Journal of Power Sources 230 (2013) 261–266

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

The effect of 24c-site (A) cation substitution on the tetragonal–cubic phase transition in $Li_{7-x}La_{3-x}A_xZr_2O_{12}$ garnet-based ceramic electrolyte

Ezhiylmurugan Rangasamy [a], Jeff Wolfenstine [b], Jan Allen [a], Jeff Sakamoto [a,*]

[a] *Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA*
[b] *Army Research Laboratory, RDRL-SED-C, 2800 Powder Mill Road, Adelphi, MD 20783, USA*

HIGHLIGHTS

- ► Substitution of La with Ce stabilizes the cubic LLZO garnet phase.
- ► CeO_2 precipitation at grain boundaries increases grain boundary resistance.
- ► Super-valent cation substitution likely stabilizes the cubic LLZO phase.

ARTICLE INFO

Article history:
Received 15 July 2012
Received in revised form
16 November 2012
Accepted 6 December 2012
Available online 27 December 2012

Keywords:
Solid-electrolyte
Garnet
Ce
Cubic
Li vacancies
Hot-pressing

ABSTRACT

The garnet-type ceramic electrolyte of nominal composition $Li_7La_3Zr_2O_{12}$ can exist in the tetragonal and cubic form. This article investigates the tetragonal to cubic phase transition based on super-valent cation substitution on the 24c site typically occupied by La (3+) in the garnet structure. Ce (4+) was selected as the super-valent cation represented as x in $Li_{7-x}La_{3-x}Ce_xZr_2O_{12}$. The doping study showed that cubic LLZO was stabilized for Ce $\geq$ 0.2. These data agree with most literature reports suggesting that the creation of Li vacancies, while maintaining oxygen stoichiometry, is necessary to stabilize cubic LLZO. Moreover, this work suggests a critical Li vacancy concentration (0.12–0.4 mol per mole of $Li_7La_3Zr_2O_{12}$) is necessary to stabilize cubic LLZO. While the addition of Ce stabilized cubic LLZO, the total ionic conductivity (0.014 mS cm^{-1}) was considerably lower compared to Al and Ta doped LLZO (0.4–0.9 mS cm^{-1}, respectively). The lower conductivity is likely due to CeO_2 precipitation at grain boundaries.

1. Introduction

Li-ion batteries have played a vital role in the development of current generation mobile devices, microelectronics and electric vehicles [1]. Due to the flammability of conventional electrolytes [2], considerable research has been conducted to develop solid state Li-ion conductors [3–5]. Ceramic Li ion conductors have high thermal, chemical and electrochemical stability vs. Li/Li^+ [4], which could enable the use of ultrahigh voltage cathodes. The unique combination of high ionic conductivity, chemical and electrochemical stability could also enable the development of Li-air, redox flow and Li–S secondary batteries.

A number of solid state Li-ion conductors demonstrate potential for use in advanced battery technology [3–5]. Of these, the most common has been the family of perovskite titanates ($Li_{3x}La_{2/3-x}TiO_3$) (LLTO) and NASICON type $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) [3–7]. Despite having a high bulk Li-ion conductivity of 1 mS cm^{-1}, polycrystalline LLTO typically has low grain boundary conductivity, thus reducing the total conductivity to the 10^{-5} to 10^{-6} S cm^{-1} range [5–7]. Additionally, the presence of Ti limits the voltage stability vs. Li/Li^+ to approximately 1.7 V in the perovskite LLTO and 2.5 V in LATP [8,9], thus preventing use with metallic Li or other low potential anodes. $Li_7La_3Zr_2O_{12}$ (LLZO) with the garnet structure is a promising ceramic electrolyte, because it exhibits the unprecedented combination of high room temperature total conductivity of 0.9×10^{-3} S cm^{-1} [10] and electrochemical stability against metallic lithium [11,12].

It has been reported that tetragonal LLZO has a Li-ion conductivity that is approximately between two and three orders of magnitude lower than the cubic LLZO [13–16]. Thus, the challenge has been to stabilize the cubic form of LLZO. The first reported stabilization of the cubic LLZO resulted from the adventitious

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* Corresponding author. Tel.: +1 517 432 7393; fax: +1 517 432 1105.
E-mail address: jsakamot@msu.edu (J. Sakamoto).

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http://dx.doi.org/10.1016/j.jpowsour.2012.12.076

doping of Al as a result of contamination from alumina crucibles [10,17]. Later Al was intentionally added [18,19] and a dense (relative density $> 90\%$) material with a cubic structure was obtained. Geiger et al. [17] have suggested that Al substitutes for Li and thereby stabilizes the cubic phase. A similar stabilization of cubic phase is observed with Ga substitution, where Ga substitutes for Li [20,21]. One hypothesis is that super-valent cation substitution reduces the Li content and/or increases Li vacancy concentration, while maintaining oxygen stoichiometry, and hence stabilizes the cubic phase [16,17,19]. In Kroger–Vink notation [24], the relationship for Al and Ga substitution for Li are as follows [17,19,21]:

$$2\left[\mathrm{Al}_{\mathrm{Li}}^{\cdot\cdot\cdot}\right] = \left[\mathrm{V}_{\mathrm{Li}}'\right] \tag{1}$$

$$2\left[\mathrm{Ga}_{\mathrm{Li}}^{\cdot\cdot\cdot}\right] = \left[\mathrm{V}_{\mathrm{Li}}'\right] \tag{2}$$

However, substitutions for Li^+ (as is the case for Al and Ga) result in the obstruction of ionic pathways, thus reducing the conductivity [20]. Another super-valent substitution scheme involves either Nb (5+) or Ta (5+) on the 16a site (Zr 4+), that reduces the Li content and/or increases Li vacancy concentration to stabilize the cubic structure [22,23]. Substitution on the Zr (4+) site will not block the Li-ion pathways and thus leads to higher conductivity than that observed for the Al and Ga substitutions [20]. For example, when 0.25 mol of Ta was substituted for 0.25 mol of Zr, the conductivity more than doubled compared to comparable levels of doping with Al [16,20]. In Kroger–Vink notation, the relationships for Ta and Nb substitution for Zr are as follows [20,22,23]:

$$\left[\mathrm{Ta}_{\mathrm{Zr}}^{\cdot}\right] = \left[\mathrm{V}_{\mathrm{Li}}'\right] \tag{3}$$

$$\left[\mathrm{Nb}_{\mathrm{Zr}}^{\cdot}\right] = \left[\mathrm{V}_{\mathrm{Li}}'\right] \tag{4}$$

Likewise, super-valent substitution on the 24c (La 3+) is another approach to create Li vacancies without obstructing the Li sublattice, that could stabilize the cubic LLZO phase. At present there is no information regarding the stabilization of cubic LLZO by the substitution of super-valent cation (4+) on the La (3+).

It follows that the purpose of this work is to investigate the tetragonal to cubic phase transition based on super-valent substitution of Ce (4+) for La (3+) in the formula $\mathrm{Li}_{7-x}\mathrm{La}_{3-x}\mathrm{Ce}_x\mathrm{Zr}_2\mathrm{O}_{12}$. In Kroger–Vink notation, the proposed substitution would be:

$$\left[\mathrm{Ce}_{\mathrm{La}}^{\cdot}\right] = \left[\mathrm{V}_{\mathrm{Li}}'\right] \tag{5}$$

In 8-fold coordination, the radius of Ce (4+) (128 pm) is similar to La (3+) (130 pm), thus substitution is expected [24]. The proposed range of x is $0.0 < x < 0.8$ and is based on similar work involving Al, Ga, Nb and Ta where the Al was intentionally added [18–23].

In this work, a series of Ce doped LLZO powder samples were prepared using a conventional solid state reaction technique. Measures were taken to eliminate Al contamination from alumina crucibles as a variable has been reported previously [19]. The powders were characterized using X-ray diffraction (XRD) to determine the phase(s) present, followed by densification to >94% relative density to evaluate the ionic transport of selected formulations. SEM analysis was used to characterize the microstructures and phase impurities. Additionally, the ionic transport was characterized using electrochemical impedance spectroscopy and the activation energies were measure between 298 and 378 K.

2. Experimental

2.1. Synthesis

Lithium carbonate (Alfa Aesar 99.998%), lanthanum hydroxide (Alfa Aesar 99.95%), zirconium oxide (30–60 nm 99.9% Inframat Advanced Materials), and cerium oxide (50–80 nm 99.97% Inframat Advanced Materials) powders were used as precursor materials during the synthesis procedure. The precursor powders were weighed according to the formula $\mathrm{Li}_{7-x}\mathrm{La}_{3-x}\mathrm{Ce}_x\mathrm{Zr}_2\mathrm{O}_{12}$ where $x = 0.0$, 0.2, 0.4, 0.6 and 0.8 mol. (no excess Li precursor was added). The precursors were milled in a planetary mill for 4 h (Planetary Mill PM 100 – Retsch) using agate media, cold pressed and calcined at 1000 °C for 4 h in air in a tube furnace (Thermo Scientific Lindberg Blue M Mini-Mite). To prevent Al contamination, powders were calcined on pristine zirconia surfaces. Powders were placed in graphite dies and hot pressed at 1050 °C under flowing argon for 1 h under 40 MPa pressure.

2.2. Characterization

Specimen densities were calculated using geometric and gravimetric measurements. Identification of crystal phases was carried out using XRD (Bruker D8 Advance with Da Vinci) and microstructure analysis was carried out using SEM (JEOL JSM 7500F). Grain sizes were established using a linear intercept method on the SEM micrographs. Energy Dispersive Spectroscopy (EDS) analysis was carried out in a Carl Zeiss variable pressure SEM (EVO LS25). Elemental analysis carried out using EDS utilized five line scans per sample with a resolution of 0.1 μm on the line scan, with each line being averaged over 6 scans. Samples for EDS analysis were mounted in a conductive epoxy and mechanically polished to a final finish using a 50 nm $\mathrm{Al}_2\mathrm{O}_3$ – water slurry. Volume fraction of ceria was calculated using the histographic analysis of Back Scattered Electron (BSE) imaged samples. Li ion conductivity was determined using AC electrochemical impedance spectroscopy (EIS) with a VersaSTAT4 potentiostat over a frequency range of 10 Hz–800 kHz and potential amplitude of 100 mV. For electrochemical measurements, the sintered pellets were coated with Au films of an approximate thickness of 105 nm using sputter coating. A load frame applied a constant 0.34 MPa pressure during EIS measurements.

3. Results and discussion

3.1. Effect of Ce on the crystal structure of LLZO

The X-ray diffraction (XRD) patterns for the range of $0.0 < x < 0.8$ Ce in the formula $\mathrm{Li}_{7-x}\mathrm{La}_{3-x}\mathrm{Ce}_x\mathrm{Zr}_2\mathrm{O}_{12}$ are shown in Fig. 1. When $x = 0.0$ Ce, tetragonal LLZO forms as is evident from peak doublets associated with primary peaks, which is in agreement with previous work [13–16]. In previous work [19] the peak at $2\Theta = 34°$ was used to identify peak doublets. However, in this work, a high intensity peak, from the secondary phase CeO_2 at $2\Theta = 34°$, obscured the tetragonal peak doublets at $2\Theta = 34°$. Thus, the 50–55° 2Θ range was used to determine if the cubic or tetragonal LLZO phase was present. If LLZO is cubic, there are three peaks and if LLZO is tetragonal there are six peaks in the 50–55° 2Θ range. A box highlights these peaks in Fig. 1.

When x is increased (Ce added), several observations can be made. First, it is clear that the addition of Ce stabilizes the cubic LLZO phase. The peak doublet intensities decrease as x increases, indicating that the addition of Ce is what drives the transformation from tetragonal to cubic LLZO. The peak doublet intensities significantly decrease between $x = 0.2$ Ce and $x = 0.4$ Ce diminishing to