Influence of precursor calcination temperature on sintering and conductivity of Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ ceramics

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ABSTRACT

Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ (LATP) is the most promising electrolytes. LATP precursor was prepared by the co-precipitation method and calcined at 500–900°C to examine the influence of the calcination temperature on LATP pellets sintered at 1000°C. The calcination temperature exerted a large effect on the morphology of sintered LATP pellets, even though the sintering temperature was same for all the samples. Formation of voids was observed in the precursor powders calcined at 500, 600, 700, and 900°C, while no void was formed in the powder calcined at 800°C. The precursor powders calcined at low temperatures (500–700°C) were crystallized during sintering. This caused shrinkage of the particles, leading to the void formation. The precursor powder calcined at 900°C was more stable at the sintering temperature. Resulting in formation of porous pellets. These voids increase the grain-boundary resistance. As a result, the LATP pellets prepared from the precursor powder calcined at 800°C showed the highest conductivity ($\sigma$$_{\text{total}}$ = 5.1×10$^{-4}$ S cm$^{-1}$) due to the relatively high crystallinity and stability of the precursor powder. It was concluded the calcination temperature applied to the precursor powders influences the properties of final sintered LATP pellets. The calcination temperature must thus be chosen carefully.

1. Introduction

Electrolytes for lithium-ion batteries generally contain flammable organic solvents that sometimes can cause serious safety problems, such as electrolyte leakage and fire hazard [1]. All-solid-state lithium batteries consisting of solid electrodes and nonflammable solid electrolytes are expected to overcome these safety problems [2]. Many kinds of Li-ion conductive ceramics, i.e., solid electrolytes for all-solid-state batteries, have been reported thus far [3–5]. NASICON (Na-ion superconductor) structure phosphates Li$_{1+x}$M$^{n+}$M$^{n+}$′$_{2-x}$(PO$_4$)$_3$ (M$^+$ = Al, Y, Fe, etc., M$^{n+}$′ = Ti, Ge, Hf, etc.) are considered as possible electrolyte candidates for all-solid-state lithium batteries [6,7]. Among these, expectations are especially high for the application of Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ (LATP) in all-solid-state batteries because of its high lithium ion conductivity (−10$^{-3}$ S cm$^{-1}$) [8]. Hoshina et al. fabricated an all-solid-state thin-film battery composed of an LATP solid electrolyte and a LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode. Their thin-film battery performed successfully [9]. Kotobuki et al. also fabricated an all-solid-state battery with a three-dimensional ordered structure using an LATP solid electrolyte and an Li$_4$Mn$_3$O$_{12}$ electrode and observed its charge and discharge behaviors [10]. One of the problems hindering practical application of LATP is the difficulty of conducting mass production of the batteries. Most studies on LATP have adopted solid-state reactions and melting-quenching methods for its preparation [11–18]. These methods cannot be easily applied to mass production due to their high energy consumption and contamination of the final products by impurities of the final products. The coprecipitation method makes the materials react uniformly at the molecular level and offers the advantages of a lower polycrystalline-synthesized temperature and shorter sintering time [19–21]. Lowering the synthesized temperature and shortening the sintering time allow us to reduce the processing cost for LATP production. It is expected that mass production of LATP solid electrolytes can be enabled by application of the coprecipitation method for LATP preparation. In our previous study, we succeeded in preparing an LATP solid electrolyte by the coprecipitation method [22]. The bulk and total conductivities of the LATP sintered at 1050°C were 1.4×10$^{-3}$ and 1.5×10$^{-4}$ S cm$^{-1}$, respectively, which were comparable to reported values. The LATP was prepared through two-step heating, i.e., the precursor coprecipitant was first calcined to eliminate organic and volatile compounds and then sintered at high temperature to obtain sintered pellets. The calculation condition of the precursor is thought to influence the properties of the LATP pellets. Schell et al. studied the effect of the calcination temperature of sol–gel-prepared precursor powder on the Li-ion conductivity of LATP pellets [23]. They reported that...
calcinated powder required high crystallinity to obtain dense, homogeneous pellets with high Li-ion conductivity. Liu et al. prepared LATP, moreover, using CO(NH$_3$)$_2$ as a molten flux [24]. The precursor powder was calcined at 600–900°C and the LATP pellets prepared using the powder calcined at 700°C revealed the highest Li conductivity. However, no such study using precursor powder prepared by coprecipitation has yet been reported.

In this study, the effect of the calcination temperature applied to precursor powder prepared by coprecipitation on the properties of LATP sintered pellets was examined.

2. Experimental

An LATP solid electrolyte was prepared by the coprecipitation method [22]. Li$_3$C$_6$O$_4$ and Al(NO$_3$)$_3$·9H$_2$O were dissolved in purified water. The resultant solution was dropped into an NH$_4$HCO$_3$ solution under vigorous stirring to obtain a coprecipitant. To compensate for evaporation of Li during calcination and sintering, a 10% excessive amount of Li was added to the precursors. Ti(C$_2$H$_7$)O$_4$ and NH$_4$H$_2$PO$_4$ solutions were then dropped into the coprecipitant. The mixture was dried at 100°C to remove the solvent and then calcined at 500–900°C for 30 min (denoted as P500, P600, P700, P800, and P900, respectively; see Table 1). The obtained precursor powder was ground by ball-milling at 650 rpm for 1 h (Pulver Risette 7, Fritsch) with a 0.5 mm Zirconia ball to initiate sintered pellet preparation. The milled powder was pressed at 200 MPa to form pellets with 20 mm diameters and then sintered at 1000°C for 6 h in air (Figure 1). All reagents were purchased from Wako Chemical Co., Ltd, Tokyo, Japan and used without further purification. The as-prepared and milled powders and the sintered pellets were measured by X-ray diffraction (XRD, Rigaku Ultima-IV) using Cu Kα radiation to identify their crystal phases. Scanning electron microscopy (SEM, JEOL, JSM-6300LA) was used to observe the morphologies of the powders and cross-sections of the pellets. Before measurement, the specimens were sputtered with gold to eliminate the charge effect.

The Li-ion conductivity was measured by the AC impedance method. Both surfaces of the sintered pellets (with a diameter of 20 mm) were polished to obtain flat surfaces and to control their thickness (~1 mm) before measuring their Li-ion conductivity. Prior to measurement, Au sputtering was conducted on both sides of the pellets to prepare Li blocking electrodes and to ensure electrical contact between the pellets and Cu current collectors. AC impedance data were collected using a ±10-mV voltage signal in the frequency range of 100–1 MHz with a chemical impedance meter (HIOKI Chemical Impedance Meter 3352-80). The measurement was performed at 30°C.

3. Results and discussion

3.1. Crystal structure and morphology of the precursor powders

Figure 2 shows SEM images of the precursor powders before ball-milling. It can be observed that the particle sizes of the precursor powders increased with the calcination temperature as grain growth was promoted. Most notably, large particles formed by incorporating small particles (a few µm in diameter) were clearly observed in Figure 2(d,e). The XRD patterns of the precursor powders before ball-milling are depicted in Figure 3. The precursor powders calcined at 500 and 600°C showed a halo pattern at around 2θ = 15°–35°. This was attributed to the amorphous nature of the Li–Al–Ti–PO$_4$ phase. Diffraction peaks assigned to Li$_3$PO$_4$ (PDF 87-39) were also observed at P500 and Li$_4$P$_2$O$_7$ peaks (PDF 87-409) as well as Li$_3$PO$_4$ were confirmed at P600. Small LATP peaks appeared in the precursor powder calcined at 600°C, and the peak intensities of LATP increased with the calcination temperature. The amorphous broad halo pattern disappeared at P800, indicating that the LATP was completely crystallized. SEM images of the precursor powders after ball-milling are displayed in Figure 4. In all samples, the particles were crushed to 100–200 nm in diameter by ball-milling. No difference in morphology was observed among the samples. Figure 5 shows XRD patterns of the precursor powders after ball-milling. The halo pattern and the
diffraction peaks of Li$_3$PO$_4$ were observed at P500, but the peaks were broader compared with those before ball-milling due to amorphization caused by the ball-milling. LATP and Li$_4$P$_2$O$_7$ peaks also appeared in addition to the Li$_3$PO$_4$ peaks at P600. The LATP peaks became sharper at P700 and P800 with increases in the calcination temperature, while small Li$_3$PO$_4$ peaks were still observed. Only LATP peaks could be confirmed at P900.

### 3.2. Morphology, crystal structure, and conductivities of sintered pellets

The precursor powders calcined at various temperatures were supplied for pellet formation. Figure 6 reveals the XRD patterns of LATP pellets sintered at 1000°C for 6 h using the precursor powders calcined at various temperatures. Most of the diffraction peaks could be attributed to LATP. All LATP peaks were sharp, indicating that high-crystallinity LATP had been obtained. Small diffraction peaks of TiO$_2$ were confirmed at P500, P600, P700, and P900, while no impurity phase was observed at P800.

SEM images of the LATP specimens are displayed in Figure 7. Crystallized particles with sharp edges were observed in the LATP pellets from P500 (Figure 7(a)). Large numbers of voids were also observed between the

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**Figure 2.** SEM images of the precursor powders calcined at various temperatures before ball-milling: (a) P500, (b) P600, (c) P700, (d) P800, and (e) P900.

**Figure 3.** XRD patterns of the precursor powders calcined at various temperatures before ball-milling.

**Figure 4.** SEM images of the precursor powders calcined at various temperatures after ball-milling: (a) P500, (b) P600, (c) P700, (d) P800, and (e) P900.
particles. These voids decreased in number and size with increases in the calcination temperature applied to the precursor powder; the voids became less and smaller until the voids and grain boundaries were scarcely visible at P800. The voids between particles appeared again, however, at P900.

The densities of the LATP pellets were calculated by their weights and dimensions (Table 2). The relative densities increased with the calcination temperature until reaching a maximum at P800. After that, the density decreased.

The Li-ion conductivity of the LATP pellets was examined by the AC impedance method at 30°C. Complex impedance plots of the results are depicted in Figure 8. All the profiles clearly show a semicircle with a tail in the low-frequency range. The tail originated from the ion-blocking electrodes, while the semicircle was due to the ionic conductivity of the specimens. Similar behavior has been observed in other solid electrolytes with ion conductivity [2,25,26]. The bulk and total (bulk + grain boundary) resistances of the specimens were estimated from an intercept of the semicircle on the high- and low-frequency sides, respectively. The bulk ($\sigma_b$), grain boundary ($\sigma_{gb}$), and total ($\sigma_{total}$) conductivities were then calculated from the dimensions of the specimens and the resistance of each. The calculated conductivities are summarized in Table 3. Bulk conductivity showed no large difference among the samples. By contrast, the grain-boundary conductivity increased with the calcination temperature and reached the maximum value at P800. The grain-boundary conductivity then dropped with further increases of the calcination temperature. The highest bulk, grain boundary, and total conductivities were obtained at P800 where the values were $3.0 \times 10^{-3}$, $5.9 \times 10^{-4}$, and $5.1 \times 10^{-4}$ S cm$^{-1}$, respectively.

The influence of the calcination temperature applied to the precursor powders on the properties of LATP pellets was studied. The calcination temperature had a
Table 2. Relative density of samples.

| Sample | Relative density (%) |
|--------|----------------------|
| P500   | 84                   |
| P600   | 91                   |
| P700   | 93                   |
| P800   | 97                   |
| P900   | 89                   |

Figure 8. Complex impedance plots of LATP pellets sintered at 1000°C for 6 h using various precursor powders: □: P500, ○: P600, ●: P700, ☼: P800, and ●: P900.

Table 3. Bulk, grain-boundary, and total conductivities of various samples measured at 30°C.

| Sample | \( \sigma_b \) (S cm\(^{-1} \)) | \( \sigma_{gb} \) (S cm\(^{-1} \)) | \( \sigma_{total} \) (S cm\(^{-1} \)) |
|--------|-------------------------------|-------------------------------|-------------------------------|
| P500   | \( 1.3 \times 10^{-3} \)       | \( 5.8 \times 10^{-5} \)       | \( 5.3 \times 10^{-5} \)       |
| P600   | \( 2.0 \times 10^{-3} \)       | \( 1.6 \times 10^{-4} \)       | \( 1.4 \times 10^{-4} \)       |
| P700   | \( 2.2 \times 10^{-3} \)       | \( 2.5 \times 10^{-4} \)       | \( 2.1 \times 10^{-4} \)       |
| P800   | \( 3.0 \times 10^{-3} \)       | \( 5.9 \times 10^{-4} \)       | \( 5.1 \times 10^{-4} \)       |
| P900   | \( 2.6 \times 10^{-3} \)       | \( 1.2 \times 10^{-4} \)       | \( 1.1 \times 10^{-4} \)       |

4. Summary

The influence of the calcination temperature applied to precursor powders on the properties of LATP sintered pellets was studied. The calcination temperature significantly affected the morphology, impurity formation, and grain-boundary conductivity of the sintered pellets, but their bulk conductivity was not significantly influenced. A low calcination temperature of 500–700°C produced low-crystallinity particles. These shrunk due to crystallization during sintering, resulting in the formation of voids in the sintered pellets. By contrast, the precursor powder calcined at 900°C was stable at the sintering temperature. The sintering was therefore insufficient, and voids still remained in the sintered pellets. The precursor powder calcined at 800°C possessed relatively high crystallinity and stability, resulting in well-sintered LATP pellets with less void formation. No impurities were observed, moreover, in the LATP pellets prepared from the precursor powder calcined at 800°C. Impurities are formed at the grain boundaries and hinder Li-ion conduction. This is clearly another reason for the large variation in grain-boundary conductivity. It was found that the calcination temperature used for the precursor powder is also a key to determining the properties of sintered LATP pellets. The calcination temperature should thus be carefully considered.

Disclosure statement

No potential conflict of interest was reported by the authors.

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