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Low-temperature processing of Garnet-type ion conductive cubic $Li_7La_3Zr_2O_{12}$ powders for high performance all solid-type Li-ion batteries

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ABSTRACT

Synthesis of lithium stuffed cubic $Li_7La_3Zr_2O_{12}$ (*c*-LLZO) garnet at low-processing temperatures is hampered by the lack of deep understanding on powder processing technology. The present article proposes a hybrid solid-state approach to accomplish controllable synthesis of Al doped LLZO cubic garnet oxide nanoparticles at low-processing temperatures. In this procedure, powders of ZrO_2 and $La(OH)_3$ in ethanol based suspension were mechanochemically (MC) treated along with 1 wt.% of AlOOH in a planetary ball mill with increasing milling time to increase the homogeneity of the precursor. Lithium acetate in the form of an ethanolic solution was subsequently added for the solid-state synthesis of single phase LLZO. Cubic LLZO phases were obtained at temperatures *i.e.* 700 °C within 3 h. The ease of lithium diffusion in these MC activated La-Zr precursor materials is attributed to the formation of single phase LLZO with the lowest Al^{3+} doping content. The sintered pellets (94% relative density at 1100 °C for 3 h in air) of the newly obtained $Li_{6.61}La_3Zr_2Al_{0.13}O_{11.98}$ deliver high bulk Li-ion conductivity of 1.35×10^{-4} Scm^{-1}. The new low-temperature processing of typical garnet and the use of *c*-$Li_{6.61}La_3Zr_2Al_{0.13}O_{11.98}$ nanoparticles could open pathways toward future solid electrolyte–electrode assembly options for all-solid state Li-ion batteries.

1. Introduction

Replacing the aprotic electrolytes with the fast ion conductive inorganic solid state electrolytes (SSE) is highly strived for the next generation Li-ion batteries with higher energy density, fire retardant and safer with greater electrochemical stability [1]. Cubic garnet phase $Li_7La_3Zr_2O_{12}$ (*c*-LLZO) is unique in satisfying the conditions described above and has attracted much attention among all other current oxide electrolyte systems (NASICON-type, perovskite-type etc.) as already reported [2,3]. Immense attention has been paid to *c*-LLZO ($Ia\bar{3}d$ symmetry) as it exhibits high room temperature ionic conductivity (~1–2 mS cm^{-1}), low activation energy and 3D Li-ion conduction paths with superior stability for use in high-voltage batteries [4,5]. Furthermore, it is electrochemically inert over a wider voltage range than the conventional liquid electrolytes [6]. Unlike sulfides, *c*-LLZO does not require a controlled environment for processing, and safer because it does not emit toxic hydrogen sulphide [7].

The main drawbacks of current state-of-art *c*-LLZO are its elevated synthesis temperature ($>$ 750 °C) and low sinterability. These limit the adaptability of the hard ceramics for the development of industrially viable all solid state Li-ion batteries (ASLB's) [8]. Low-temperature processing is preferable, since the chances of Li evaporation at higher calcination temperatures results in the formation of the second phase of pyrochlore to reduce the Li-ion conductivity [9]. Hence, synthesis of phase pure LLZO fine powders and its densification at lower sintering temperatures have become the subject research till date [10]. Meanwhile, favorable interfacial compatibility and stable solid-solid interfaces between the solid electrolyte and the electrodes have become a greatest challenge for the next generation energy storage devices, which should be realized at lower processing temperatures. The development of high ion conductive solid electrolyte coupled with a high voltage/capacitive electrode materials without any reactions, degradation, and inter-

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diffusion is very important [11,12]. We think that low-temperature preparation of c-LLZO fine powders is essential for these purposes.

The conventional garnet structure has the general chemical formula of $A_3B_2(CO_4)_3$, where A, B and C reside at 8, 6 and 4 oxygen-coordinated sites, respectively. In a Li-stuffed garnet, *i.e.* in *c*-LLZO, lithium occupies the B (L1) sites as well as unoccupied distorted octahedral (L2) sites. Therefore, Li-ions could be accommodated within six octahedral and two trigonal prismatic free interstitial sites, in addition to the three fully occupied tetragonal interstitial sites on a conventional $A_3B_2(CO_4)_3$ garnet. We should take this crystal structure into account for the low-temperature preparation of c-LLZO fine powders. Many of the preparation methods for *c*-LLZO have been done mostly via liquid phase or solid state synthesis, in which powders were calcined at temperatures above 750 °C and at longer heating duration, as summarized in our previous report [13]. In order to synthesize such complex garnet structure at low calcination temperatures and time, we need to overcome the low reactivity of the starting oxide mixture ascribed to the larger grain sizes. From the structural consideration mentioned above, we proposed that uniform mixing and/or reaction of La and Zr precursor before mixing the Li source for the low-temperature preparation in the previous paper, which should decrease the diffusion path lengths and increase the reactivity of each species. Moreover, Li shows the smallest electron negativity and ionic radius, compared to the other elements contained in *c*-LLZO. Therefore, Li could easily diffuses across the three dimensional interstitial sites. Such synergetic modifications to the reactants decrease the calcination temperatures and duration, thereby, the size of the particles.

Based on this perspective, we aim to crystallize the single-phase *c*-LLZO at low processing temperature by two-step synthesis. In the first step, we tried to prepare a highly reactive La-Zr precursor by mechanochemical (MC) reaction using a high energy planetary ball mill. In the second step, attempt was made to uniformly react La-Zr precursor with Li by solid-liquid reaction. The main objective of this paper is to demonstrate the inter-relation between the homogeneity and high reactivity of La-Zr precursors and the low temperature processing of single-phase *c*-LLZO powder via a solid state route. Further, emphasis is laid on the sinterability and the ionic conductivity of the resultant fine powders of *c*-LLZO to be used as an advanced ion conducting inorganic materials for the development of all solid state Li-ion batteries (ASLB).

2. Experimental

2.1. Sample preparation

LLZO was synthesized by a novel solid-state reaction route based on the previous paper [13]. Raw powders of ZrO_2 fine powders (Tosoh ~99.9%, average particle diameter, $d_{avg.} = 270$ nm) and $La(OH)_3$ (Aldrich ~99.9%, $d_{avg.} = 190$ nm) were used as precursor materials. In this case, Al ingredient (1 wt.% AlOOH, Wako ~97%, $d_{avg.} = 50$ nm) which stabilize the cubic garnet frame work was added together at the same time. They were mixed intimately in a planetary mill (Fritsch, Pulverisette 6) at 500 rotations per minute (RPM) with 3 mm diameter ZrO_2 media in ethanol (EtOH). In this work, grinding time was varied from 1 to 100 h in order to investigate the influence of milling time on the homogeneity of La-Zr precursor. The slurries were then carefully dried in air in 3 steps, *i.e.* 70 °C for 2 h, 100 °C for 0.5 h and 200 °C for 1 h. Thus prepared La-Zr precursor was dispersed in absolute ethanol containing stoichiometric amount of lithium acetate stirred for 0.5 h and ultrasonicated for 10 min followed by drying under the same conditions to LLZO precursor. After that, we aim to synthesize cubic phase pure LLZO powder by calcining these precursor powders at 700 °C for 3 h in the open atmosphere.

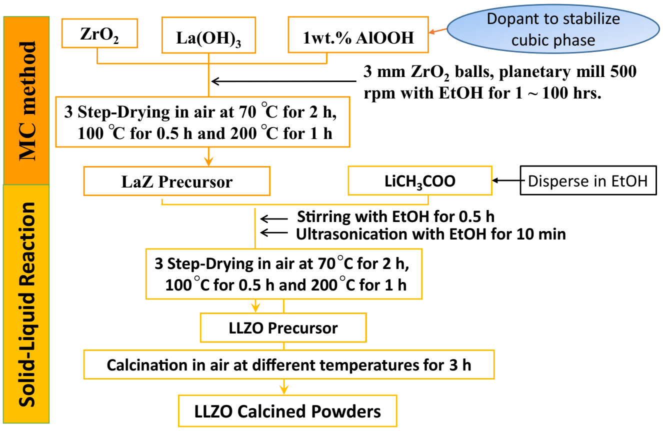

Fig. 1. Schematic diagram representing two-step synthesis to modified solid route synthesis of *c*-LLZO nanoparticles.

On the other hand, stoichiometric amounts of ZrO_2, $La(OH)_3$, $LiCH_3COO$ and AlOOH fine powders were mixed at once to prepare LLZO using conventional solid state reaction method, and the results were compared. It should be noted that these powders were synthesized at stoichiometric ratios of elements and no excess Li was added. Powders were compressed by CIP at 60 MPa for 0.5 h. The green compact was subjected to sintering in a muffle furnace at 900 °C, 1000 °C and 1100 °C for 3 h in air. Fig. 1 representing the schematic representation of two step synthesis approach for LLZO.

2.2. Sample characterization

Crystal structures of the samples were examined using an X-ray diffractometer (D8 Advance; Bruker Analytik, Germany) equipped with a Cu anode ($\lambda = 1.5418$ Å) operated at 40 kV and 40 mA with a scanning rate in 2θ of 0.01 s^{-1}. The phase composition was analyzed using TOPAS software utilizing the ICSD PDF database. The external morphology of the powder samples calcined and the cross-sectional view of the pellet sintered were observed by field emission scanning electron microscopy (FESEM) (Model JSM-700F, JEOL Ltd., Tokyo, Japan) with an accelerating voltage of 15 kV. For the measurements the samples were prepared by attaching the powder/broken pellet to an aluminum stub with silver paste, which then was coated with osmium by sputtering to prevent surface charging. The microstructure of calcined LLZO samples was investigated using scanning transmission electron microscopy (STEM) (Model JEM-2100F; JEOL Ltd.) equipped with energy dispersive spectroscopy (EDS) operating at an accelerating voltage of 200 kV. For TEM evaluations powder samples were dispersed in ethanol using ultrasound for 10 min and one droplet was dropped on a carbon coated grid and dried overnight before analysis. Inductively coupled plasma optical emission spectrometry (ICP-OES) studies were performed to determine the concentration of trace elements in synthesized LLZO powders by Optima 2100DV (PerkinElmer, USA). Impedance spectroscopy (IS) measurements at room temperature were conducted using HP 4194A impedance/gain-phase analyzer in the frequency range between 100 Hz and 10^7 Hz with voltage ramp of 100 mV s^{-1}.

3. Results and discussion

3.1. Importance of wet MC treatment of La-Zr precursor for c-LLZO

3.1.1. XRD

Fig. 2(a) and (b) compares the X-ray diffraction patterns of the LLZO precursor powders calcined at 750 °C for 3 h synthesized

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