Preparation of Sintered Li₅La₃Nb₂O₁₂ Garnet-type Li Ion Conductor via Spark Plasma Sintering Synthesis

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ABSTRACT: Spark Plasma Sintering (SPS) synthesis can sinter ceramics powders quickly at a relatively low temperature. In this study, the SPS synthesis is applied for preparation of sintered Li₅La₃Nb₂O₁₂ (LLNb) pellet which is a member of fast Li ion conductor with garnet structure. Well-sintered LLNb pellet is obtained by the SPS synthesis at 1000 °C only for 5 min, although the sintered pellet cannot be obtained in conventional sintering process using electric furnace at same temperature for 6 h. The Li ion conductivity of the sintered pellet is 6.0 × 10⁻⁶ S cm⁻¹, which is same order as that of the conventional method. It is concluded that the SPS synthesis can be applied to prepare the garnet-type Li ion conductor.

Keywords: Solid electrolyte; Garnet-type Li ion conductor; Spark plasma sintering; Lithium battery

1. Introduction

A series of garnet-like structural compounds have been widely investigated as a novel family of fast Li ion conductors since Wepner and co-workers reported Li ion conductive nature of Li₅La₃Nb₂O₁₂ (LLNb) and Li₅La₃Ta₂O₁₂ (LLTa) [1]. Because the compounds are one of the promising candidates as solid electrolytes for all-solid-state lithium batteries, which can overcome safety issues present lithium batteries are facing on.

So far, a preparation of the garnet-like structural Li ion conductor has been performed by solid state reaction [2-4] and sol-gel method [5, 6]. In order to obtain pure phases and well-sintered pellets, they require a long time and high temperature sintering process. This time and energy consuming process would appear as a shortcoming when the Li ion conductors applied to mass production.

The Spark Plasma Sintering (SPS) synthesis is an expeditious and effective heat treating method, which can sinter ceramics powders at a relatively low temperature within a much shorter time compared with conventional sintering methods [7]. During the SPS processing, a DC current applies to and pressure is uploaded on a sample. The current runs through the graphite die that plays a role as an external heat sources. This heating method enables the samples to be heated very effectively, leading to a very short time and low temperature sintering process.

The SPS synthesis has been applied to preparation of Li ion conductive ceramics [8]. Xu et al. [9] reported a preparation of Li₅Al₄O₁₀Ti₄O₁₃ (LATP) with NASICON (Na ion super conductor) structure using the SPS synthesis. They succeeded in obtaining sintered LATP for 8 min of the sintering time. Mei et al. [10] used the SPS synthesis to prepare sintered Li₀.₃₅La₀.₅₅TiO₃ (LLT). They obtained the dense LLT only for 3 min of the sintering time. Therefore, the SPS synthesis is thought to be a very useful technique to prepare the Li ion conductive ceramics. However, an application of the SPS synthesis for the garnet-type Li ion conductors has not been reported thus far.

In this paper, the SPS synthesis was used to prepare the LLNb, which is a member of the garnet-like Li ion conductors. By using the SPS synthesis, well-sintered LLNb pellet could be obtained in much shorter sintering time compared with conventional sintering process using the electric furnace. The Li ion conductivity of the pellet prepared by the SPS synthesis was 6.0 × 10⁻⁶ S cm⁻¹, which was same order as that of conventional method.

2. Experimental

A precursor powder to obtain sintered LLNb was prepared by a conventional solid state reaction [1]. LiNO₃, La(OH)₃, and Nb₂O₅ in a molar ratio of 5.5:3:1 were ball-milled (Pulver Risette 7, Fritsch) with zirconia ball for 1 h in 2-propanol. 10 % excess LiNO₃ was added to compensate for a loss of lithium during heat treatment. All reagents were purchased from Wako Chemical Co. Ltd, Japan and used without further purification. Obtained mixture was heated at 700 °C for 12 h to prepare the precursor powder for the sintered LLNb. The precursor powder was milled by a planetary ball mill at 650 rpm for 1 h.

The precursor powders were subsequently sintered in the form of pellet using SPS furnace (CSP-1-05203, SS Alloy Co. Ltd.). The powders were placed into a graphite die (15 mm in diameter) and the SPS system was evacuated below 5 Pa. The electric current of 500 A was applied through the graphite die. A pressure of 200 MPa and a heating rate of 100 °C/min were set for the sintering process. The sintering
was performed at 1000 °C for 5 min.

For comparison, conventional sintering process using an electric furnace was also carried out. The precursor powder was pressed into a pellet form with 20 mm diameter. The pellet was subjected to calcine at 1000 °C for 6h.

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

The Li ion conductivity of LLNb prepared by the SPS synthesis was measured by the AC impedance method. Prior to measurement, the sintered pellet was polished to obtain flat surfaces and to control its thickness. Then, Au was sputtered onto both sides of the pellet to ensure electrical contact. The AC impedance data was collected at 10 mV voltage signal in a frequency range of 50 ~ 1 MHz using a chemical impedance meter (HIOKI Chemical Impedance Meter 3532-80). The measurement was performed at 30 ~ 125 °C to clarify the temperature dependency of the Li ion conductivity. The analysis of obtained impedance spectra was performed using HIOKI IM9000 software.

3. Results and discussion

Fig. 1 shows the XRD pattern of the precursor powder after heat-treatment at 700 °C for 12 h. All diffraction peaks were well-matched with the standard pattern of LLNb (PDF 45-0109) having the garnet structure. Weppner et al. [1] also reported garnet LLNb powder could be obtained by similar starting materials and under similar heating condition.

SEM images of the precursor powders before and after the ball-milling are displayed in Fig. 2a and b, respectively. Notably, both powders had completely different morphologies. Before ball-milling (Fig. 2a), small particles with approximately 1 µm in diameter were observed and these particles were fused each other, resulting in a formation of large second particles. After the ball-milling, the particles were crushed well and the large particles were no longer observed. The particle size was approximately 1 µm.

The milled precursor powder was pelletized and heat-treated by the SPS synthesis and conventional sintering process using electric furnace. Cross-sectional SEM images of the pellet sintered by the SPS and conventional method are revealed in Fig. 3. In the conventional sintering, the precursor particles sintered each other, however, lots of voids were still observed in the cross-section, indicating that the pellet was not sintered well (Fig. 3a and b). Contrary, in the SPS synthesis (Fig. 3c and d), well-sintered pellet was obtained. The densities of the pellets prepared by the SPS and conventional method were 4.4 and 2.7 g cm⁻³, respectively. The precursor particles were fused well and no void could be observed in the cross-section although some grains seem remaining. It is thought that the SPS synthesis can provide well-sintered LLNb pellet at much shorter sintering period (5 min) compared with that of the conventional method (6 h).

![Figure 1 XRD pattern of the precursor powder after heat-treatment at 700 °C for 12 h](image-url)
Figure 2 SEM images of the precursor powder (a) before and (b) after ball-milling

Figure 3 Cross-sectional SEM images of sintered LLNb pellets prepared by the conventional sintering process ((a), (b) and the SPS synthesis ((c), (d))

The XRD pattern of sintered pellet by the SPS synthesis is depicted in Fig. 4. The diffraction peaks could be attributed to mainly LLNb and small peaks of La2O3 were observed. Unknown phase was also confirmed in the pellet sintered by the SPS. A possible reason of these impurities formation is thought to occur undesired reactions at high temperature, not SPS because these phases were confirmed in the XRD pattern of the pellet prepared by the conventional method. By ICP measurement, a metal composition in the pellet prepared by SPS was estimated to Li:La:Nb=4.1:2.9:2.

Fig. 5 shows a complex impedance plot of the LLNb pellet sintered by the SPS synthesis using Au blocking electrodes. The pellet prepared by the conventional sintering process could not be subjected to the AC impedance measurement because it was too brittle. The complex impedance profile of the SPS pellet 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 ceramics conductor [11-15]. The Li ion conductivities were estimated by using equivalent circuit of \((R_gQ_g)(R_{gb}Q_{gb})(Q_{el})\) (where R is the resistance, Q is the constant phase element, and the subscripts g, gb, and el refer to the grain, grain boundary, and electrode). The total conductivity (the conductivity of both the grain bulk and the grain boundary) estimated from the intercepts of the semicircle at the low-frequency side was \(6.0 \times 10^{-6} \text{ S cm}^{-1}\). This value is a little lower than that in previous report \((9.0 \times 10^{-6} \text{ S cm}^{-1})\). The reason for the lower value of conductivity is thought to be due to impurity phase as shown in the XRD pattern of LLNb pellet sintered by the SPS synthesis (Fig. 4), in which La2O3 and unknown phase were confirmed. These impurities would obstruct Li ion conduction in the pellet.

The Arhenius plot of total conductivity of the LLNb pellet in the temperature range of 30 ~ 125 °C is shown in Fig. 6. The plot was fit well by a straight line and the fitting
accuracy ($R^2$ factor) was greater than 0.99, indicating that the ion-conductive mechanism of the prepared LLNb was identical in this temperature range. The activation energy estimated from the slopes of the fitting line was 0.48 eV. In our knowledge, there is only one paper which reported the activation energy of the LLNb [1]. The reported value was 0.43 eV, almost same as this study.

The SPS synthesis was applied to shorten sintering time of the LLNb Li ion conductor with garnet structure and its structure was compared with that prepared by the conventional method. As shown in Fig. 3, the SPS synthesis could form well-sintered LLNb pellet. On the other hand, in the sintering conventional process using the electric furnace, lots of voids could be observed in the pellet cross-section, although same sintering temperature was applied for in both cases. As for the sintering time, the SPS synthesis could provide the well-sintered pellet much shorter period (5 min) than the conventional process (6 h). The DC current running through the graphite die worked as an external heat source in the SPS synthesis. It is thought that the external heat fuses the precursor particles with garnet structure very well and promotes the sintering very efficiently, resulting in extraordinary reduction of sintering time. The Li ion conductivity of the LLNb pellet was a little lower than that in previous report. This is due to formation of $\text{La}_2\text{O}_3$ and unknown phase as impurities. The estimated activation energy was comparable to the reported value. It is thought the Li ion conduction mechanism in the LLNb prepared by the SPS synthesis was same as that prepared by the conventional method and the SPS-prepared LLNb can work as the Li ion conductive ceramics.

It is concluded that the SPS synthesis can be applied to prepare sintered garnet-type Li ion conductor as a very useful sintering technique. Although the optimization of procedure to suppress impurity formation is needed, the extraordinary reduction of sintering time is very attractive for mass production. The optimization is going on now in our group. New findings will be reported in due course.

4. Conclusion

The SPS synthesis was applied for preparation of LLNb garnet-type Li ion conductor. Well-sintered LLNb pellet was obtained by the SPS synthesis at 1000 °C for 5 min, although the sintered pellet could not be formed in conventional sintering process using electric furnace at same temperature for 6 h. The XRD result indicated that the sintered LLNb pellet by the SPS synthesis included impurity phase like $\text{La}_2\text{O}_3$. The Li ion conductivity of the sintered pellet was $6.0 \times 10^{-6}$ S cm$^{-1}$, it is a little lower than that of conventional method. This was thought to be due to impurity phase in the
SPS pellet. The activation energy was 0.48 eV and this value was comparable to previous report. It is concluded that the SPS synthesis can be applied to prepare the garnet-type Li ion conductor although the optimization of the process to suppress impurity formation is needed.

References

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