepare the electrolyte sheets by the tape-casting method. The effect of the compositional uniformity of the LLZT powder has on the morphology, and conductive properties of the sintered sheets was thereby investigated.
2. Experimental

2.1. Preparation of the precursor oxide and the garnet-type powder

The precursor oxide, Ga$_{0.15}$Al$_{0.1}$La$_3$Zr$_{0.175}$Ta$_{0.225}$O$_{9}$, was prepared by a polymerized complex method based on a previous report [15]. Ga(NO$_3$)$_3$·H$_2$O (99%, Kojundo Chemical Lab. Co., Ltd), Al(NO$_3$)$_3$·9H$_2$O (99.9%, FUJIFILM Wako Pure Chemical Co., Ltd), La(NO$_3$)$_3$·6H$_2$O (99.9%, FUJIFILM Wako Pure Chemical Co., Ltd), ZrOCl$_2$·8H$_2$O (99.0%, FUJIFILM Wako Pure Chemical Co., Ltd), and TaCl$_5$ (99.9%, Rare Metallic Co., Ltd) were used as starting materials. An appropriate amount of TaCl$_5$ was firstly dissolved in ethanol and then mixed with a stoichiometric amount of other starting materials. After that, citric acid (95%, FUJIFILM Wako Pure Chemical Co., Ltd) and ethylene glycol (99.9%, FUJIFILM Wako Pure Chemical Co., Ltd) were used as a chelating and complexing agent, respectively, and were added to the solution so that the molar ratio of metal: citric acid: ethylene glycol was 1:6:8. The final solution was stirred at 150°C overnight, heated at 350°C for 2 h, and then calcined at 700°C for 4 h in air. Li$_2$O (99.9%, FUJIFILM Wako Pure Chemical Co., Ltd) was used as the Li source. To prepare the garnet-type Li$_6$Ga$_{0.15}$Al$_{0.1}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ using the precursor oxide (PRE-LLZ), Li$_2$O and the obtained precursor oxide were mixed with agate mortar and pestle for 15 min in a dry, Ar-filled glove box. Afterward, the mixtures were calcined at 600°C for 15 h in Ar. The Li$_6$Ga$_{0.15}$Al$_{0.1}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ formation reaction in the presence of the precursor and Li$_2$O is as follows:

$$ \text{Ga}_{0.15}\text{Al}_{0.1}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_9 + 3 \text{ Li}_2\text{O} \rightarrow \text{Li}_6\text{Ga}_{0.15}\text{Al}_{0.1}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12} (1) $$

For comparison, the Li$_6$Ga$_{0.15}$Al$_{0.1}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ sample was also prepared using the conventional solid-state method (SS-LLZ). Li$_2$CO$_3$ (99.9%, FUJIFILM Wako Pure Chemical Co., Ltd), La$_2$O$_3$ (99.9%, FUJIFILM Wako Pure Chemical Co., Ltd), ZrO$_2$ (99.9%, Kanto Chemical Co., Inc.), Ta$_2$O$_5$ (99.9%, FUJIFILM Wako Pure Chemical Co., Ltd), Ga$_2$O$_3$ (99.9%, Kojundo Chemical Lab. Co., Ltd) and Al(OH)$_3$ (99.9%, Kojundo Chemical Lab. Co., Ltd) were used as starting materials. An excess amount of 10 mol% of Li$_2$CO$_3$ was added to prevent the loss of Li during calcination. The mixed starting materials were calcined at 850°C for 3 h in air.

The obtained LLZTGA powder was dispersed in a toluene and n-butanol mixed solution. Adipic acid, poly (vinyl butyral), and diamine were added as a dispersant, a binder, and a plasticizer into the mixed slurry, respectively. After that, the mixed slurry was uniformly stirred using a mixer (ARE-310, Thinky) and was de-formed to remove the air bubbles by using a planetary vacuum mixer (ARV-310, Thinky) before tape casting. The Li$_6$Ga$_{0.15}$Al$_{0.1}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ green sheet was prepared with a single doctor blade on a moving polyester film, and the solvent was removed during heating onto a touching polyester film. The tape was removed from the supporting polyester film and dried at room temperature to obtain the green sheet. Finally, the green sheet was sintered at 1100°C for 4 h in air. The relative density of obtained PRE-LLZ and SS-LLZ sheet was 91% and 73%, estimated from their sheet size and weight, respectively.

2.2. Preparation of the Li$_6$Ga$_{0.15}$Al$_{0.1}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ sheet using the tape-casting process

The thin ceramic sheets of Li$_6$Ga$_{0.15}$Al$_{0.1}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ were prepared by the conventional tape-casting method using a single doctor blade. Then, the SS-LLZ powder was ball-milled for 10 min using a Multi-beads shocker (MP3000, YASUI KIKAI) without solvent in air.

The phase identification was performed using X-ray diffraction (XRD; SmartLab, RIGAKU) with Cu Kα radiation at a scanning step of 0.02 ° at room temperature. The cross-section morphologies of the prepared sheets were observed using scanning electron microscope (SEM; JSM-6000Plus, JEOL) at an acceleration voltage of 15 kV. Specimens for cross-sectional observation were prepared by Ar ion milling using a cross section polisher (CP, IB-19510CP, JEOL). The electrochemical impedance spectra measurements of the LLZTGA sheets were performed using an impedance analyzer (SP-300, BioLogic) from 0°C to 40°C with an amplitude of 10 mV AC and a frequency range from 0.01 Hz to 7 MHz. To measure the ionic conductivity, the Au electrode was deposited by vacuum evaporation on both sides of the LLZTGA sheet. At each different temperature, the samples were held for 30 minutes at a constant temperature to reach thermal equilibrium before the measurement.

3. Results and discussion

3.1. Phase identification of the prepared samples

The phase identification of the precursor oxide, the PRE-LLZ powder and the sintered sheet was performed by XRD. Figure 1(a) shows the XRD patterns of the precursor oxide and the as-prepared PRE-LLZ powder. Although an unknown peak was detected around 25 °, the main diffraction peaks of the precursor oxide could be attributed to a cubic system with a pyrochlore-type (space group: Fd-3 m) crystal structure. The lattice parameter of the precursor oxide, calculated by the least-
square method, was $a = 1.08975(9)$ nm. On the other hand, all the observed diffraction peaks of the as-prepared P-LLZGA powder were indexed as those of the cubic system (space group: $Ia3d$) with the garnet-type structure. The XRD patterns of the PRE-LLZ and SS-LLZ sintered sheet were summarized in Figure. (b). The PRE-LLZ and SS-LLZ have garnet-type cubic structures, and no impurity phase was identified in both patterns. The lattice parameters of the as-prepared PRE-LLZ powder, sintered PRE-LLZ sheet, and sintered SS-LLZ sheet, calculated by the least-square method, were $a = 1.29660(4)$ nm, 1.29653(4) nm, and 1.29694(4) nm. The lattice parameter of PRE-LLZ was smaller

Figure 1. X-ray diffraction patterns of (a) the precursor oxide ($Ga_{0.15}Al_{0.1}La_3Zr_{1.75}Ta_{0.25}O_9$) and PRE-LLZ powder and (b) PRE-LLZ and SS-LLZ sheet calcined at 1100°C for 4 h.
than that of SS-LLZ. This difference in the lattice parameter may be attributed to the slightly different composition of the fabricated electrolyte sheets.

### 3.2. Particle and cross-sectional morphology of the prepared samples

Figure 2(a) and (b) show the SEM images of the particle morphology of the as-prepared PRE-LLZ powder and the milled SS-LLZ powder. The particle size of the as-prepared PRE-LLZ was smaller than that of the milled SS-LLZ powder due to synthesize at a relatively lower temperature (600°C). Figure 3(a) and (b) show the SEM images of the cross-sectional morphologies of the sintered PRE-LLZ and SS-LLZ sheets. The cracks at the top of the PRE-LLZ sheet occurred seemingly during sample processing. The thickness of the sintered PRE-LLZ and SS-LLZ sheets was 110 μm and 140 μm, respectively. The cross-sectional morphology of the PRE-LLZ sheet showed that it consists of a dense and single-grain layer along the vertical direction, although some small closed pores were present. The SS-LLZ was observed to have many pores and a particle size of approximately 10 μm. Figure 4(a) and (b) show the results of chemical composition analysis using EDS for the sintered PRE-LLZ and SS-LLZ sheets. In the case of PRE-LLZ, metallic elements excluding Li were found to be uniformly diffused. On the other hand, in SS-LLZ, Al and Ga were unevenly distributed at the grain boundaries, and Ta\(^{5+}\), which is partially replaced at the Zr\(^{4+}\) site, was not uniformly diffused, which agrees with the EDS line profile across the grain boundary (Figure 4(c) and (d)). It has been reported that Al has low diffusivity and a tendency to segregate at the grain boundaries has also been observed [13,14].

A similar trend was observed in the present study, indicating that not only Al but also Ga segregated at the grain boundaries in these sheets prepared by the conventional solid-phase synthesis method. The reason for the rapid diffusion of metallic elements in the precursor-synthesized sheets could be attributed to the synthesis of garnet-type oxides using precursor oxides with metallic elements occupying the 16c and 16d sites in the crystal structure (Fd-3 m). Since the reaction mechanism during the synthesis between Li\(_2\)O and the precursor oxide is not clear, in-situ observation of the synthesis process using advanced spectroscopic techniques is necessary to understand the crystal structure change of the precursor oxide.
3.3. Electrical conductivity measurement

The Li-ion conductive properties of the sintered PRE-LLZ and SS-LLZ sheets were determined using electrochemical impedance spectroscopy (EIS). Cole-Cole impedance plots obtained at 25°C for the sintered PRE-LLZ and SS-LLZ sheets are shown in Figure 5. In general, two semicircles are observed in the Cole-Cole plots of LLZ, one representing the material's bulk resistance in the high-frequency range and one for grain boundary resistance in the low-frequency range. The Cole-Cole plot of the PRE-LLZ sheet contains only one semicircle corresponding to the bulk resistance (Figure 5(b)). This result agrees with the observed PRE-LLZ sheet's cross-sectional morphology as the sheet consisted of a single-grain-layer and therefore should not have any grain boundary resistance parallel to the sheet surface. The bulk conductivity of the PRE-LLZ sheet was calculated to be $6.7 \times 10^{-4}$ S·cm$^{-1}$ from the semi-circle's diameter. We speculate that the ionic conductivity of PRE-LLZ is reduced by the closed pores inside the grain. To avoid the vaporization of lithium in the system, the heating rate during sintering of the sheets was relatively fast at 5°C/min. Since this heating rate was too fast for grain growth, many pores may have been created inside of the grain. On the other hand, the Cole-Cole plots for the SS-LLZ sheet displayed two semi-
circles on the high-frequency side. The resistance components in the high and low-frequency ranges were attributed to bulk and grain boundary resistance, respectively. The Li-ion conductivity of bulk and grain boundary calculated from the diameter of each semicircle were $1.0 \times 10^{-4}$ S·cm$^{-1}$ and $9.4 \times 10^{-5}$ S·cm$^{-1}$, respectively. Cross-sectional observation clearly showed grain boundaries, which may be responsible for the large grain boundary resistance. The concentration of Ta in the middle of the particles was higher than that in the vicinity of pores. (Figure 4(b)). It has been reported that the conductive properties of garnet-type electrolytes with cubic systems depend on the amounts of dopants [16,17]. Therefore, we speculate that the grains with low Ta dopant concentration may have acted as a resistive layer, resulting in decreased ionic conductivity. The temperature dependences of the bulk and grain boundary conductivity of the samples are shown in Figure 5(c). The Li-ion conductivity is fitted using an Arrhenius equation ($\sigma = A/T \exp(-E_a/kB/T)$), where $A$ is the frequency factor, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant ($1.381 \times 10^{-23}$ J/K), and $T$ is the absolute temperature. The Li-ion conductivities of the sintered PRE-LLZ and SS-LLZ sheets were all linear against the $1/T$ function, which indicates that the ionic conduction routes did not change in the

**Figure 4.** Continued.
measured temperature range. From the slope of the log\(\sigma\)T vs. 1000/T plot from 273 K to 313 K, the activation energies of the bulk conductivity of PRE-LLZ, the bulk and grain boundary conductivity of SS-LLZ sheets were estimated to be 0.33 eV, 0.43 eV and 0.38 eV, respectively. The activation energy of the bulk conductivity of PRE-LLZ was obviously lower than the one of SS-LLZ. In general, a lattice parameter enlargement leads to increased ionic conductivity and the decrease of activation energy. From experimental and theoretical points of view, lattice parameter change on lithium-ion diffusion was studied. It was suggested that the lattice parameter in which ion diffuse is an essential factor for ion diffusion [18–20]. However, in the present study, PRE-LLZ had a higher conductivity and smaller activation energy than SS-LLZ, despite the smaller lattice parameter. This result suggests that the uniformity of the elemental distribution strongly affects the conductive property than the difference in lattice volume observed in this study. Therefore, in order to improve the properties, it is necessary to consider in detail the effect of the uniformity of the elemental distribution within the grains and at the grain boundaries on the ionic conductivity as well as the change in the lattice parameter.

4. Conclusion

The garnet-type LLZT co-doped with Al and Ga sheet was successfully fabricated using fine raw powder prepared by the precursor method. The PRE-LLZ sheet is 110 \(\mu\)m thick and has almost no grain boundaries parallel to the sheet surface.
Therefore, the grain boundary resistance was significantly reduced compared to the SS-LLZ sheet prepared by the conventional solid-state reaction. The Li-ion conductivity of the PRE-LLZ sheet was 6.7 x 10^{-4} S cm^{-1} at room temperature, higher than that of the ones prepared by conventional solid-state reaction. Al, Ga, and Ta dopants diffused rapidly and were observed to be evenly distributed in PRE-LLZ grain, which resulted in the electrolyte sheets showing high conductivity and good sinter ability.

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