



# Grain boundary modification to suppress lithium penetration through garnet-type solid electrolyte



Rajendra Hongahally Basappa<sup>a</sup>, Tomoko Ito<sup>a</sup>, Takao Morimura<sup>a</sup>, Raman Bekarevich<sup>b</sup>, Kazutaka Mitsuishi<sup>b</sup>, Hirotochi Yamada<sup>a,\*</sup>

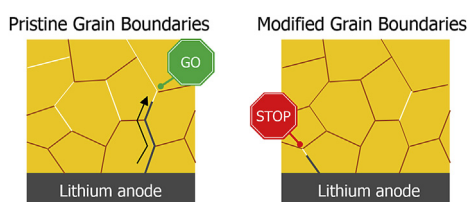
<sup>a</sup> Graduate School of Engineering, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852-8521, Japan

<sup>b</sup> Global Research Center for Environment and Energy Based on Nanomaterials Science (GREEN), National Institute for Materials Science, 1-2-1, Sengen, Tsukuba 305-0047, Japan

## HIGHLIGHTS

- Grain boundaries of garnet-type solid electrolytes are modified.
- Microstructure of LLZT is studied by SEM, STEM and EIS techniques.
- Influence of microstructure on short-circuit prevention is investigated.
- $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}$  fill voids and facilitate sintering on the grain boundaries.
- Grain boundary modification suppresses short circuit up to  $0.6 \text{ mA cm}^{-2}$ .

## GRAPHICAL ABSTRACT



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## ABSTRACT

Garnet-type solid electrolytes are one of key materials to enable practical usage of lithium metal anode for high-energy-density batteries. However, it suffers from lithium growth in pellets on charging, which causes short circuit. In this study, grain boundaries of  $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$  (LLZT) pellets are modified with  $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}$  to investigate the influence of the microstructure of grain boundaries on lithium growth and to study the mechanism of the lithium growth. In spite of similar properties (relative density of ca. 96% and total ionic conductivity of  $7 \times 10^{-4} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ ), the obtained pellets exhibit different tolerance on the short circuit. The LLZT pellets prepared from  $\text{LiOH}$ -modified LLZT powders exhibit rather high critical current density of  $0.6 \text{ mA cm}^{-2}$ , at which short circuit occurs. On the other hand, the LLZT pellets without grain boundary modification short-circuited at  $0.15 \text{ mA cm}^{-2}$ . Microstructural analyses by means of SEM, STEM and EIS suggest that lithium grows through interconnected open voids, and reveal that surface layers such as  $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}$  are not only plug voids but also facilitate the sintering of LLZT to suppress the lithium growth. The results indicate a strategy towards short-circuit-free lithium metal batteries.

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## 1. Introduction

Rechargeable Li-metal-based batteries are considered to be one of the most promising technologies for electrochemical energy storage devices due to its high theoretical capacity, and thus, it is

\* Corresponding author.

E-mail address: [h-yama@nagasaki-u.ac.jp](mailto:h-yama@nagasaki-u.ac.jp) (H. Yamada).

anticipated that Li metal anode would be applied to Li-S and Li-O<sub>2</sub> batteries [1–4]. However, lithium dendrite growth during cycling has prevented its practical application, especially when organic electrolyte solutions are used. In this respect, inorganic solid electrolytes (ISEs) are potential candidates to replace organic electrolyte solutions and thereby to improve the safety of next-generation energy storage devices [5]. To achieve satisfactory lithium metal batteries, it is important to employ ISEs with high lithium ion conductivity and high electrochemical stability against lithium metal. According to a theoretical model by Monroe and Newman, shear modulus of ISEs are more than two times higher than that of metallic Li, which would suppress lithium growth in ISEs [6].

Among various high-performance ISEs, garnet-type lithium ion conductors, with nominal composition of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZ), are promising candidates for electrolytes that enable the safe use of the lithium metal anode due to its high ionic conductivity of  $3 \times 10^{-4}$  S cm<sup>-1</sup> at room temperature (RT) and electrochemical stability against lithium metal [7,8]. Further, they exhibit high shear modulus of ca. 55 GPa [9,10].

However, for the past few years, it has been reported that short circuit occurs during electrochemical lithium deposition on the garnet-type solid electrolytes, which is due to lithium growth inside the solid electrolytes. Imanishi and co-workers reported short circuit of symmetric cells of Li | doped LLZ | Li on direct current (DC) [11–13]. They prepared all solid electrolytes with relative density of 92.8–96.7% by a conventional sintering process, and these solid electrolytes short-circuited within 1000 s at a current density of 0.5 mA cm<sup>-2</sup>. The obtained results indicated that lithium growth through the garnet-type solid electrolytes was independent of dopants that were added to stabilize cubic garnet-type structure. On the other hand, the relative density of sintered pellets showed positive correlation to lithium growth in Ta-doped LLZ (LLZT) pellets [14], which suggests that lithium eventually grows through open pores on grain boundaries in the LLZT pellets to short-circuit the cells. In terms of safety and reliability of batteries, short circuit must be avoided.

To suppress the lithium growth, several strategies have been attempted. Suzuki et al. prepared an Al-doped LLZ (Al:LLZ) pellet with a very high relative density of 99.1% by combination of conventional sintering (1180 °C for 36 h) and subsequent hot isostatic press (1160 °C, 127 MPa for 2 h) [15]. The obtained pellet included partly transparent regions, which exhibited high tolerance against short circuit and voltage drop was not observed at 0.5 mA cm<sup>-2</sup> up to 1000 s, above which all lithium on the anode was dissolved. Cheng et al. investigated critical current density (current density at which short circuit occurs) of Al:LLZ with various microstructures [16]. Al:LLZ consisting of small grains showed higher critical current density than Al:LLZ consisting of large grains. Tsai et al. demonstrated lithium growth was suppressed by using gold thin layers inserted between a Ta-doped LLZ (LLZT) pellet and Li metal electrodes [17]. These results suggest that homogeneous distribution of current on the interfaces of electrodes | solid electrolyte would improve the critical current density.

The critical current density also depends on preparation methods of garnet-type solid electrolytes. Sharifi et al. prepared Al:LLZ by hot press, which exhibited rather low critical current density of 0.05 mA cm<sup>-2</sup> at 30 °C, in spite of relatively high relative density of 97% [18]. In the previous works, we reported that LLZT pellets prepared by spark plasma sintering (SPS, or field assisted sintering technique: FAST) exhibit high critical current density of 0.2 mA cm<sup>-2</sup> [19], which were further improved to 0.4 mA cm<sup>-2</sup> by preparing lithium thin layers by vacuum evaporation [20]. The rather high critical current density for the specimens prepared by SPS may be due to the plastic deformation of grains on the sintering process [19].

Although the critical current density has been improved, it does not satisfy required values for the practical application. For example, when an all-solid-state battery (ASSB) was assembled using a LiCoO<sub>2</sub> cathode with a thickness of 50 μm and volume fraction of 80%, its area specific capacity is 2.8 mAh cm<sup>-2</sup>. To charge this ASSB in 1 h, i.e. at 1 C-rate, current density of 2.8 mA cm<sup>-2</sup> is applied. Therefore, it is necessary to develop solid electrolytes with much higher critical current density.

Based on the previous works, it is supposed that the short circuit on the DC polarization is mainly caused by lithium growth through interconnected open pores, and is facilitated by the inhomogeneous distribution of local current density. However, the reported pellets exhibit rather high relative density of 92–99% and it would be difficult to densify further. In order to completely eliminate interconnected open pores, another strategy should be proposed. In this study, we prepared LLZT pellets with different microstructures by modifying the surface of LLZT powders. The powders were covered with Li<sub>2</sub>CO<sub>3</sub>, LiOH or nothing. By combination of SPS and the surface-modified LLZT powders, we improved tolerance of the short circuit. Mechanism of the short circuit prevention was also studied by investigating influence of the microstructure.

## 2. Experimental section

### 2.1. Materials and preparation of LLZT pellets

LLZT powders and pellets were prepared by a solid-state reaction and following SPS as reported in our previous works [19,20]. Stoichiometric amounts of LiOH·H<sub>2</sub>O (Kishida Chemical Co. Ltd., 99.0%), La<sub>2</sub>O<sub>3</sub> (Kishida Chemical Co. Ltd., 99.99%), ZrO<sub>2</sub> (Kishida Chemical Co. Ltd., 99.9%) and Ta<sub>2</sub>O<sub>5</sub> (Wako Pure Chemical Industries Ltd., 99.9%) were used as starting materials to prepare various types of LLZT powders. Excess lithium by 10% was added to compensate decrease in lithium on a high temperature process. LiOH·H<sub>2</sub>O was dried at 200 °C and La<sub>2</sub>O<sub>3</sub> was heated at 800 °C in advance to remove water and CO<sub>2</sub>, respectively. The mixture of the starting materials was calcined at 900 °C for 12 h to obtain LLZT powder. The obtained powders were pelletized with a graphite die and punches by the SPS technique at 950 °C for 10 min with uni-axial pressure of 25 MPa under reduced pressure (<5 Pa). The surface of the pellets was polished to remove the residual graphite sheets on their surface using emery papers (grit number #400 and #1500). The diameter and the thickness of the pellet were 10 mm and 0.8–0.9 mm, respectively.

In this work, we prepared three types of LLZT pellets with the same procedures. For the first specimen, all the processes (except for the SPS) were carried out in air, which is named as LLZT-air. The second specimen was prepared without exposure to air, namely LLZT-w/o-air: LiOH·H<sub>2</sub>O was dried under vacuum and LLZT was calcined in pure O<sub>2</sub> using a furnace directly connected to an Ar-filled glovebox (O<sub>2</sub>: <0.1 ppm, H<sub>2</sub>O < 1 ppm) and the specimen were handled, stored and analyzed without air exposure. The last one, named as LLZT-2calc, was prepared by modifying LLZT-air with LiOH: LLZT-air was once calcined and mixed with 2 wt-% of additional LiOH (corresponding to 0.65Li in composition) using a planetary ball-mill with a ZrO<sub>2</sub> pot and balls (3 mm in diameter, ball-powder ratio was 1: 1 by vol.) at 300 rpm for 1 h. Then, the mixture was calcined at 900 °C for 12 h in air again.

### 2.2. Structural characterization

The relative density of the pellets was calculated from the ratio of experimental density to the theoretical density. The experimental density was obtained from weight and volume of each sintered pellets, and theoretical density of pellets was calculated

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