

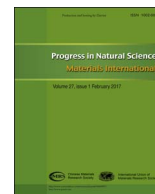
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Original Research

Properties of garnet-type  $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$  solid electrolyte films fabricated by aerosol deposition method<sup>☆</sup>Ryoji Inada<sup>\*</sup>, Takayuki Okada, Akihiro Bando, Tomohiro Tojo, Yoji Sakurai

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## ABSTRACT

The garnet-type  $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$  (LLZT) solid electrolyte films were fabricated by aerosol deposition (AD) method. Ball-milled LLZT powder with a cubic garnet structure and a particle size of 1–2  $\mu\text{m}$  was used as raw material and deposited directly on a SUS316L or a glass substrate via impact consolidation. As-deposited LLZT film has a cubic garnet structure but contains  $\text{Li}_2\text{CO}_3$  and  $\text{La}_2\text{Zr}_2\text{O}_7$  phases. SEM observation revealed that the film consists of LLZT particles fractured into submicron size. The impurity phase formation during AD process was caused by the local heating by the collision between LLZT particles and deposition surface and reaction with  $\text{CO}_2$ . The  $\text{Li}^+$  ion conductivity of LLZT film was estimated to be  $0.24 \times 10^{-8} \text{ S cm}^{-1}$  at room temperature. Electronic conductivity of LLZT film was confirmed to be around  $10^{-12} \text{ S cm}^{-1}$ , indicating the dominant  $\text{Li}^+$  ion conduction of LLZT film.

## 1. Introduction

All-solid-state lithium-ion batteries (LiBs) are expected to be one of the next generation of energy storage devices because of their high energy density, high safety and excellent cycle stability [1–4]. The materials used for solid electrolyte must have not only high lithium-ion conductivity above  $10^{-3} \text{ S cm}^{-1}$  at room temperature but also possess chemical stability against electrode materials, air and moisture. Although oxide-based SE materials have rather lower conductivity and poor deformability compared to sulfide-based ones, they have other advantages such as their chemical stability and ease of handling.

Among the various oxide-based SE materials, lithium-stuffed garnet-type oxide with the formula of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZ) has been widely studied because of its high conductivity above  $10^{-4} \text{ S cm}^{-1}$  at room temperature, excellent thermal performance and stability against metallic lithium [5]. LLZ has two different crystal phases, one is the cubic phase and the another is tetragonal one [6–8], but high total (bulk+grain boundary) conductivity at room temperature above  $10^{-4} \text{ S cm}^{-1}$  is mostly confirmed in cubic LLZ sintered at high temperature from 1100 °C to 1200 °C in alumina crucible and/or substituted  $\text{Al}_2\text{O}_3$  [5,9–12]. During the high temperature sintering,  $\text{Al}^{3+}$  enters from the crucible and/or substituted  $\text{Al}_2\text{O}_3$  into the LLZ pellet and works as sintering aid. In addition, it has been pointed out that some amount of  $\text{Al}^{3+}$  enters into LLZ lattice, modifies the  $\text{Li}^+$  ion

vacancy concentration and stabilizes the cubic structure [11,12]. Partial substitution of  $\text{Zr}^{4+}$  by  $\text{Nb}^{5+}$  [13] or  $\text{Ta}^{5+}$  [14–18] in LLZ is reported to be effective to stabilize the cubic garnet structure, and their room temperature conductivity was greatly enhanced up to  $10^{-3} \text{ S cm}^{-1}$  by optimizing doping level.

Film-shaped solid electrolyte provides low electrical resistance, small size of a device and increasing volumetric energy density for all-solid-state battery. LLZ film fabrication by using pulsed laser deposition (PLD) [19,20], radio-frequency (RF) magnetron sputtering [21] and sol-gel process [22] has been reported, but their room temperature conductivities were in the range of  $10^{-7}$ – $10^{-5} \text{ S cm}^{-1}$ , which is nearly two digits lower than sintered LLZ pellets [5–12]. These film fabrication methods are efficient for fabricating uniform film and controlling the film thickness, but in some cases, it is difficult to control elementary composition. Moreover, increasing substrate temperature during deposition and/or post-annealing should be needed to obtain well-crystallized films. Since high temperature treatments may lead to undesired reactions at the interface or uncontrolled diffusion between electrode and solid electrolyte, these methods are not recommended in some cases for fabricating all-solid-state batteries.

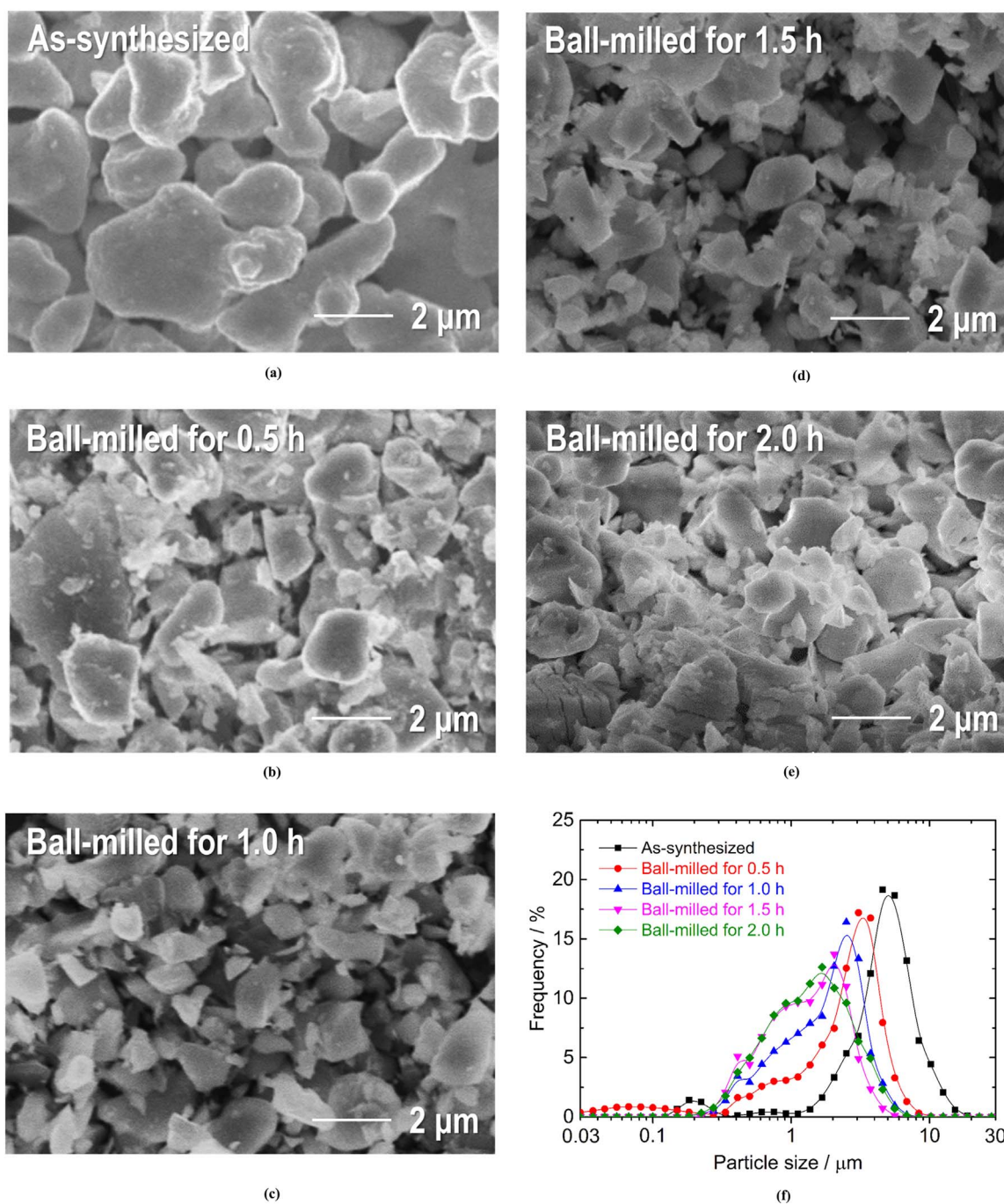
Aerosol deposition (AD) has several advantages compared to other conventional thin film deposition methods as mentioned above, including deposition of polycrystalline film without any heat treatments, a fast deposition rate and high adhesion strength with a

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**Fig. 1.** SEM images of LLZT powders: (a) as-synthesized, (b) ball-milled for 0.5 h and (c) ball-milled for 1.0 h, (d) ball-milled for 1.5 h and (e) ball-milled for 2.0 h. The particle size distributions of all LLZT powders are summarized in (f). The powders (a), (b), (c) and (d) are used for LLZT film fabrication by AD but the film can be formed only using the powder (e).

substrate [23,24]. A film is deposited through impact and adhesion of fine particles on substrate at room temperature. In general, the film fabricated by AD has similar properties with raw powder material, such as crystal structure, composition and physical property. By addressing these attractive features, numerous studies for the film fabrication by AD have been reported in various functional ceramic materials, including  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT) [24],  $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$  [25] and  $\text{Ca}_3\text{Co}_4\text{O}_9$  [26]. Recently, several works have been also reported in the battery field. The electrochemical properties of Si alloy or composite [27],  $\text{LiMn}_2\text{O}_4$  [28],  $\text{LiFePO}_4$  [29],  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  [30],  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [31],  $\text{Fe}_2\text{O}_3$  [32] and graphite [33] film electrodes were investigated to verify the feasibility of AD. It has been also reported that AD  $\text{Li}_{1+x}\text{Al}_x\text{M}_{2-x}(\text{PO}_4)_3$  ( $\text{M} = \text{Ti, Ge}$ ) solid electrolyte films with NASICON (Na superionic conductor) structure showed the room

temperature ionic conductivity of  $10^{-6}$ – $10^{-5} \text{ S cm}^{-1}$  [34,35].

Very recently, Ahn et al. reported the properties of LLZ film fabricated by AD, but the conductivity of the film was limited to only  $10^{-8} \text{ S cm}^{-1}$  even at  $140^\circ\text{C}$  [36]. In their work, Al-doped LLZ powder with a particle size around 7–10  $\mu\text{m}$  is used as raw material and the LLZ film was composed of strongly fractured LLZ nanoparticles with the size of several 10 nm. They have concluded that much lower conductivity than sintered LLZ is mainly attributed to the degradation of crystallinity, significant increase of the volume ratio between grains and grain-boundaries, and possible impurity phase formation in LLZ film due to moisture. However, it is known that both the microstructure and properties of the films fabricated by AD are strongly influenced by the size and the morphology of raw powder materials [31,35], so that the conductivity of LLZ film would be improved by controlling the

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