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Ceramics International 40 (2014) 5043–5047
CERAMICS INTERNATIONAL
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Short communication

Preparation of $Li_7La_3Zr_2O_{12}$ solid electrolyte via a sol–gel method

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Received 2 August 2013; received in revised form 3 September 2013; accepted 3 September 2013
Available online 9 September 2013

Abstract

In this research, $Li_7La_3Zr_2O_{12}$ (LLZ), which has been recognized as a promising solid electrolyte for next-generation Li-ion batteries, is prepared by a sol–gel method to lower the calcination temperature. A precursor sol is prepared from lithium acetate, lanthanum acetate and zirconium tetrabutoxide. After gelation, the gel is heated at 700 °C, and a white powder, which consisted mainly of $La_2Zr_2O_7$, is obtained. Sintered pellets are prepared by calcination at 1000 °C or 1100 °C. The tetragonal-phase LLZ with low Li-ion conductivity is contained in the pellet calcined at 1000 °C. After the calcination at 1100 °C, the tetragonal LLZ transforms into a cubic phase which possesses high Li-ion conductivity. With the sol–gel method, the cubic-phase LLZ can be obtained after calcination at 1100 °C, which is 130 °C lower than the temperature in conventional solid-state reaction. The Li-ion conductivity of the prepared cubic LLZ is 1.5×10^{-4} S cm^{-1}, which is comparable with the previously reported values. It is concluded that the cubic LLZ with high Li-ion conductivity can be successfully prepared at low temperature using the sol–gel method.

Keywords: Solid electrolyte; Lithium battery; Sol–gel method; Garnet-type electrolyte

1. Introduction

In our current information-rich society, energy storage devices, such as batteries, are a key component [1]. Among the various types of batteries, rechargeable lithium-ion batteries have been widely used as energy sources for a variety of electronic devices, such as mobile phones and laptop computers because of their high energy densities. However, fast progress of new electronic devices has required further improvement in the energy density of lithium-ion batteries.

Compounds with a composition of $Li_xLa_3M_2O_{12}$ ($x=5$ or 7, M = Ta, Nb, Zr) have been discovered as a novel family of fast lithium-ion conductors [2]. Among them, $Li_7La_3Zr_2O_{12}$ (LLZ) has recently gained high interest as a solid-state lithium-ion conductor in the all-solid-state lithium rechargeable batteries because of its high lithium-ion conductivity ($\sigma_{Li} > 10^{-4}$ S cm^{-1}) and chemical stability when in contact with metallic lithium [3–8]. The metallic lithium anode exhibits the largest capacity among all anode materials for the lithium-ion batteries because it does not contain matrix components. The theoretical capacity of Li metal is 3862 mA h g^{-1} [9], which is approximately 10 times larger than the capacity of present graphite anodes (372 mA h g^{-1} [10]). Therefore, all-solid-state batteries with the metallic lithium anode can satisfy the requirement for the improvement of energy density. Kotobuki et al. reported reversible Li deposition and extraction in Li/LLZ/Li [4] and Li/LLZ/$LiCoO_2$ cells [6–8]; their results imply that the all-solid-state batteries with the metallic lithium anode can be fabricated using the LLZ solid electrolyte. However, the preparation of LLZ requires high-temperature calcination (1230 °C) which causes the formation of $La_2Zr_2O_7$ as an impurity phase, and this high-temperature has made the LLZ preparation difficult.

To resolve this issue, some groups have attempted to reduce the calcination temperature. Huang et al. prepared Ge-doped LLZ solid electrolyte calcined at 1200 °C which has high Li-ion conductivity (7.63×10^{-4} S cm^{-1}) [11]. Wolfenstine et al. examined the effects of Ga addition to LLZ on the calcination temperature and reduced the calcination temperature to 1000 °C [12]. Kotobuki et al. investigated the effects of Al_2O_3 addition on the calcination temperature for LLZ preparation [6]. They prepared the LLZ solid electrolyte by

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http://dx.doi.org/10.1016/j.ceramint.2013.09.009

calcination at 1000 °C and operated Li/LLZ/$LiCoO_2$ cell successfully.

The preparation of LLZ using a sol–gel method, which allows preparation of inorganic materials at low temperatures [13], has also been reported. Kokal et al. used the sol–gel process to prepare LLZ and obtained the LLZ solid electrolyte at calcination temperature of 900 °C. They also reported that Li-ion conductivity of obtained LLZ was 3.12×10^{-7} S cm^{-1} [14]. In their research, Li_2CO_3 and La_2O_3 were used as Li and La sources, respectively, and were dissolved into HNO_3 to prepare a precursor sol. Their procedure would be simplified if water-soluble Li and La salts were used. Janani et al. also reported the preparation of LLZ by the sol–gel method using water-soluble $LiNO_3$ and $La(NO_3)_3\cdot 6H_2O$; however, they did not report the Li-ion conductivity [15].

In this paper, we report the preparation of LLZ solid electrolyte via a sol–gel process using water-soluble lithium acetate and lanthanum acetate as starting materials. The LLZ solid electrolyte was obtained after calcination at 1100 °C, which is 130 °C lower than the temperature of the conventional solid-state reaction, and the Li-ion conductivity was comparable with those reported previously.

2. Experimental

LLZ solid electrolyte was prepared by the sol–gel method. A precursor sol containing Li, La and Zr was prepared by mixing CH_3COOLi, $La(CH_3COO)_3\cdot 1.5\,H_2O$, $Zr(C_4H_9O)_4$, CH_3COOH, C_3H_7OH, and H_2O in a molar ratio of 7.7:3:2:25:25:1000. All reagents were purchased from Wako Chemical Co. (Tokyo, Japan) and were used without further purification. After gelation, the obtained gel was ground in an agate mortar and then heated at 700 °C for 4 h in air to obtain a precursor powder. The powder was crushed by a planetary ball-mill at 650 rpm for 1 h (Pulver Risette 7, Fritsch) with ϕ0.5 mm zirconia balls. The crushed powder was pressed into a pellet form 20 mm in diameter and was then calcined at 1000 °C for 6 h, 1000 °C for 9 h, or 1100 °C for 6 h in air.

The crystalline phases of the precursor powder and the calcined pellet were identified by X-ray diffraction (XRD, Rigaku Ultima-IV) using Cu Kα radiation. Scanning electron microscopy (SEM, JEOL, JSM-6300LA) was used to observe the morphologies of the powder and the pellet cross-section.

Both surfaces of the pellet calcined at 1100 °C were polished to obtain flat surfaces and control its thickness before measurement of the Li-ion conductivity. The Li-ion conductivity was measured by the ac impedance method. Prior to the measurement, Au was sputtered onto both sides of the pellet to prepare Li-ion blocking electrodes and ensure electrical contact between the pellet and Cu current collectors. The ac impedance data was collected at a voltage signal of ±10 mV in a frequency range of 500 Hz–1 MHz using a chemical impedance meter (HIOKI Chemical Impedance Meter 3352-80). The measurement was performed at 30–100 °C to clarify the temperature dependence of the Li-ion conductivity.

3. Results

When the gel was heated at 600 °C, the obtained powder showed gray color, indicating that the organic components still existed in the powder. A white powder could be obtained after heat treatment at 700 °C for 4 h. SEM images of the heated powder before and after ball-milling are shown in Fig. 1. Before ball-milling (Fig. 1a), small particles of approximately 1 μm in diameter were observed; the particles were fused to each other and formed large particles with diameters greater than 20 μm. Notably, the morphology of the powder after being ball-milled was completely different (Fig. 1b). In this case, large particles were no longer observed. The powder was crushed to a diameter of ~100 nm by the ball-milling.

The XRD pattern of the ball-milled powder is revealed in Fig. 2. Broad diffraction peaks were observed because of the low crystallinity of the sample. The main peak appeared at 2θ=28.6° and some low-intensity peaks were assigned to pyrochlore-structured $La_2Zr_2O_7$ (LZ; PDF 71-2363). The other low-intensity peaks matched the standard pattern of the $Li_5La_3Nb_2O_{12}$ garnet phase (PDF 45-0109), indicating that garnet-structured LLZ was also formed during the heat treatment at 700 °C for 4 h [3–8].

Fig. 3 depicts the XRD patterns of the calcined pellets at various temperatures. Two phases of garnet LLZ are known: tetragonal and cubic phases [4–16]. The tetragonal phase can be identified by peak doublets, and the most pronounced doublet is centered at 2θ=30.5° [17]. The peaks in the pellet heated at 1000 °C for 6 h (Fig. 3a) matched well the standard pattern of garnet and the occurrence of the doublet peak at 2θ=30.5° was confirmed, indicating that the tetragonal-phase LLZ was produced. Moreover, a peak assigned to the pyrochlore LZ at 2θ=28.6° was also observed. The diffraction pattern of the pellet calcined at 1000 °C for 9 h (Fig. 3b)

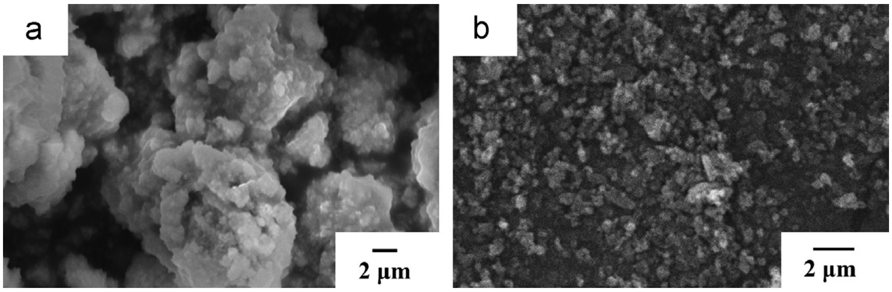

Fig. 1. SEM images of powders prepared by a sol–gel method after heat treatment at 700 °C: (a) before ball-milling and (b) after ball-milling.

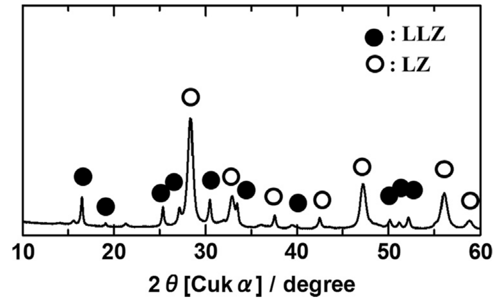

Fig. 2. XRD pattern of the heated powder after ball-milling.

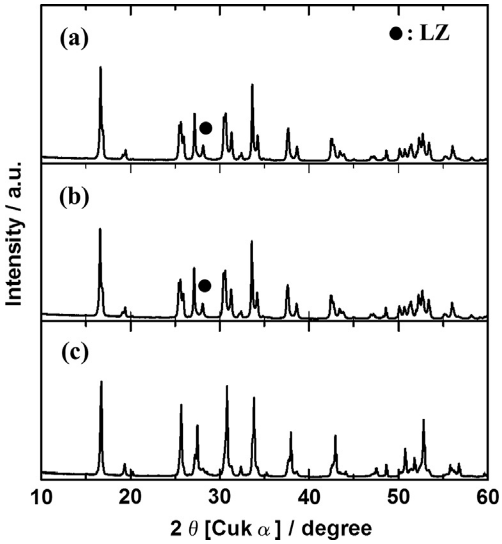

Fig. 3. XRD patterns of LLZ pellets calcined at (a) 1000 °C for 6 h, (b) 1000 °C for 9 h, and (c) 1100 °C for 6 h.

exhibited the same features. The calcination time did not strongly affect the crystal structure of LLZ. However, a large difference in the diffraction pattern was observed in the pellet calcined at 1100 °C (Fig. 3c). All the doublet peaks were no longer observed, and only singlet peaks, which were attributed to cubic-phase LLZ [17], were observed. The clear peak of the pyrochlore LZ was also not observed.

Cross-sectional SEM images of LLZ pellets calcined at 1000 °C for 6 h, at 1000 °C for 9 h, and at 1100 °C for 6 h are displayed in Fig. 4. In the pellet calcined at 1000 °C for 6 h, the particles fused each other during calcination; however, numerous voids were observed. These voids became fewer in number and smaller when the calcination time was extended to 9 h. By the calcination at 1100 °C, the particles fused well and the voids were much fewer and smaller than those in the pellets calcined at 1000 °C for 6 h and 9 h, although some voids were still observed.

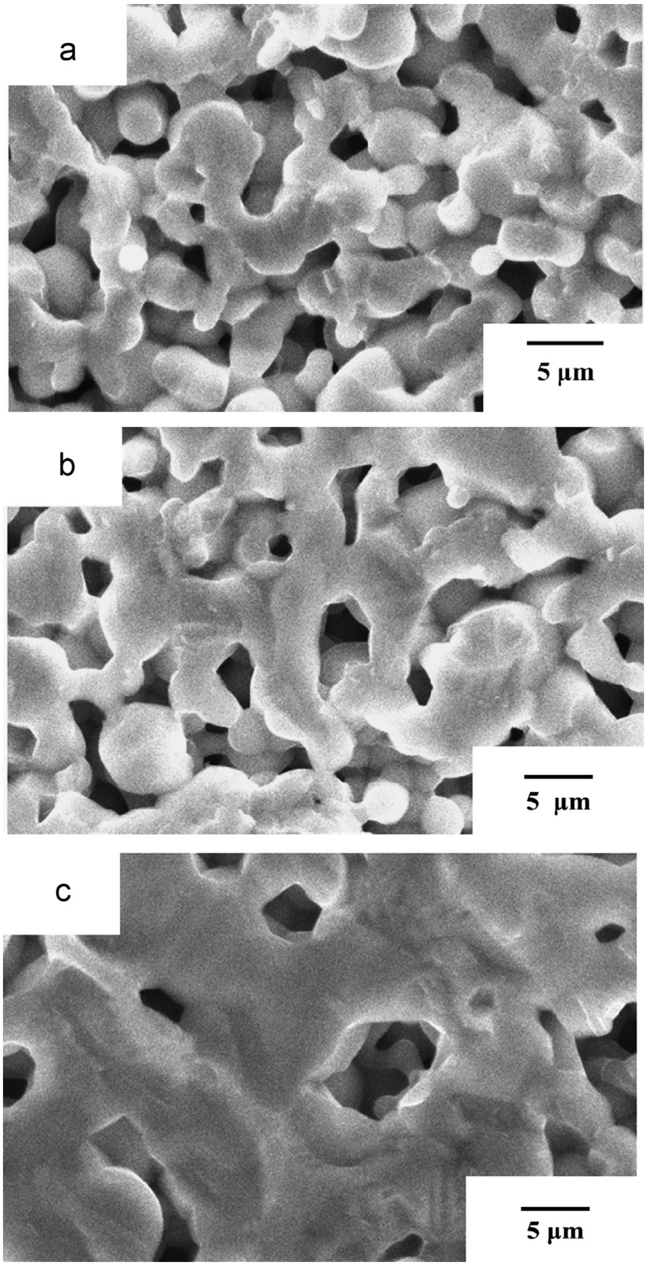

Fig. 4. Cross-sectional SEM images of LLZ pellets calcined at (a) 1000 °C for 6 h, (b) 1000 °C for 9 h, and (c) 1100 °C for 6 h.

A complex impedance plot of the LLZ pellet calcined at 1100 °C for 6 h using Au as Li-ion blocking electrodes is shown in Fig. 5. The profile clearly shows a semicircle and a tail. The tail measured in the low-frequency region originated from the ion-blocking electrodes, whereas the semicircle measured in the high-frequency range was due to the ionic conduction in the grain bulk and grain boundaries. A similar behavior has been observed in other garnet-type Li-ion conductors [18,19]. The Li-ion conductivities of the grain bulk, σ_{bulk}, and of the total, σ_{total} (i.e., the conductivities of both the grain bulk and the grain boundary), estimated from the intercepts of the semicircle at the high- and low-frequency sides were 1.5×10^{-4} and 3.5×10^{-6} S cm^{-1}, respectively. The Arrhenius plot of the grain bulk and total conductivities of the LLZ pellet in the temperature range of 30–100 °C is shown in Fig. 6. Both plots were fit well by a straight line, indicating that the ion-conduction mechanism of the prepared LLZ was identical in this temperature range. This observation is consistent with previous reports [3,6,14]. The activation

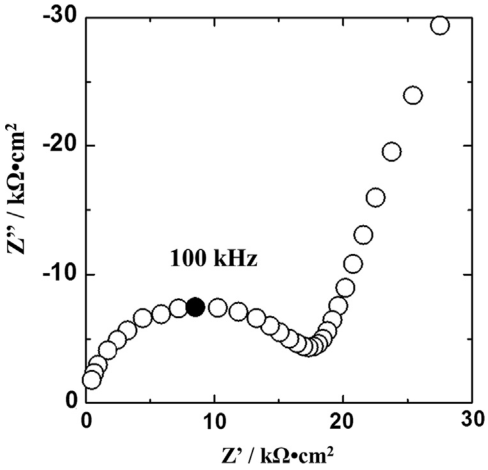

Fig. 5. Complex impedance plot of LLZ pellet calcined at 1100 °C for 6 h; the measurement was conducted at 30 °C.

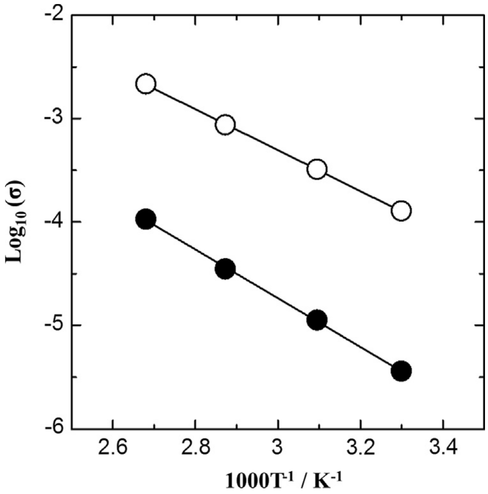

Fig. 6. Arrhenius plot of the grain-bulk (open circles) and the total (closed circles) conductivities of LLZ pellet calcined at 1100 °C for 6 h.

energies estimated from the slopes of the lines were 0.39 and 0.47 eV for the grain bulk and the total conductivities, respectively.

4. Discussion

In this paper, LLZ solid electrolyte was prepared via the sol–gel method. The precursor powder contained both LZ and LLZ, as shown in Fig. 2. The XRD pattern of the pellet calcined at 1000 °C contained doublet peaks, which was attributed to tetragonal LLZ, and LZ peaks. In the XRD pattern of the pellet calcined at 1100 °C, the doublet peaks changed into singlet peaks, implying that cubic LLZ was produced. On the basis of these results, the reactions during the heat treatment and calcination can be summarized as follows. The La and Zr species in the gel reacted with each other during the heat treatment at 700 °C and then produced LZ. Any lithium species could not be detected by XRD, implying that the Li species dispersed among the LZ particles. Some Li species reacted with LZ during the heat treatment, resulting in the LLZ formation. During the calcination at 1000 °C, the tetragonal LLZ was formed because the LZ particles reacted with the Li species. The tetragonal LLZ changed into the cubic phase during the 1100 °C calcination. Janani et al. also observed the formation of LZ intermediate during the conversion of gel to LLZ [15]. In a previous report, calcination temperatures of 1230 °C were required to obtain the cubic LLZ [3]. In our experiments, the cubic LLZ was produced at 1100 °C, which implies that a reduction of calcination temperature for preparation of the cubic LLZ is possible using the sol–gel process.

The grain bulk conductivity of the prepared cubic LLZ was 1.5×10^{-4} S cm^{-1}. This value is comparable with previously reported values [3–7]. It is concluded that the cubic LLZ with high Li-ion conductivity was successfully prepared by the sol–gel method and with low calcination temperature. However, the total conductivity of the prepared LLZ pellet is still insufficient for its use in practical applications. The reason for the low total conductivity is thought to be low grain boundary conductivity due to voids in the pellet, as observed in Fig. 4 [20]. To improve the total conductivity, i.e., the grain boundary conductivity, an addition of a sintering promoter is very useful [6]. The LLZ electrolyte would be useful in practical applications if the Li-ion conductivity could be improved through the addition of the sintering promoter, and an investigation of this approach is currently underway in our laboratory. New findings will be reported in due course.

5. Conclusion

A sol–gel method was used to prepare LLZ at lower calcination temperatures than that of the conventional solid-state method. The precursor gel containing Li, La, and Zr was transformed into a white powder, that consisted of LZ and LLZ, by a heat treatment at 700 °C. The white powder was pressed into pellets, and the pellets were calcined at 1000 °C or 1100 °C. The pellet calcined at 1000 °C contained tetragonal LLZ with low Li-ion conductivity, whereas the tetragonal LLZ transformed into the high-Li-ion-conductive cubic phase after the calcination at 1100 °C. The cubic LLZ can be prepared using the sol–gel method with calcination at 1100 °C, which is 130 °C lower than the temperature in the conventional solid-state reaction method. The Li-ion conductivity of the cubic LLZ was 1.5×10^{-4} S cm^{-1}, which was comparable with previously reported values. It is concluded that the cubic LLZ with high Li-ion conductivity can be successfully prepared at low temperatures using the sol–gel method, although the total conductivity (i.e., the grain-boundary conductivity) was still low for its practical use. Improvement of the grain-boundary conductivity is required.

Acknowledgment

This work was supported by JSPS KAKENHI Grant number 24750187 and the Suhara Memorial Foundation. The authors appreciate their support.

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