



## Short communication

## Co-sinterable lithium garnet-type oxide electrolyte with cathode for all-solid-state lithium ion battery



Shingo Ohta\*, Juntaro Seki, Yusuke Yagi, Yuki Kihira, Takao Tani, Takahiko Asaoka

Toyota Central R&amp;D Labs. Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan

## H I G H L I G H T S

- The sintering temperature of garnet electrolyte was found to significantly lower by addition.
- The simultaneous interdiffusion of elements was important to lower sintering temperature.
- Garnet oxide exhibited high lithium ion conductivity despite of the low sintering temperature.
- All-solid-state lithium ion battery using garnet oxide was fabricated by co-sintering.

## A R T I C L E I N F O

## Article history:

Received 3 February 2014

Received in revised form

11 April 2014

Accepted 14 April 2014

Available online 24 April 2014

## Keywords:

Solid electrolyte

Garnet oxide

All-solid-state lithium ion battery

Co-sintering

Lithium ion conductor

## A B S T R A C T

We investigated the development of a novel lithium garnet-type oxide electrolyte, which is co-sinterable with a metal oxide cathode, for practical all-solid-state lithium ion batteries using metal oxide electrolytes. The sintering temperature of  $\text{Li}_{6.8}(\text{La}_{2.95}\text{Ca}_{0.05})(\text{Zr}_{1.75}\text{Nb}_{0.25})\text{O}_{12}$  was found to significantly lower to 790 °C by addition of  $\text{Li}_3\text{BO}_3$  and  $\text{Al}_2\text{O}_3$ , due to simultaneous interdiffusion of Al and Ca elements between garnet-type oxide and additives. The sintered electrolyte exhibited high lithium ion conductivity of  $0.36 \text{ mS cm}^{-1}$  at 25 °C despite of the low sintering temperature. An all-solid-state lithium ion battery was successfully prepared by co-sintering of the electrolyte and  $\text{LiCoO}_2$  (cathode), followed by coating of Li metal (anode), and confirmed to function well as a secondary battery with charge and discharge capacities of 98 and 78 mAh  $\text{g}^{-1}$ , respectively. These results opened the potential for fabrication of all-solid-state lithium ion batteries by a simple and well-established co-sintering process.

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## 1. Introduction

Lithium ion secondary batteries have been widely used as power sources for electric vehicle (EV), a mobile phone and etc., and are now indispensable for our daily lives. At the same time, safety of the batteries has been becoming an important issue with the progress of their performance (e.g. capacity and energy density). From this viewpoint, all-solid-state lithium ion batteries using solid electrolytes have attracted much attention as a next-generation battery due to non-use of flammable organic liquid electrolytes.

Especially, specific focus has been placed on “metal oxide” electrolytes rather than others (e.g. sulfide electrolyte) because metal oxides are stable in air and thus never release toxic gases even in case of breaking down. In addition, metal oxide electrolyte has several advantages such as high chemical and thermal stability and

a low charge transfer resistance between the electrode/electrolyte interfaces [1–3]. Furthermore, metal oxide electrolyte/electrode systems have a great merit to construct a bi-polar structure for high capacity, because a layer-by-layer structure of electrolyte, electrode and metal is easily fabricated by a simple co-sintering process, which has been widely used in production of multi-layered ceramic capacitors. However, low lithium ion conductivities of metal oxide electrolytes (e.g.  $1 \mu\text{S cm}^{-1}$  at R.T.) limited their use for all-solid-state batteries.

The important breakthrough in this field was achieved in 2007 by R. Murugan, who first reported  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) and its derivatives with high lithium ion conductivity ( $\sim 0.1 \text{ mS cm}^{-1}$  at R.T.) [4–13]. The discovery motivated researches on the use of metal oxide electrolytes for all-solid-state batteries. We also investigated the electrochemical performance of a model battery using an as-sintered Nb doped LLZO (LLZO-Nb,  $0.8 \text{ mS cm}^{-1}$  at 25 °C) pellet and  $\text{LiCoO}_2$  (LCO, one of typical cathodes), and found that the model battery exhibited good charge–discharge capacities and low interfacial resistance between LCO and LLZO-Nb comparable with

\* Corresponding author. Tel.: +81 561 71 7659; fax: +81 561 71 5743.

E-mail address: [sohta@mosktytlabs.co.jp](mailto:sohta@mosktytlabs.co.jp) (S. Ohta).

that of lithium ion batteries with liquid organic electrolytes [2,14]. The results confirmed the availability of LLZO-Nb as a metal oxide electrolyte for all-solid-state batteries. The next challenge is co-sintering of electrolyte and electrode materials with high densities but without the formation of other compounds by interdiffusion.

Here, we investigated the design of LLZO-Nb for co-sintering with LCO (cathode) for the first step because it is one of the most important issues to suppress the reaction of LLZO-Nb and cathode by drastically lowering the sintering temperature of LLZO-Nb to less than 900 °C [15]. In order to overcome this difficulty, our strategy is to enhance interdiffusion between LLZO-Nb and a grain boundary phase (not LCO) by an appropriate selection of additives. As the result, addition of Al<sub>2</sub>O<sub>3</sub> and Li<sub>3</sub>BO<sub>3</sub> to Ca and Nb doped LLZO (LLZO-CaNb) lowered the sintering temperature to 790 °C with maintaining high lithium ion conductivity but without the reaction with LCO. The developed electrolyte pellet was stacked on a LCO (cathode) pellet, co-sintered at 790 °C and coated with Li metal (anode). The obtained model battery was confirmed to work properly with charge–discharge capacities of 72% and 58%, respectively, to the theoretical value. The present results opened the potential to produce all-solid-state lithium ion battery by a simple co-sintering process.

## 2. Experimental

Commercial reagents were purchased from Sigma–Aldrich and Kojundo Chemical Lab. Co. Ltd. and used as received for Li(OH), La(OH)<sub>3</sub>, Ca(OH)<sub>2</sub>, ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Li<sub>2</sub>CO<sub>3</sub>, B<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. LLZO-CaNb was prepared by conventional solid state reactions. The starting materials, Li(OH), La(OH)<sub>3</sub>, Ca(OH)<sub>2</sub>, ZrO<sub>2</sub>, and Nb<sub>2</sub>O<sub>5</sub> were mixed by planetary ball-milling, and then calcined at 700 °C for 48 h. The composition of the samples were evaluated by inductively coupled plasma spectroscopy (ICP: Rigaku Co. CIRIOS 120 EOP). Li<sub>3</sub>BO<sub>3</sub> powder as an additive was prepared by heating a mixture of Li<sub>2</sub>CO<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> at 600 °C. The calcined LLZO-CaNb powder was mixed with the additives (both Al<sub>2</sub>O<sub>3</sub> and Li<sub>3</sub>BO<sub>3</sub>, only Al<sub>2</sub>O<sub>3</sub> or only Li<sub>3</sub>BO<sub>3</sub>) by planetary ball-milling. The mixture was die-pressed at 10 MPa into a pellet (green density: ca. 40% (2.10 g cm<sup>-3</sup>)) and sintered at 790 °C for 40 h in air. The crystal structure and the lattice parameter of the samples were evaluated by X-ray diffraction (XRD: Rigaku Co. Ultima IV, CuK $\alpha$  radiation, 40 kV, 30 mA). The electrical conductivity of the samples was measured using a two-probe AC impedance method (Agilent 4294A) in the frequency range of 110 MHz–40 Hz from 25 to 150 °C. The distribution of the elements was measured by EPMA (JEOL Ltd. JXA-8500F). The cathode/electrolyte stacked pellet was prepared by co-sintering process. A commercial LiCoO<sub>2</sub> powder (average particle size: 5  $\mu$ m, Nippon Chemical Industrial Co., Ltd.) as a cathode was mixed with Li<sub>3</sub>BO<sub>3</sub> and the calcined LLZO-CaNb powder in the ratio of 42:35:23 (wt%). The mixed powder was put on the LLZO-CaNb electrolyte pellet and co-die-pressed at 10 MPa. The stacked pellet was sintered at 790 °C in air. The morphology and the elemental distribution of the cathode/electrolyte interface were observed by FIB-SEM (Hitachi NB5000 FIB-SEM, 5 kV) and EDX (EDAX Inc. GenesisAPEX2), respectively. The charge–discharge curves were obtained using a potentiostat galvanostat (Solartron 1480) under galvanostatic conditions of 1  $\mu$ A g<sup>-1</sup> (rate: ~0.01C) in the range from 3.0 to 4.2 V.

## 3. Results and discussions

Li<sub>6.8</sub>(La<sub>2.95</sub>Ca<sub>0.05</sub>)(Zr<sub>1.75</sub>Nb<sub>0.25</sub>)O<sub>12</sub> (LLZO-CaNb) was chosen as the base garnet-type oxide compound due to its high lithium ion conductivity (~0.6 mS cm<sup>-1</sup> at 25 °C) and lower sintering

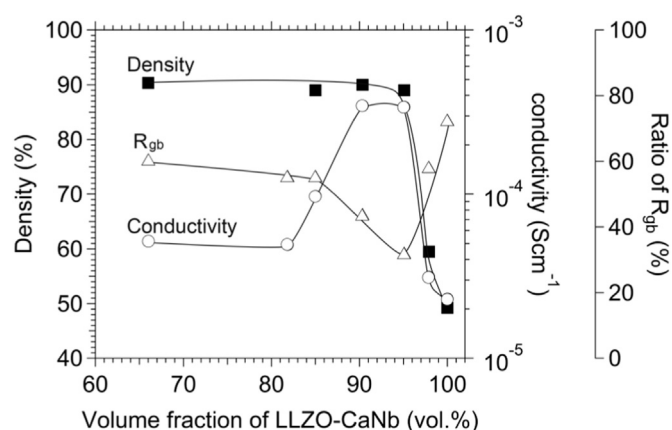


Fig. 1. Effects of Li<sub>3</sub>BO<sub>3</sub> addition on density (square), lithium ion conductivity (open circle) and the ratio of resistance due to grain boundary (open triangle) for LLZO-CaNb with Al<sub>2</sub>O<sub>3</sub> (0.2 mol%).

temperature (1050 °C) than those of other lithium garnet-type oxides [16]. The composition ratio of Li/La/Ca/Zr/Nb in calcined LLZO-CaNb powder which was evaluated by ICP was 6.81/2.96/0.05/1.75/0.25, where this ratio was normalized according to Zr at 1.75. Al<sub>2</sub>O<sub>3</sub> and Li<sub>3</sub>BO<sub>3</sub> were selected as additives for lowering the sintering temperature due to the following reasons. The Al<sup>3+</sup> ion can be substituted to the Li<sup>+</sup> site in LLZO-CaNb by interdiffusion into the LLZO-CaNb grain, which can improve the sinterability of LLZO-CaNb. The Al<sup>3+</sup> ion was added until its solubility limit (0.2 mol %) to LLZO-CaNb [17–19]. Li<sub>3</sub>BO<sub>3</sub> can form a liquid phase due to its low melting point (ca. 700 °C) and thus enhance liquid phase sintering of LLZO-CaNb without reactions with it [20]. The effects of Li<sub>3</sub>BO<sub>3</sub> addition on sinterability and lithium ion conductivity were preliminarily evaluated for LLZO-CaNb with Al<sub>2</sub>O<sub>3</sub> (0.2 mol%) is shown in Fig. 1. The addition of ≥5 vol.% was effective for densification, whereas the addition of >10 vol.% resulted in the decrease of the lithium ion conductivity due to the large increase of the grain boundary resistance. This can be explained by the mechanism that Li<sub>3</sub>BO<sub>3</sub> tends to exist at the grain boundaries in addition to the triple points, which leads to insufficient contact between LLZO-CaNb grains. Thus, the amount of Li<sub>3</sub>BO<sub>3</sub> addition was determined as 5–10 vol.% to LLZO-CaNb according to these results.

Sinterability of LLZO-CaNb was drastically improved by co-addition of Al<sub>2</sub>O<sub>3</sub> and Li<sub>3</sub>BO<sub>3</sub>. Table 1 lists the relative densities for die-pressed pellets of a calcined LLZO-CaNb powder with or without the additives (both Al<sub>2</sub>O<sub>3</sub> and Li<sub>3</sub>BO<sub>3</sub>, only Al<sub>2</sub>O<sub>3</sub>, only Li<sub>3</sub>BO<sub>3</sub> and no additives) after sintering at 790 °C in air. It is clear that (i) the formation of a liquid phase (addition of Li<sub>3</sub>BO<sub>3</sub>) is effective for densification of LLZO-CaNb and (ii) the relative density increases up to nearly 90% only in the case of co-addition of Al<sub>2</sub>O<sub>3</sub> and Li<sub>3</sub>BO<sub>3</sub>. The XRD pattern of all the diffraction peaks confirmed the formation of a cubic garnet type structure (space group: Ia-3d, JCPDS: 84-1753) with the lattice parameter of 12.95 Å (Fig. 2). The ICP analysis showed that the composition ratio of Li/La/Ca/Zr/Nb/

Table 1  
Relative density and lithium ion conductivity of the samples.

Base	Additive	Rel. dens. (%) <sup>a</sup>	Li <sup>+</sup> $\sigma$ (mS cm <sup>-1</sup> )
LLZO-CaNb	Al <sub>2</sub> O <sub>3</sub> , Li <sub>3</sub> BO <sub>3</sub>	90	0.36
LLZO-CaNb	–	49	0.004
LLZO-CaNb	Al <sub>2</sub> O <sub>3</sub>	49	0.008
LLZO-CaNb	Li <sub>3</sub> BO <sub>3</sub>	52	0.006

<sup>a</sup> The theoretical density was calculated based on the ideal densities of LLZO-CaNb (5.08 g cm<sup>-3</sup>) and LBO (2.16 g cm<sup>-3</sup>) and their mixing ratio (90/10) in volume.

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