



Low temperature synthesis of garnet type solid electrolyte by modified polymer complex process and its characterization



ARTICLE INFO

Article history:

Received 15 October 2015
 Received in revised form 22 February 2016
 Accepted 27 February 2016
 Available online 2 March 2016

Keywords:

A. Inorganic compounds
 B. Sol–gel chemistry
 C. X-ray diffraction
 D. Ionic conductivity

ABSTRACT

Polycrystalline tetragonal and cubic with garnet related type structured $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has been successfully synthesized at 700 °C (tetragonal) and 1100 °C (cubic), respectively by modified polymer complex synthesis. Citric acid was used for a chelating agent and ethylene glycol was applied for polymer complex agent. Thermal analysis indicated that the crystallization has been completed at the low temperature in case of applying high energy ball-milling process. It is presumed that applied mechano-chemical energy promotes the earlier crystallization at lower temperature, which induces the reduction of particle size effectively. LLZOs with tetragonal and cubic phase showed ionic conductivities of $6.2 \times 10^{-7} \text{ Scm}^{-1}$ and $1.4 \times 10^{-4} \text{ Scm}^{-1}$, respectively. Prepared LLZO powders, having relatively small size, are expected to provide the large surface area for Li-ion conducting path in the design of all solid electrodes.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Much interest has been given to lithium batteries because of their high energy density and long cycle life [1–3]. However, there are unsolved issues with respect to safety. The battery safety should be addressed more as a battery gets larger and stores more energy. Especially, the battery for electric propulsion vehicles is demanded to have extra features on safety. The organic liquid electrolyte applied to lithium batteries is one of the major contributors on these safety issues [4]. Therefore, the solid electrolyte has been proposed as one of the possible solutions to resolve safety issues over lithium batteries [5–8].

Several kinds of solid electrolytes (i.e., NASICON, Thio-LISICON, and Garnet types, etc.) have been mainly focused on getting high ionic conductivity comparable with liquid type of conventional electrolyte system. NASICON type $[\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}(\text{PO}_4)_3]$ of solid electrolyte shows high ionic conductivity of $10^{-3} \sim 10^{-4} \text{ S/cm}$, but it has critical issue of instability at interface with anode (in reduction potential range) [9]. Thio-LISICON type [Li-Ge-P-S] system has been reported to be the highest value of ionic conductivity of 10^{-3} S/cm , but generate H_2S gas in the atmosphere due to high reactivity with residual water [10,11].

On the contrary, Garnet type $[\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}]$ system shows excellent electrochemical stability in wide potential range and chemical stability in atmosphere with relatively high ionic conductivity ($\sim 10^{-4} \text{ S/cm}$) [12,13].

First of all, if all-solid electrode will be designed by applying garnet type solid electrolyte powder, the conventional electrode preparation process is supposed to be most preferable to get comparable energy density to current system. The content of solid

electrolyte powder should be, however, controlled as small as possible, while minimizing void space between adjacent electrolyte particles in the all-solid type electrode unlike liquid electrolyte fluid. Therefore, the preferable solid electrolyte powder to all-solid electrode design is required to have nano-size specification with uniform particle size distribution.

In general, the garnet type solid electrolyte with tetragonal and cubic phases has been obtained through solid state synthesis process at high temperature of 900 °C and 1250 °C, respectively [14,15]. It is, however, difficult to avoid the grain growth and particle coarsening, resulting in being larger particle with well-developed crystalline during calcination at high temperature.

It is important to promote an earlier crystallization at the lower temperature resulting in synthesizing smaller fine particles without sacrificing ionic conductivity for solid electrolytes.

Many researchers have reported the studies on low temperature synthesis of oxide based solid-electrolyte powder by applying conventional sol–gel, Pechini sol–gel process, etc. [16–21]. Kokal et al. reported that the garnet solid electrolyte with well-developed cubic phase could be synthesized by calcination at the lower temperature of 700 °C through conventional sol–gel method. Recent reports have only been focused on the evaluation of ionic conductivity for sintered membrane using oxide based solid electrolyte. So far, although many efforts have been made to synthesize the solid electrolyte powder calcined at low temperature, there are little reports on practical approaches of all-solid electrode design using nano-sized solid electrolyte synthesized by low temperature calcination. It is important to promote the low temperature synthesis resulting in smaller particles without sacrificing ionic conductivity for solid electrolytes.

In this work, we have applied newly modified polymer complex process based on in-situ poly-esterification reaction. Citric acid

(CA) and ethylene glycol (EG) were applied to synthesize nano-sized garnet type solid electrolyte under lower calcination temperature. The micro-structural and electrochemical characteristics of solid electrolyte are compared with that of non-modified synthesis process.

2. Experiment and details

2.1. Material synthesis

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ precursors were prepared by a conventional Pechini-type polymer complex method using citric acid as organic complex agent and ethylene glycol as a surface active agent, described in Fig. 1. LiNO_3 (Sigma-Aldrich), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich), and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich) with high purity were used to prepare nitrate precursor. The appropriate amount of nitrate precursors were dissolved in distilled water, and then citric acid and ethylene glycol were added to the solution. Extra Li nitrate (10 wt.%) was added to compensate for expected Li loss during heat treatment. The amount of citric acid used was twice the total moles of cations in the precursor solution. Applied ratio of ethylene glycol and citric acid was 1:2. The resultant solution was vigorously stirred at 40°C for 10 h. The solvent was slowly evaporated and then a transparent gel was obtained at 60°C . The obtained gel was further heated under stirring for several hours. The gel became highly viscous, changing in color from colorless to yellow, and finally it turned to brown precursor powder by heat treatment at 200°C for 5 h under air atmosphere. The precursor powder was finely ground by mechanical ball milling. The morphological changes were observed for the precursors having various milling conditions (Fig. 2). The obtained fine powder was spread on an alumina or platinum crucible, first heated slowly to 400°C at $5^\circ\text{C}/\text{min}$, then hold for 2 h, sintered at a designed temperature ($600\text{--}1250^\circ\text{C}$) and maintained for 5 h.

2.2. Characterization

Thermal analysis (TG/DTA) of the gels dried at 200°C for 5 h, followed by mechanical ball milling, was conducted by using SDT Q600 (TA) in air flow with a heating rate of $10^\circ\text{C}/\text{min}$. The crystal structure of resulting powder was identified by the X-ray diffraction method (Siemens D5000). Diffraction patterns were acquired with nickel-filtered $\text{Cu K}\alpha$ radiation at room temperature between scattering angles of 10° and 90° in increments of 4° with a step size of 0.01° . Structural refinements of the resulting compounds were performed with the Full Prof software. The morphological change of powders after modification was characterized by field emission-scanning electron microscope (FE-SEM, HITACHI S-4800N). Ionic conductivity of powder samples were measured using a potentiostat with frequency response analyzer (VMP3, Bio-Logic). Pellet-type samples were prepared with 12 mm diameter and 1 mm thickness by pressing the powder followed by sintering at 700°C for 3 h. The measurement condition was a potential perturbation of 100 mV and a frequency range of 100 Hz to 1 MHz. Prior to measurements, Au paste was applied on both sides of the pellets and then cured at 100°C in air to ensure electrical contact and form the ionically blocked electrodes. Finally, to evaluate the electrochemical performances of test cell applying the as-prepared LLZO solid electrolyte, a coin cell (2032 type) was assembled, using Li metal anode, Ni-based cathode, and composite solid electrolyte in an argon-filled glove box. In particular, to prepare cathode electrode based on optimum composition, the cathode slurry was first prepared by mixing the five components: NCM622 (56 wt.%, $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$, L&F Co., Ltd.) as active material, PEO (15 wt.%, $M_w = 6 \times 10^6$, Aldrich Co., Ltd.), as-synthesized LLZO (21.5 wt.%, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, tetragonal phase) powders, LiClO_4 (2.5 wt.%, Aldrich Co., Ltd.) as composite electrolyte, and finally SPB (5 wt.%, Super-p black) as conducting agent.

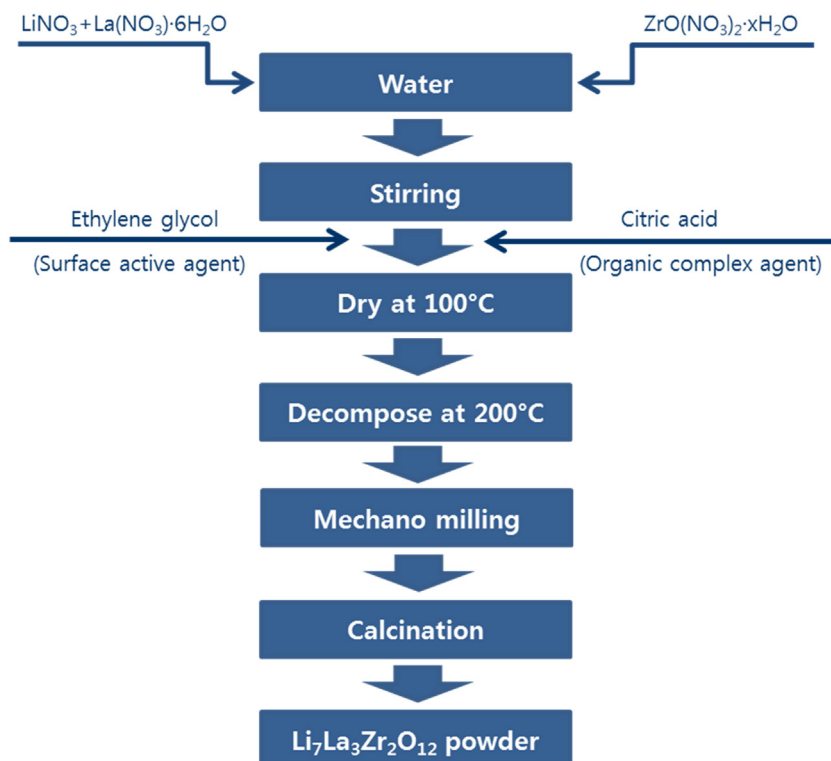


Fig. 1. Flow chart for synthesizing sub-micron sized $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ powder by modified polymer complex method.

Download English Version:

<https://daneshyari.com/en/article/1487084>

Download Persian Version:

<https://daneshyari.com/article/1487084>

[Daneshyari.com](https://daneshyari.com)