Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Ionic conductivity of Ga-doped LLZO prepared using Couette–Taylor reactor for all-solid lithium batteries

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ARTICLE INFO

Article history:
Received 2 June 2017
Received in revised form 28 July 2017
Accepted 30 July 2017
Available online xxx

Keywords:
All-solid battery
Co-precipitation
Couette–Taylor
Q3 Garnet-like structure
Sintering temperature
Cubic phase
Ionic conductivity

ABSTRACT

A Couette–Taylor reactor and a batch reactor were used to synthesize garnet-related LLZO materials ($Li_{7-3x}M_xLa_3Zr_2O_{12}$, M = Ga, Al) for all-solid batteries, and the properties of the resulting samples were compared. Ga-doped LLZO synthesized with the Couette–Taylor reactor comprised cubic phase primary nanoparticles; the calculated lattice parameter and crystallite size for the Couette–Taylor and batch reactor samples were $a = 12.98043$ Å and 129.8 nm and $a = 12.97568$ Å and 394.5 nm, respectively. The parameters for the Al-doped LLZO congener synthesized with the Couette–Taylor reactor were $a = 13.10758$ Å, $c = 12.67279$ Å, and 132.5 nm. The cross-section of the Ga-doped LLZO pellet synthesized with the Couette–Taylor reactor showed a denser microstructure than that of the other pellets, with a relative density of 98%. The total ionic conductivity of the Ga-doped LLZO pellets synthesized with the Couette–Taylor reactor was $1.2–1.75 \times 10^{-3}$ S/cm at 25 °C. This value contrasts sharply with that of the sample from the batch reactor (3.9×10^{-4} S/cm). This is may be related to the large size of Ga doped into the LLZO crystallite structure and the primary nanoparticles, which promoted sintering of the pellet.

Introduction

Despite the safety risk, lithium ion batteries have been applied to small electric devices, such as mobile phones, for a long time due to their high energy density. With the recent advances in renewable energy and the electric vehicle industry, the development of a large and safe lithium ion battery is required. All-solid lithium ion batteries are considered as an alternative for next-generation batteries. It is well known that the electrochemical properties of all-solid lithium batteries depend greatly on the character of the solid electrolyte materials, such as the ionic conductivity, electrochemical potential window, chemical stability, et cetera [1]. The recent investigations on lithium ion conductors encompass a wide range of compounds with different structure types, such as $70Li_2S\text{-}30P_2S_5$ with the binary-sulfide structure, $Li_{0.34}La_{0.51}TiO_{2.94}$ with the perovskite structure, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ with the NASICON structure, and lately, $Li_5La_3M_2O_{12}$ (M = Nb, Ta) with the garnet-related structure. Garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) has been intensively investigated [2–4] as a metal oxide with excellent ionic conductivity, a desirable electrochemical window, and as a solid electrolyte since the first report by Murugan et al., in which LLZO was prepared via the conventional solid-state reaction [4]. However, one major drawback of LLZO is that it is difficult to prepare cubic phase pellets with fine sintering properties as these properties are sensitively affected by the preparation conditions, such as the composition, synthesis process, and calcination temperature. Cubic phase LLZO tends to exhibit excellent lithium ion conductivity relative to the tetragonal phase [4]. The differences between cubic phase and tetragonal phase LLZO materials prepared via solid-state, sol–gel, and co-precipitation processes have been reviewed in the literature [4–7], where the lithium ion conductivity of the two polymorphs differs by about 2 orders of magnitude (10^{-4}–10^{-6} S/cm) [7] and the co-precipitation process is particularly attractive for mass production.

Current attempts to improve the lithium ion conductivity of LLZO materials involve doping with transition or non-transition metal cations [8–10]. However, the use of transition metal cations (e.g., Nb, Ta) may undesirably impart mixed conductor properties to LLZO, along with electronic and ionic conductivity. Therefore, LLZO materials have been doped with non-transition metal cations

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http://dx.doi.org/10.1016/j.jiec.2017.07.041
1226-086X/© 2017 Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry.

Please cite this article in press as: S.H. Yang, et al., Ionic conductivity of Ga-doped LLZO prepared using Couette–Taylor reactor for all-solid lithium batteries, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.07.041

such as Ga, Al, etc., via a modified sol–gel process; the resulting Ga-doped LLZO had a typical cubic structure, with an ionic conductivity of 3.5×10^{-4} S/cm [11]. The highest ionic conductivity of LLZO oxide materials synthesized via the conventional methods is approximately $3–8 \times 10^{-4}$ S/cm [12,13].

To evaluate the main factors affecting the ionic conductivity of LLZO materials, the primary particle size and the calcination process must be tailored based on the dopant used. Herein, we report a new method of producing nano-grade Ga or Al doped-LLZO materials with high yields in a significantly shortened reaction time. The setup used herein, termed the Couette–Taylor reactor, is a modified co-precipitation process in which two coaxial cylinders with the inner one rotating are utilized, and toroidal vortices are created and regularly spaced along the cylinder axis at a critical rotating speed [14–17].

The metal ions and additives(i.e., La, Zr, Ga, Al, and NH_4OH) are accelerated by the turbulent Couette–Taylor vortex flow. It is reported that this toroidal motion of the fluids leads to highly efficient radial mixing of the metal ion solution and chelating agents in the system [18]. In this work, LLZO materials doped with Ga or Al, prepared by using a Couette–Taylor reactor, are discussed in detail on the basis of the particle morphology, crystal structure, and ionic conductivity.

Experimental

Synthesis of non-transition element-doped LLZO powders

Ga-doped LLZO (sample name: Ga-Taylor powder) and Al-doped LLZO (sample name: Al-Taylor powder) with the general formula $Li_{7-3x}M_xLa_3Zr_2O_{12}$ (M = Ga, Al) were prepared by using the Couette–Taylor reactor. $La(NO_3)_3$, $ZrOCl_2$, and $Ga(NO_3)_3$ were used as the starting materials for the Ga-Taylor powder and $La(NO_3)_3$, $ZrOCl_2$, and $Al(NO_3)_3$ were used for the for Al-Taylor powder. All chemicals (Aldrich) used in the synthesis were of regular grade purity. The starting materials were first dissolved in a fixed quantity of distilled water by stirring at room temperature. The wet precursor (as the metal hydroxide) was obtained by adding ammonium, and sodium solution to the metal ion solution, which brought the pH of the solution to 11 during the chemical reaction in the Couette–Taylor reactor. Fig. 1 shows a conceptual diagram of the vortex structure in the Couette–Taylor reactor. The reactor with Taylor fluid flow is composed of two cylinders, in which a round bar-type cylinder is inserted into a pipe-type cylinder. This leads to unique flow characteristics as the outer cylinder is fixed and the inner cylinder rotates. The fluid flows in the direction of rotation as the inner cylinder rotates, but a force acts on the fluids in the inner cylinder to move them in the direction of the outer cylinder via a centrifugal force and a coriolis force; thus, the fluid flow becomes gradually unstable as the rotation speed increases, thereby creating vortexes of a ring pair array rotating regularly and in the counter directions along the axial direction.

The wet precursor was continuously collected at the end nozzle of the reactor cylinder and washed through a filter paper with deionized water to remove impurities; the precursors were dried overnight in an oven under air atmosphere. In order to fabricate the Ga-doped LLZO material and Al-doped LLZO material, the dry precursor was mixed with the required amount of lithium hydroxide (calculated for the target ratio). The lithium content in all samples was about 10 wt% (as excess lithium due to the loss of lithium by sintering at high temperature), and the mixture was homogenized in a planetary ball-mill for 15 min and then calcined at 900 °C for 2 h. For reference, the Ga-doped LLZO material (sample name: Ga-batch powder) was also prepared by the conventional co-precipitation method in the batch type reactor [7]. Furthermore, after calcination, the powders were pressed and sintered at 1200 °C for 5 hr in a disc mold to measure the ionic conductivity. After sintering, the Ga-doped LLZO pellet prepared with the Couette–Taylor reactor (sample name: Ga-Taylor pellet), Ga-doped LLZO pellet prepared by using the batch reactor (sample name: Ga-batch pellet), and Al-doped LLZO pellet prepared by using the Couette–Taylor reactor (sample name: Al-Taylor pellet) were obtained as the final products.

Characterization of non-transition element-doped LLZO powders

The thermal characteristics of the mixture precursor before calcination were analyzed to determine the transition state of the mixture with increasing temperature by using thermal analysis systems (TGA/SDTA851, Mettler Toledo, Switzerland). The crystalline structures of the powder samples were identified by using an X-ray diffractometer (XPert Pro, PANalytical, Netherlands), employing Cu-Kα radiation ($\lambda = 1.5406$ Å). The crystal parameters, such as the lattice parameters, crystallite size, etc., were estimated by the Rietveld refinement method. The morphology of the powders and the microstructure of the pellet were observed via field emission scanning electron microscopy (FESEM, HITACHI S-4700, Japan).

The bulk density of the pellets was determined from the weight and physical dimensions of the rectangular parallelepipeds. The relative density values were determined by dividing the bulk density by the theoretical density of cubic $Li_7La_3Zr_2O_{12}$

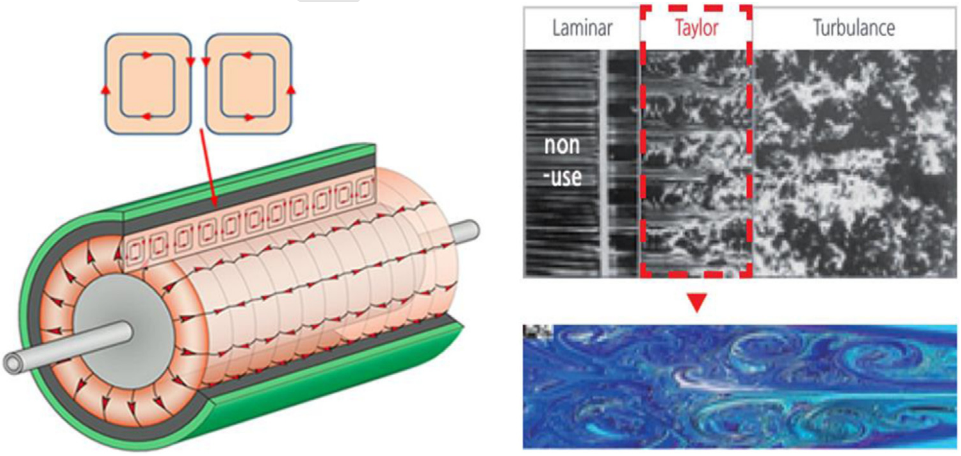

Fig. 1. Conceptual diagram of vortex structure in the Couette–Taylor reactor.

Please cite this article in press as: S.H. Yang, et al., Ionic conductivity of Ga-doped LLZO prepared using Couette–Taylor reactor for all-solid lithium batteries, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.07.041