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Dense garnet-like $Li_5La_3Nb_2O_{12}$ solid electrolyte prepared by self-consolidation method

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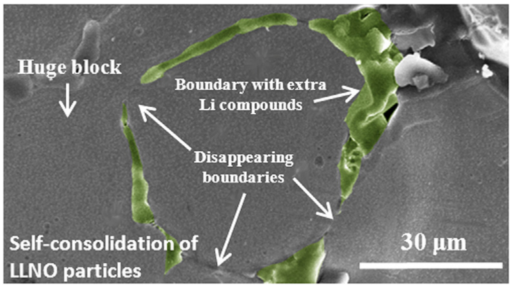
HIGHLIGHTS

- High-density cubic LLNO is first prepared by self-consolidation method.
- Surface tension is utilized as the intrinsic power for sample's self-consolidation.
- The bulk ionic conductivity of LLNO is promoted up to $1.61 \times 10^{-4}\,S\,cm^{-1}$ at 30 °C.
- Huge particles in size over 80 μm are observed in the fracture surface of LLNO.

GRAPHICAL ABSTRACT



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ABSTRACT

$Li_5La_3Nb_2O_{12}$ (LLNO) is a typical garnet-like solid electrolyte with solitary cubic structure. However, its ionic conductivity is relatively low due to the low relative density when prepared by cold isostatic pressing method, which usually involves high-pressure machines, poor productivity, tedious pressing operations, and low density. In this paper, self-consolidation method is developed to sinter dense LLNO electrolyte. Although not any pressing operations are employed in the entire process, the relative density of LLNO is promoted up to 95%, which is much higher than the reported values of 45–80%. SEM images reveal that the sample is built by huge particles in size of 80 μm indicating that there are few boundaries in the sample. Moreover, a rich content of Li-Al-O compounds is detected out in the boundary areas, which may act as sintering aids for the sample to consolidate automatically. According to the highest density, the bulk ionic conductivity of LLNO sample reaches up to $1.61 \times 10^{-4}\,S\,cm^{-1}$ at 30 °C, which is in the same order of magnitude as the value of cubic $Li_7La_3Zr_2O_{12}$ electrolyte. This work verifies the self-consolidation mechanism for the sintering of ceramic electrolytes and could significantly facilitate the development of LLNO membrane technology.

1. Introduction

Lithium ion battery (LIB) is becoming the dominant storage device for commercial applications. However, its safety issues still haven't been resolved due to its liquid organic electrolytes which are volatile and flammable. All-solid-state LIB is viewed as a potential solution for the safety issues [1]. Instead of liquid electrolytes, all-solid-state LIB employs stable ceramic solid electrolytes with super ionic conductivity as both separators and ion conductors.

Among current super-ionic conducting oxide electrolytes, ceramic solid electrolytes are typically synthesized by sintering in air atmosphere. Accordingly, they are relatively stable in ambient air. Their

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thermal, chemical, and electrochemical stability could significantly simplify the cell fabrication and improve the cell safety [2]. Compared with NASICON-like LATP ($Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$) and perovskite-like LLTO ($Li_{3x}La_{2/3-x}TiO_3$), garnet-like oxides are the only candidates exhibiting the unique combination of high ionic conductivity and excellent chemical stability against Li metal [2–8]. LLNO ($Li_5La_3Nb_2O_{12}$) with solitary cubic phase is the first example of fast lithium ion conductors possessing garnet-like structure. It was first synthesized and characterized by H. Hyooma and K. Hayashi in 1988 [9,10]. In 2003, V. Thangadurai and the co-works reported a bulk ionic conductivity of $\sim 10^{-6}$ S cm^{-1} at room temperature (RT) for LLNO that initiated the family of garnet-like lithium ion conductors [11]. Soon, cubic LLZO ($Li_7La_3Zr_2O_{12}$) with a high bulk ionic conductivity over 10^{-4} S cm^{-1} at RT was synthesized and became a new star of the garnet family [8,12–16]. After that, the ionic conductivity of LLZO was promoted much further by doping. On the contrary, few attentions were paid on the research of LLNO due to its relatively lower conductivity.

In general, the sample's density is a critical factor for ceramic solid electrolytes to improve their ionic conductivity. LLNO is usually prepared by cold isostatic pressing (CIP) method which always involves costly high-pressure machines, poor productivity, tedious pressing operations, and low sample's density. The reported value of LLNO samples' relative density is as low as 45–80% [17,18]. There is still a large space for us to improve the sample's density. Accordingly, the ionic conductivity of LLNO electrolyte could be promoted much further. In our previous work, we developed a novel method defined as "self-consolidation". It employed the surface tension of "liquid" molten Li_2O as the intrinsic power for the powder sample to consolidate automatically. By that, a tetragonal LLZO sample with a relative density of 93% was successfully synthesized without the assist of any pressing operations [19]. We noticed that, in the raw materials of LLNO, Nb_2O_5 possesses an even lower melting point than that of Li_2O. Therefore, in addition to Li_2O or Li-Al-O eutectic, Nb_2O_5 might also act as a sintering aid. As a result, LLNO should have a better "self-consolidation" sintering property than that of LLZO. In this regard, we applied self-consolidation method to prepare high-density LLNO solid electrolyte. To our expectation, a dense cubic LLNO bulk sample with a highest relative density of 95% was obtained. Accordingly, its bulk ionic conductivity is promoted up to 1.64×10^{-4} S cm^{-1} at 30 °C, which is in the same order of magnitude as the value of cubic LLZO electrolyte. This work would facilitate the development of LLNO membrane technology and is also favorable for us to understand the self-consolidation mechanism of ceramic electrolytes.

2. Experimental

2.1. Preparation of LLNO powder

Schematic illustration for the preparation of LLNO sample by self-consolidation method is shown in Fig. 1. The primary LLNO powder was prepared through conventional solid reaction. All reagents are analytically pure and bought from Sinopharm Chemical Reagent Co. Ltd. At first, stoichiometric amounts of Li_2CO_3, La_2O_3, and Nb_2O_5 raw powders were ball-milled with ethonal in a ZrO_2 jar under 350 rpm for 10 h. In order to compensate the expected loss of lithium during the high-temperature treatments, excess of 10 mol% Li_2CO_3 was added into the raw materials. After being ball-milled, the slurry was dried at 120 °C for 6 h and calcined at 1150 °C for 10 h in alumina crucible with a heating rate of 10 °C min^{-1} up from RT. The primary LLNO powder was ground by an agate mortar and ball-milled again in a ZrO_2 jar at 500 rpm for 10 h. Then, the LLNO powder was sieved by 100$^{\#}$ nylon meshes to be kept in a loosened state.

2.2. Preparation of LLNO pellets

The loosened LLNO powder was put in a cylinder-type crucible and compacted through manual vibration (the vibration process is shown in Fig. S1). The packed powder sample was heated up stepwise. The sintering rule is confirmed by thermal analysis, which is shown in Fig. S2. From RT to 900 °C, the heating rate is 10 °C min^{-1}, followed by a heating rate of 1 °C min^{-1} from 900 °C to 1150 °C. It was finally sintered into a dense bulk at 1150 °C for 15 h in air atmosphere. The bulk sample was sliced by a diamond saw and polished by a 1000$^{\#}$ diamond chip. Then, LLNO pellet ($\sim$0.97 cm in diameter and 0.20 cm in thickness) was prepared for further characterization.

2.3. Characterization

The particle size distribution of the primary LLNO powder before sintering was measured by Malvern Mastersizer 2000 laser-diffraction particle size analyzer. The density of LLNO bulk was determined from its weight and volume according to Archimedes principle. The sample's relative density was calculated through dividing its bulk density to the theoretical density of LLNO ($\sim$5.170 g cm^{-3}) [10].

Crystalline phase of the sintered LLNO pellet was characterized by X-ray diffraction (XRD, Bruker D8 advance X-ray diffractometer, Cu Kα radiation). The morphology of the sample was characterized by scanning electron microscopy (SEM, Hitach S-4800 Field Emission). Combined with SEM measurement, composition distribution of the elements was measured by energy dispersive X-ray spectroscopy (EDS, Horiba EMAX).

Using two probes method, electrical conductivity measurements were performed on the LLNO pellet in air atmosphere. Li-ion blocking Au electrodes were sputter-coated on both the bottom and top sides of the sample to form Au|LLNO|Au structure. Electrochemical impedance spectras (EIS) were collected with a frequency response analyzer (Solartron 1260, Solartron Analytical) and an electrochemical gain-phase analyzer (Solartron 1287, Solartron Analytical) under open circuit voltage. The frequency range was arranged from 1 Hz to 1 M Hz with an AC amplitude of 10 mV. From 30 °C to 120 °C, the temperature-dependent ionic conductivities were measured.

The electronic conductivity was detected through Hebb-Wagner polarization measurement. A constant DC voltage of 5 V was undertaken for 10,000 S between the two probes of Au|LLNO|Au. According to Hebb-Wagner principle, the electronic conductivity was calculated from the constant voltage, end current, and dimension of the sample.

3. Results and discussion

As shown in Fig. 1, during the calcination process, the gas components such as CO_2 and H_2O were basically eliminated, and LLNO were preliminarily synthesized in puff type due to the exhausting of gas components. Since the loosened LLNO powder was just compacted by manual vibration before sintering, without the assistance of any pressing operations, packing density becomes a crucial factor for the self-consolidation of the packed LLNO powder during sintering. Herein, the packing density is directly determined by the particle size distribution of the powder. Fig. 2 shows the size distribution of LLNO powder, which is not uniform with an average particle size of 15 μm and three main Gaussian distributions around $\sim$0.6, 5, and 30 μm. The LLNO powder can be viewed as particles with consecutive distribution and the volume of large particles is several times larger than the volume of small ones. According to the optimized packing theories, the small particles could distribute in the intersticial space among the large particles after being packed [20]. Therefore, the porosity of the packed LLNO powder would be minimized, which is favorable for the self-consolidation of the packed powder sample during sintering.

Fig. 3 shows the photographs of LLNO sample at different stages. As shown in Fig. 3c and d, the sintered bulk is in a dense cylinder shape in accordance with its sintering holder. It indicates that the packed LLNO powder was shrinking towards its center during sintering, and the sintering powder should contain a solid-state frame to keep the shape