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Short communication

Low temperature synthesis of highly ion conductive $Li_7La_3Zr_2O_{12}$–Li_3BO_3 composites

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ABSTRACT

Highly lithium ion conductive composites with Al-doped $Li_7La_3Zr_2O_{12}$ (LLZ) and amorphous Li_3BO_3 were prepared from sol–gel derived precursor powders of LLZ and Li_3BO_3. Precursor LLZ powders with cubic phase were obtained by a heat treatment of the precursor dried gel at 600 °C. Pellets of the mixture of the obtained LLZ and Li_3BO_3 were first held at 700 °C, and then successively sintered at 900 °C. Density of the sintered pellet with Li_3BO_3 was larger than that of the pellet without Li_3BO_3. From the TEM observation, the pellets were found to consist of cubic LLZ and amorphous Li_3BO_3. Total electrical conductivity of the obtained LLZ–Li_3BO_3 composite was 1×10^{-4} Scm^{-1} at 30 °C.

1. Introduction

All-solid-state lithium ion secondary batteries with inorganic solid electrolytes attract attention because of their high safety, reliability and energy density [1]. We have been developing sulfide-based electrolytes such as Li_2S–P_2S_5 glasses and glass ceramics with high lithium ion conductivities of over 10^{-3} Scm^{-1} at room temperature. Compared with sulfide-based materials, lithium ion conductive oxide glasses have rather low conductivity [2]. However, oxide materials have advantages such as their chemical stability and handling.

Recently, garnet-type $Li_7La_3Zr_2O_{12}$ (LLZ) has been studied extensively because LLZ has high lithium ion conductivity ($\sigma_{total} > 10^{-4}$ Scm^{-1} at room temperature) in cubic phase and chemical stability against lithium metal [3–6]. Although the bulk conductivity is close to 10^{-3} Scm^{-1}, very high temperature is needed for the sintering to reduce grain boundary resistance. To obtain a dense pellet with cubic LLZ, a heat-treatment at around 1200 °C is required in the conventional solid state reaction method. Such a heat-treatment at high temperatures causes a lithium loss, and to suppress the lithium loss, samples must be covered with mother powders. Thus, low temperature synthesis and sintering of cubic LLZ are desired. Addition of γ-Al_2O_3 to LLZ [7–9] or synthesis by sol–gel process [10–12] has been reported to lower the sintering temperature. Nevertheless, the densification of cubic LLZ at rather low temperature has not been achieved.

To lower the sintering temperature, the addition of sintering additives that have low melting points and make liquid phases below sintering temperature is effective. The liquid phase promotes the densification and coarsening at low temperature [13,14].

Here, we propose a composite electrolyte of LLZ and lithium borate glass as a novel solid electrolyte with high lithium ion conductivity, and with the maximum process temperature of 900 °C. In the heat-treatment at 900 °C, the lithium loss during heat-treatment is assumed to be suppressed. During sintering of precursor powders of LLZ and lithium borate, the liquid phase of lithium borate acts as an accelerator for inter-reaction of grains at grain boundaries and the grain growth. In the obtained composite, amorphous lithium borate would be formed as a thin layer at the grain boundaries. These glassy phases will reduce the grain boundary resistance, and thus the composite can achieve high total lithium ion conductivity.

When this composite is used for the lithium ion conductive path in composite electrodes with active materials, the lithium borate glass can act as a binder for electrolyte and active materials, and thus a small interfacial resistance will be expected.

In the present study, we have prepared a composite of Al-doped LLZ and Li_2O–B_2O_3 glass. The heat treatment of the LLZ precursor particles and Li_3BO_3 at 700 °C and successive sintering at 900 °C led to the formation of a dense LLZ and Li_3BO_3 glass composite, and the total ion conductivity of this composite is about 1×10^{-4} Scm^{-1} at 30 °C.

2. Experimental

Al-doped LLZ were prepared by a sol–gel process. Firstly, $LiNO_3$ and $La(NO_3)_3 \cdot 6H_2O$ were dissolved in ethanol. Separately, $Zr(O\text{-}n\text{-}C_3H_7)_4$ and $Al(O\text{-}sec\text{-}C_4H_9)_3$ were reacted with Ethylacetoacetete (EAcAc).

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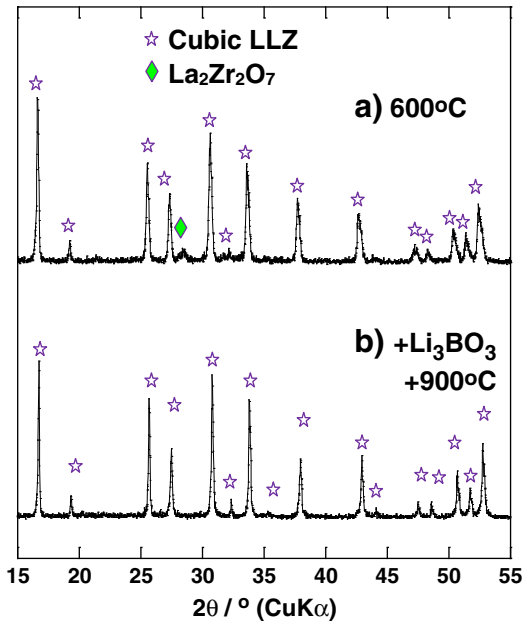

Fig. 1. XRD patterns of (a) Al-doped LLZ powder calcined at 600 °C and (b) sintered pellet with Li_3BO_3 at 700 and then 900 °C.

These two solutions were mixed, and the obtained solution was stirred at room temperature for 1 h to obtain gel. The mole ratio of $LiNO_3$:$La(NO_3)_3 \cdot 6H_2O$:$Zr(O\text{-}n\text{-}C_3H_7)_4$:$Al(O\text{-}sec\text{-}C_4H_9)_3$:EAcAc:ethanol is 7.7:3:2:0.3:1.6:50. The gel was dried at 80 °C for 12 h, and then successively at 150 °C for 5 h. The dry gel was ground well and calcinated at 600 °C for 5 h. Al-doped LLZ powders obtained at 600 °C were ball-milled with zirconia balls for 12 h. Li_3BO_3 and the milled powders were mixed in an agate mortar, where the mole ratio of Li_3BO_3/LLZ was 0.68. Effects of Li_3BO_3 contents will be reported elsewhere [15]. Mixed powders were pressed into pellets at a pressure of 200 MPa, and the pellets were first held at 700 °C for 5 h, and then successively sintered at 900 °C for 36 h in an alumina crucible.

X-ray diffraction (XRD) patterns were obtained by X-ray diffractometer (XRD-6000, Shimadzu). A scanning electron microscope (SEM) (JSM-6610A, JEOL) was used for the observation of the particles or polished fracture surface of sintered pellets. The sintered pellets were polished with sandpapers (#1000) and Au (0.5 cm^2) was sputter-coated onto the both surfaces of the pellets. AC impedance was measured by an impedance analyzer (SI 1260; Solartron) in a frequency range of 0.1Hz to 1 MHz. Porosity was calculated by the density of the pellets determined from the weight and physical dimensions. A symmetrical cell with Li/LLZ–Li_3BO_3 composite/Li configuration was fabricated through the deposition of lithium by vacuum-evaporation on both sides of the composite, and the reversibility of its dissolution and deposition was evaluated by galvanostatic cycling of 9×10^3 C. This corresponds to the dissolution and deposition of 9.3×10^{-8} mol of Li (about 3.4% of the deposited Li).

3. Results and discussion

Fig. 1 shows XRD patterns of (a) Al-doped LLZ powder calcined at 600 °C and (b) sintered pellet with Li_3BO_3 at 700 and then 900 °C. In

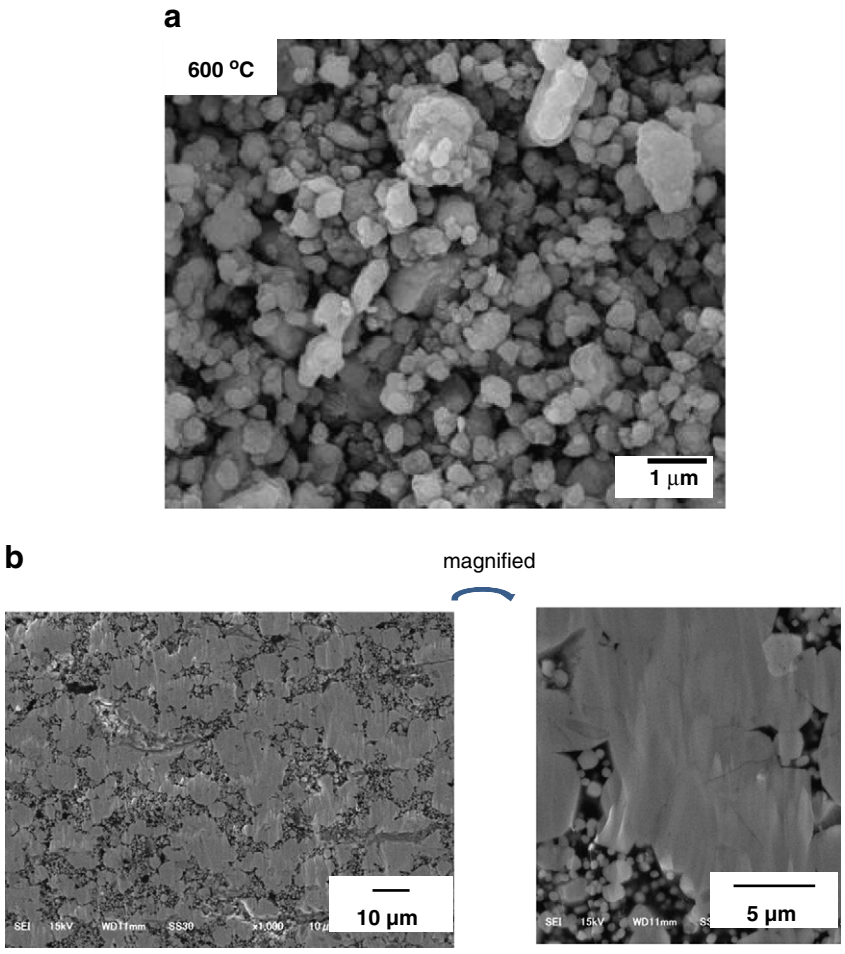

Fig. 2. SEM image of Al-doped LLZ powder calcined at 600 °C (a), and the cross-sectional SEM image of the LLZ pellet sintered at 900 °C with Li_3BO_3 (b).