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# Interface behavior between garnet-type lithium-conducting solid electrolyte and lithium metal

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$Al_2O_3$ was doped (0.5, 1.0. and 2.0 wt.%) into the garnet-type lithium ion-conducting solid electrolyte with a nominal composition of $Li_7La_3Zr_2O_{12}$ (LLZ) by solid state reaction at 1180 °C. The effect of the $Al_2O_3$ content in LLZ on the interface behavior with lithium metal was investigated. The lowest interface resistance was observed for 0.5 wt.% $Al_2O_3$-doped LLZ, which had the highest relative density of 93.7%. The Li/$Al_2O_3$-doped LLZ/Li cell showed a short circuit after a limited polarization period. Short circuiting is considered to be due to lithium dendrite formation. The longest period until short circuit was 1000 s of polarization at 0.5 mA $cm^{-2}$ and room temperature for the 0.5 wt.% $Al_2O_3$ doped LLZ.

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## 1. Introduction

The high lithium ion conducting and lithium stable solid electrolyte of $Li_7La_3ZrO_{12}$ (LLZ) was reported by Weppner's group in 2007 [1]. The ionic conductivity of a sintered pellet (92% theoretical density) was reported to be $2.44 \times 10^{-4}$ S $cm^{-1}$ at 25 °C. This lithium conducting solid is quite attractive for application in all-solid-state lithium batteries and also in aqueous lithium–air batteries because it is stable under atmosphere and in contact with lithium metal, as well as in water with a high content of LiCl [2]. However, for such applications, the interface properties between LLZ and lithium metal should be clarified to establish the optimal conditions for excellent battery performance. The interface behavior between lithium metal and solid lithium conductors has not been well studied except for that with lithium conducting solid polymer electrolytes [3–5]. Lithium dendrite formation on lithium metal electrodes is a serious problem in non-aqueous solutions [6]. Lithium dendrite formation was suppressed by using polymer electrolytes, but is still observed at a high current density [3]. We expect that lithium dendrite formation could be completely suppressed by the use of a hard solid electrolyte. Kotobuki et al. reported abnormal behavior at high current density from chronopotentiograms measured for the Li/LLZ/Li cell with LLZ pellets sintered at 1230 °C for 36 h [7]. At current densities up to 10 μA $cm^{-2}$, the lithium deposition and stripping potential curves gave a mirrored relationship at least until 600 s. However, an abrupt increase in cell voltage was observed after polarization for 70 s at 50 μA $cm^{-2}$; however, no comment on this phenomenon was given. Ohta et al. [8] measured the impedance of a Li/$Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ (LLZ-Nb)/Li cell to be around 1000 Ω $cm^2$ at room temperature, where LLZ-Nb was sintered at 1200 °C for 36 h. The cell resistance is mainly due to the interface resistance between Li and LLZ-Nb. The Li/LLZ-Nb/$LiCoO_2$ cell was only operated at a low current density of 3.5 μA $cm^{-2}$; therefore, the interface resistance should be reduced to operate at a high current density. Nakata et al. [9] reported that Li/LLZ prepared at 1180 °C/Li cell had a low cell resistance of around 50 Ω $cm^2$ at room temperature. The interface behavior between LLZ and lithium metal may be dependent on the electrical conductivity, impurity phases, and the grain boundary properties of the LLZ. High conducting cubic LLZ that was previously reported contained aluminum as a contaminant from the alumina crucible used during high temperature sintering [2,10]. Aluminum is considered to stabilize the high conducting cubic phase at room temperature [10,11]. Rangasamy et al. [11] observed that at least 0.204 mol of Al is required to stabilize cubic phase LLZ at room temperature. In this study, the effects of the aluminum concentration in LLZ on the interface resistance between lithium metal and LLZ and lithium dendrite formation have been examined.

## 2. Experimental

LLZ was prepared by conventional solid state reaction using chemical grade $LiCO_3$, $La_2O_3$ and $ZrO_2$ (Nacalai Tesque). $La_2O_3$ was dried at 1000 °C for 1 h. The molar ratio of Li:La:Zr was controlled to be 7.7:3:2. Excess Li was added to compensate for expected Li loss during high temperature heat treatment. The powders were ball-milled with zirconia balls and isostatically pressed into pellets at 150 MPa and then calcined at 900 °C for 5 h. The reaction products were ball-milled again and isostatically pressed into pellets and calcined at 950 °C for 12 h. The calcined pellets were then ball-milled with γ-$Al_2O_3$ (Alfa) and pressed into pellets and placed in alumina crucibles, covered with mother powder (prepared at 950 °C for 12 h), and sintered at 1180 °C for 36 h under an air atmosphere.

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X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT 2500 diffractometer with a rotating copper cathode. Elemental analysis for Li, La, Al, and Zr was conducted using inductively coupled plasma spectroscopy (ICP; Shimadzu ICP 1000). A powder sample was dissolved into a mixed solution of concentrated nitric acid and hydrochloride acid (1:3 v/v) for ICP analysis. The electrical conductivity of sintered samples (1.0 cm diameter and ca. 0.1 cm thick) with gold-sputtered electrodes was measured using an impedance phase analyzer (Solartron 1260) in the frequency range of 0.1 Hz to 1 MHz with the voltage set at 10 mV. A Li/LLZ/Li cell was prepared by sandwiching lithium metal foil (Honjo Metal, 200 μm thick) with a Cu thin foil lead and LLZ in a plastic envelope. The envelope was then evacuated, heat-sealed and subjected to an isostatic pressure of 150 MPa to ensure good contact between the Li and LLZ. ZView software was employed for data analysis and presentation of the impedance results.

## 3. Results and discussion

All XRD peaks of undoped LLZ were assigned to the garnet-type cubic structure reported by Awaka et al. [12] with a lattice constant of 1.29679 nm, which is slightly smaller than that of a single crystal of Al-containing LLZ (1.29751 nm) [10] and is comparable with that of polycrystalline LLZ (1.29682 nm) reported by Murugan et al. [1]. The XRD patterns of the $Al_2O_3$-doped LLZ samples were also assigned to the cubic phase, and tetragonal LLZ and impurity phases such as $LaAlO_3$ and $La_2Zr_2O_7$ were below the detection limit. Rangasamy et al. [11] reported the effect of the Al and Li concentrations on the formation of cubic garnet for the nominal composition of $Li_7La_3Zr_2O_{12}$ prepared at 1000 °C for 4 h using boron nitride coated $Al_2O_3$ combustion boats. It was determined that at least 0.65 wt.% of Al is required to stabilize the cubic phase. Table 1 shows the Li and Al wt.% normalized according to the Zr content of 2 in $Li_7La_3Zr_2O_{12}$, lattice constant, and the relative density of the sintered pellets of $Al_2O_3$-doped LLZ. The Al content of the undoped LLZ was 0.6 wt.%, where the aluminum originates from the alumina crucible used during sintering. The LLZ samples sintered in alumina crucibles at 1180 °C were stabilized to the cubic phase at room temperature by the aluminum contaminant. The Al content was slightly increased by the intentional addition of $Al_2O_3$ into LLZ. The lattice constants of the $Al_2O_3$-doped LLZ samples were not changed systematically with the $Al_2O_3$ content, because the lattice constant was dependent on both the Al and Li contents. The relative density of the sintered pellets was estimated from the ratio of the density calculated from the lattice constant and that calculated from the weight and volume. The highest density of 93.7% was observed for 0.5 wt.% $Al_2O_3$-doped LLZ. The pellet density was decreased by further doping $Al_2O_3$. Kumazaki et al. [13] reported that the relative density of 1.3 wt.% $Al_2O_3$-doped LLZ sintered at 1230 °C for 36 h was 87%, and Jin and McGinn [14] reported the relative densities of 0.7 and 1.2 wt.% $Al_2O_3$-doped LLZ sintered at 1200 °C for 6 h to be 88 and 86%, respectively. These LLZ samples were sintered using alumina crucibles or alumina plate. The aluminum contents in these sintered samples were not reported. The alumina content of these sintered samples may be higher than that of the 0.5 wt.% $Al_2O_3$ doped LLZ due to the higher sintering temperatures, which suggests that the high content of alumina in LLZ reduces the relative density.

**Table 1**
Al and Li contents, lattice constant and relative density of $Al_2O_3$-doped LLZ.

| Starting materials (wt.%) | | | Al and Li content of sintered $Al_2O_3$-doped LLZ (wt.%) | | Lattice constant (nm) | Relative density (%) |
|---|---|---|---|---|---|---|
| $Al_2O_3$ | Al | Li | Al | Li | | |
| 0 | 0 | 6.28 | 0.6 | 5.4 | 1.29676 | 89.6 |
| 0.5 | 0.26 | 6.25 | 0.79 | 5.3 | 1.29684 | 93.7 |
| 1.0 | 0.54 | 6.22 | 0.98 | 5.2 | 1.29734 | 91.5 |
| 2.0 | 1.08. | 6.17 | 1.18 | 5.1 | 1.29689 | 90.0 |

Fig. 1 shows impedance profiles measured for Au/$Al_2O_3$-doped LLZ/Au at 25 °C in the frequency range of 0.1 Hz to 1 MHz as a function of the doped $Al_2O_3$ content. All the impedance profiles show a semicircle in the frequency range of 1 MHz to 100 kHz followed by a straight line. The semicircle is attributed to the grain boundary resistance and the intercept of the semicircle with the real axis at high frequency represents the bulk resistance of the sample [15]. Table 2 summarizes the conductivity data obtained for $Al_2O_3$-doped LLZ. The bulk conductivity was not significantly changed by the addition of $Al_2O_3$ into LLZ, while the grain boundary conductivity of the undoped LLZ ($4.17 \times 10^{-4}$ S $cm^{-1}$) was enhanced to $1.67 \times 10^{-3}$ S $cm^{-1}$ by the addition of 0.5 wt.% $Al_2O_3$. Further addition of $Al_2O_3$ resulted in a decrease of the grain boundary conductivity. The total conductivity of LLZ is comparable to that reported by Murugan et al. [1]. The highest total conductivity of $4.12 \times 10^{-4}$ S $cm^{-1}$ was observed for 0.5 wt.% $Al_2O_3$-doped LLZ. The total conductivity value is comparable to that of hot-pressed $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.89}$ (relative density: 98%), of which the grain boundary resistance was low [11]. Geiger et al. [10] suggested that Al substitutes for Li in LLZ, but the limit of the amount of substitution has not been clarified. A limited amount of $Al_2O_3$ may contribute to a reduction in the grain boundary resistance.

The stability of $Al_2O_3$-doped LLZ in contact with lithium is an important requirement for all-solid-state batteries and for application as the protective layer for a water-stable lithium metal electrode. The resistance of the Li/LLZ/Li cell decreased with storage period for the first one week and then became stable for one month at room temperature. Fig. 2 shows impedance profiles of the Li/$Al_2O_3$-doped LLZ/Li cell after one week at room temperature. Diminished semicircles were observed in these impedance profiles. The high frequency range semicircles in the frequency range of 1 MHz to 100 kHz were observed for Au/0, 0.5

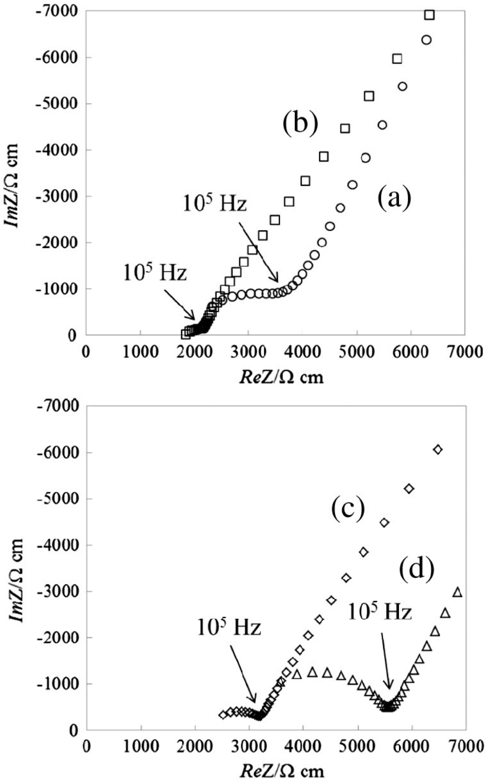

**Fig. 1.** Impedance profiles for Au/$Al_2O_3$-doped LLZ/Au measured at 25 °C. ○: LLZ, □: 0.5 wt.% $Al_2O_3$-doped LLZ, : 1 wt.% $Al_2O_3$-doped LLZ, △: 2.0 wt.% $Al_2O_3$-doped LLZ.

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