Effect of Li salts on the properties of Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ solid electrolytes prepared by the co-precipitation method

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ABSTRACT
In this study, Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ (LATP) solid electrolyte is prepared through co-precipitation using Li$_3$PO$_4$ and Li$_2$C$_2$O$_4$ salts. The co-precipitates are heated at 800°C to obtain precursor powders. The precursor powders are then ball-milled to reduce the particle size to prepare dense LATP pellets. Li salts significantly influence the morphology and crystallinity of the precursor powders. The precursor powder prepared from Li$_3$PO$_4$ possesses a smaller particle size and lower crystallinity of LATP compared with Li$_2$C$_2$O$_4$. The soft, low-crystallinity powder from Li$_3$PO$_4$ is easily crushed by the ball-milling. The average particle size is reduced to 30 nm, while the average size of particles from Li$_2$C$_2$O$_4$ is 120 nm after the ball-milling. The small particle size promotes sintering of LATP pellets. As a result, LATP pellets prepared from Li$_3$PO$_4$ show higher Li ion conductivity than those from Li$_2$C$_2$O$_4$ due to their high sinterability and large grain size (low grain-boundary resistance). The Li ion conductivity is 2.0 × 10$^{-4}$ S cm$^{-1}$ after sintering at 1050°C for 6 h. It is concluded that the Li source used to form the co-precipitate greatly influences the properties of sintered LATP pellet. The Li source is one key to obtain LATP with high Li ion conductivity.

1. Introduction
In today’s advanced information society, storage devices such as batteries are key components [1]. Among the various types of batteries, rechargeable Li ion batteries have been used as the energy source for a variety of electronic devices, especially small devices such as laptop computers, mobile phones, and digital cameras due to their high energy density. Recently, many groups have tried the application of the Li ion batteries as an energy source for electric vehicles. However, flammable organic electrolytes have sometimes caused serious safety issues, including fire hazards and leakage. In the development of large-scale Li ion batteries for electric vehicles, the safety issues are of much greater concern.

The all-solid-state battery is composed of non-flammable solid electrolyte that solves the safety issues. Na super ionic conductor (NASICON)-type oxide-based solid electrolytes [2,3] as well as pervoskite-type [4,5] and garnet-type [6,7] solid electrolytes are considered to be promising solid electrolytes due to their reasonably high Li ion conductivity. Especially, LATP (Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$) with the NASICON structure which can be formed by partial substitution of Al$^{3+}$ for Ti$^{4+}$ in LiTi$_4$(PO$_4$)$_3$ exhibits high Li ion conductivity in the order of $\sim$10$^{-3}$ S cm$^{-1}$ at room temperature [8,9].

With the co-precipitation method, the materials react uniformly at the molecular level. It is also the advantages of lower polycrystalline-synthesized temperature and shorter sintering time. Lowering the synthesized temperature and shortening the sintering time help to reduce processing cost for LATP production. We have researched preparation of LATP solid electrolyte through use of a co-precipitate and have found that the sintering temperature could be reduced by 150°C using the co-precipitation method and that PO$_4$ sources greatly influenced properties of LATP [10–12]. Therefore, it is thought that the salts used to form co-precipitation affect the properties of the LATP solid electrolyte.

In this paper, we report the preparation of the LATP solid electrolyte through co-precipitates using Li$_3$PO$_4$ and Li$_2$C$_2$O$_4$ as lithium source. Li$_3$PO$_4$ provided precursor powder with smaller grain size than that of Li$_2$C$_2$O$_4$ and well-sintered pellets. Consequently, the LATP solid electrolyte prepared from Li$_3$PO$_4$ showed higher Li ion conductivity.

2. Experimental
LATP solid electrolyte was prepared through the use of co-precipitates. First, Al(NO$_3$)$_3$·9H$_2$O was dissolved in purified water. The pH value of water after dissolution was 3.1. Li$_3$PO$_4$ was then added into the water. To compensate for the evaporation of Li during heat treatment and calcination, 10% excessive amount of Li was added. After complete dissolution, the solution was heated and NH$_4$HCO$_3$ solution was added dropwise under vigorous stirring. It was observed that...
white precipitation was formed. Then, Ti(C$_2$H$_7$O)$_4$ and NH$_4$H$_2$PO$_4$ ethanol solution were dropped into the solution. The mixture was dried at 100°C to remove the solvent. The dried mixture was heated at 800°C for 30 min. The obtained precursor powder was ground by ball-milling at 650 rpm for 1 h (Pulverisette 7, Fritsch) with 0.5 mm zirconia balls to provide sintered pellet preparation. The milled powder was then pressed into the form of pellets with 20 mm diameter and then sintered at 1000 ~ 1100°C for 6 h in air. All reagents were purchased from Wako Chemical Co. Ltd, Tokyo, Japan and used without further purification. For the purpose of comparison, the same procedure was performed using Li$_2$C$_2$O$_4$.

The as-prepared and ball-milled powders, and the sintered pellets were subjected to X-ray diffraction (XRD, Rigaku Ultima-IV) measurement using Cu $\text{K}_\alpha$ radiation to identify their crystal phases. Scanning electron microscopy (SEM, JEOL, JSM-6300LA) was used to observe the morphologies of the powders and the pellet cross-sections.

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

3. Results and discussion

SEM images of the precursor powders prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$ after calcination at 800°C for 30 min are revealed in Figure 1. The two powders showed different morphologies. The powder prepared from Li$_2$C$_2$O$_4$ was irregular in shape with a particle diameter of approximately 20–100 µm. On the contrary, secondary particles with a diameter of $\sim$10 µm were observed in the powder prepared from Li$_3$PO$_4$. Figure 2 depicts XRD patterns of the precursor powders prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$. In both cases, most diffraction peaks could be assigned to LiTi$_2$(PO$_4$)$_3$ with NASICON structure (PDF-35–0754). The powder prepared from Li$_3$PO$_4$ showed low-intensity diffraction peaks compared with powder from Li$_2$C$_2$O$_4$. This indicated that the precursor powder from Li$_3$PO$_4$ possessed low crystallinity. An impurity phase (Li$_{0.5}$TiO$_2$, PDF 38–269) was also detected.

SEM images of the powders after the ball-milling are displayed in Figure 3. Both powders were thoroughly crushed by ball-milling and reduced in particle size. The particle morphologies were totally different from those before the milling (Figure 1). The precursor power from Li$_3$PO$_4$ was more fully crushed to a smaller size than that from Li$_2$C$_2$O$_4$. The average particle sizes of the powders from Li$_3$PO$_4$ and Li$_2$C$_2$O$_4$ were approximately 30 and 120 nm, respectively.

Figure 4 depicts XRD patterns of the precursor powders prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$ after ball-milling. In both samples, the diffraction peaks became broader than those before ball-milling. This was consistent with the SEM observation, reduction of particle sizes and amorphization by ball-milling. It is noted that impurities were formed by the ball-milling in the precursor powder from Li$_2$C$_2$O$_4$. After ball-milling, the Li$_3$PO$_4$ (PDF 15–760) formation was clearly confirmed. On the contrary, no new impurity formation by the ball-milling was observed in the powder from Li$_3$PO$_4$. Li$_{0.5}$TiO$_2$ was presented in both powders before and after the ball-milling. Compared with the powder from Li$_2$C$_2$O$_4$, the diffraction peaks of the precursor powder from Li$_3$PO$_4$ were broader, indicating that the powder contained more amorphous components. This was also revealed by SEM observation, which showed the powder from Li$_3$PO$_4$ to be smaller than that from Li$_2$C$_2$O$_4$.

The milled powder was used to prepare sintered pellets. The powder was pressed using a stainless die with 20 mm diameter and sintered at 1000 ~ 1100°C for 6 h. XRD patterns of the sintered pellets are shown in Figure 5. In the sintered pellets formed from precursor powder obtained from Li$_2$C$_2$O$_4$ (Pellet-Li$_2$C$_2$O$_4$), although most diffraction peaks matched the LTP standard peaks (PDF 35–0754), LiTiOPO$_4$ (PDF 82–1998) formation was also confirmed after sintering.

Figure 1. SEM images of precursor powders prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$ after heating at 800°C for 30 min.
at 1000°C. The LiTiOPO$_4$ disappeared after sintering at 1050°C and 1100°C. The intensity of LATP peaks strengthened with increases in the sintering temperature due to the improvement of crystallinity. On the other hand, the sintered pellets prepared from the precursor powder from Li$_3$PO$_4$ (Pellet-Li$_3$PO$_4$) revealed a different behavior. Impurity formation was not observed after sintering at 1000°C and 1050°C. Impurity formation was confirmed only after sintering at 1100°C, and the impurity was AlPO$_4$ (PDF 11–500), not LiTiOPO$_4$.

Cross-sectional SEM images of the LATP pellets prepared using different Li salts sintered at various temperatures are presented in Figure 6 and average grain sizes are tabulated in Table 1. In the Pellet-Li$_2$C$_2$O$_4$, round-shaped crystals were observed in the cross-section after sintering at 1000°C, suggesting that the growth of crystals was insufficient. Many voids existed at the grain boundaries. With increases in the sintering temperature, the edges of crystal grains became sharper and the size of the grains increased, indicating that the crystallinity of LATP was enhanced. The grains were in good contact with each other after sintering at 1050°C. On the contrary, with sintering at 1100°C, small voids were observed at the grain boundary because of rapid crystallization at a high temperature. On the contrary, in the Pellet-Li$_3$PO$_4$, small grains (about 1 μm) with sharp edges were obtained even after sintering at 1000°C. Larger crystal grains were observed at high sintering temperatures. After sintering at 1050°C, the grain size was increased and the average grain size of the Pellet-Li$_3$PO$_4$ was 38.1 μm. However, the formation of pores was observed after sintering at 1100°C as in the case of Pellet-Li$_2$C$_2$O$_4$. The relative densities of the sintered pellets are tabulated in Table 2. The relative densities of Pellet-Li$_3$PO$_4$ were always higher than those of Pellet-Li$_2$C$_2$O$_4$ at the same sintering temperature.

**Figure 2.** XRD patterns of precursor powders prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$ after heating at 800°C for 30 min.

**Figure 3.** SEM images of precursor powders prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$ after ball-milling.

**Figure 4.** XRD patterns of precursor powders prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$ after ball-milling.
Figure 5. XRD patterns of LATP pellets prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$ sintered at various temperatures.

Figure 6. SEM of LATP pellets prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$ sintered at various temperatures.

Figure 7 depicts complex impedance plots of LATP pellets prepared from Li$_2$C$_2$O$_4$ and Li$_3$PO$_4$ measured at 30°C. In both plots, a semicircle and a tail were observed in the high and low-frequency ranges. This characteristic profile of the impedance

| Temperature (°C) | Li$_2$C$_2$O$_4$ | Li$_3$PO$_4$ |
|------------------|-----------------|--------------|
| 1000             | 9.4             | 1.8          |
| 1050             | 14.8            | 38.1         |
| 1100             | 16.6            | 19.2         |
plot has been observed in ion-conductive ceramics \cite{13,14}. The tail can be attributed to Warburg-type impedance, which originates from the diffusion of Li ions in the blocking electrode. The intercepts of the semicircle at high and low frequencies correspond to the bulk (inner crystal) and total (bulk + grain-boundary) resistances, respectively \cite{15}. Estimated Li ion conductivities are tabulated in Table 3. The highest bulk (\( \sigma_{\text{bulk}} \)) and total (\( \sigma_{\text{total}} \)) conductivities were observed in the LATP pellets after sintering at 1050°C independent of Li salts. When the sintering temperatures were 1000°C and 1100°C, the bulk conductivities were almost the same for the Pellet-Li\(_2\)C\(_2\)O\(_4\) and Pellet-Li\(_3\)PO\(_4\), but the Pellet-Li\(_3\)PO\(_4\) showed higher total conductivity than Pellet-Li\(_2\)C\(_2\)O\(_4\). With sintering at 1050°C, both bulk and total conductivities were higher in the Pellet-Li\(_3\)PO\(_4\).

Based on the temperature dependence of the total Li ion conductivity, the activation energies of the Pellet-Li\(_2\)C\(_2\)O\(_4\) and Pellet-Li\(_3\)PO\(_4\) sintered at 1050°C can be calculated. The Arrhenius plots of both samples could be accurately fitted by straight lines (in both samples, the fitting accuracies (\( R^2 \)) were >0.99) (Figure 8). The activation energies were 0.35 and 0.28 eV in Pellet-Li\(_2\)C\(_2\)O\(_4\) and Pellet-Li\(_3\)PO\(_4\), respectively.

The ionic transference number of Pellet-Li\(_3\)PO\(_4\) sintered at 1050°C was examined using Au/LATP/Au cell by the DC polarization technique \cite{16}. The polarization curve is shown in Figure 9. The ionic transference number could be calculated based on the initial and stabilized currents. The calculated ionic transference number was >0.999, indicating that the Pellet-Li\(_3\)PO\(_4\) was a pure ionic conductor.

### Table 2. Relative densities of LATP pellets (%).

| Temperature (°C) | Li\(_2\)C\(_2\)O\(_4\) | Li\(_3\)PO\(_4\) |
|-----------------|---------------------|------------------|
| 1000            | 82                  | 90               |
| 1050            | 94                  | 98               |
| 1100            | 85                  | 89               |

### Table 3. Li ion conductivities of LATP pellets prepared from Li\(_2\)C\(_2\)O\(_4\) and Li\(_3\)PO\(_4\) sintered at various temperatures.

| Temperature (°C) | \( \sigma_{\text{bulk}} \) (S cm\(^{-1}\)) | \( \sigma_{\text{total}} \) (S cm\(^{-1}\)) | \( \sigma_{\text{bulk}} \) (S cm\(^{-1}\)) | \( \sigma_{\text{total}} \) (S cm\(^{-1}\)) |
|-----------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 1000            | \( 1.2 \times 10^{-3} \)        | \( 6.0 \times 10^{-5} \)        | \( 1.1 \times 10^{-3} \)        | \( 1.2 \times 10^{-4} \)        |
| 1050            | \( 1.4 \times 10^{-3} \)        | \( 1.5 \times 10^{-4} \)        | \( 1.9 \times 10^{-3} \)        | \( 2.0 \times 10^{-4} \)        |
| 1100            | \( 1.3 \times 10^{-3} \)        | \( 9.3 \times 10^{-5} \)        | \( 1.1 \times 10^{-3} \)        | \( 1.0 \times 10^{-4} \)        |

### Figure 7. Complex impedance plots of LATP pellets prepared from Li\(_2\)C\(_2\)O\(_4\) and Li\(_3\)PO\(_4\) sintered at various temperatures.

### Figure 8. Arrhenius plots of LATP pellets prepared from Li\(_2\)C\(_2\)O\(_4\) and Li\(_3\)PO\(_4\) sintered at 1050°C.
4. Discussion

In this study, LATP solid electrolyte was prepared through co-precipitation using Li$_3$PO$_4$ and Li$_2$C$_2$O$_4$ salts. The co-precipitation was prepared using Li$_3$PO$_4$ and Li$_2$C$_2$O$_4$ and then heated at 800°C to prepare the precursor powders.

It was found that Li salts affected the properties of the precursor powders. The particles in the precursor powder from Li$_3$PO$_4$ were smaller in size and lower in crystallinity than those from Li$_2$C$_2$O$_4$. The mechanism for forming small particles with low crystallinity from Li$_3$PO$_4$ is not yet clear. While the co-precipitation was forming, H$_3$PO$_4$ (or NH$_4$PO$_4$) and H$_2$C$_2$O$_4$ (or (NH$_4$)$_2$C$_2$O$_4$) were produced in Li$_3$PO$_4$ and Li$_2$C$_2$O$_4$ solutions, respectively. These species would influence the co-precipitation and crystal growth of LATP in the following heating processes.

After ball-milling, the particle sizes of both precursor powders were reduced, but the powder from Li$_3$PO$_4$ was crushed more fully to a smaller size than that from Li$_2$C$_2$O$_4$. This would be due to the low crystallinity of the powder from Li$_3$PO$_4$ after heating at 800°C. A soft amorphous powder would be easily crushed by ball-milling. Therefore, smaller particles could be obtained in the powder from Li$_3$PO$_4$ after ball-milling.

The ball-milled precursor powders were supplied for pellet preparation and sintered at 1000 ~ 1100°C. It should be noted that impurity formation was affected by the precursor powders. In Pellet-Li$_2$C$_2$O$_4$, the formation of LiTiOPO$_4$ was confirmed after sintering at 1000°C, but the LiTiOPO$_4$ disappeared after sintering at 1050°C and 1100°C. Contrary, with Pellet-Li$_3$PO$_4$, although impurity formation was not confirmed after sintering at 1000°C and 1050°C, AlPO$_4$ was formed when the sintering temperature increased to 1100°C. This AlPO$_4$ impurity was also observed in other groups [17–19].

The highest Li ion conductivity appeared after sintering at 1050°C independent of Li salts. SEM showed small grains with low crystallinity and pore formation after sintering at 1000°C and 1100°C, respectively, in both cases. The small, low-crystallinity grains possess low Li ion conductivity. Davaasuren et. al. reported that crystallinity is a key factor influencing the bulk ionic conductivity [20]. Therefore, it is thought that the low bulk conductivity in the samples sintered at 1000°C was due to low crystallinity of LATP. On the other hand, Li evaporation is inevitable during high-temperature sintering. Li evaporation causes a reduction of the carrier concentration (Li ions) in solid electrolytes, resulting in lowering of the Li ion conductivity [21]. Thus, the lower bulk conductivities of the sample sintered at 1100°C would be caused by the Li evaporation.

The density of the samples also significantly influences the total conductivity [20]. Pores lead to high grain-boundary impedance, decreasing the total conductivity [22,23]. The densest pellets were obtained after sintering at 1050°C in both cases (Table 2). At 1000°C sintering, the sintering process did not proceed sufficiently due to the low sintering temperature. On the other hand, shrinkage of grains occurred with rapid crystallization when sintering was performed at 1100°C, resulting in pore formation and leading to low-density pellets. It is consequently thought that the highest Li ion conductivity appeared after sintering at 1050°C.

Additionally, XRD results (Figure 5) revealed impurity formation after sintering at 1000°C and 1100°C in the Pellet-Li$_2$C$_2$O$_4$ and Pellet-Li$_3$PO$_4$, respectively. This impurity formation is considered another reason for the low Li ion conductivity of the LATP pellets after sintering at 1000°C and 1100°C.

Compared with Pellet-Li$_2$C$_2$O$_4$, Pellet-Li$_3$PO$_4$ possessed higher Li ion conductivity after sintering at 1050°C. Additionally, the activation energy of the total conductivity of Pellet-Li$_3$PO$_4$ was lower than that of Pellet-Li$_2$C$_2$O$_4$. In SEM (Figure 6), Pellet-Li$_3$PO$_4$ showed larger grains. The grain sizes were 14.8
and 38.1 μm in Pellet-Li$_2$C$_2$O$_4$ and Pellet-Li$_3$PO$_4$, respectively (Table 1). The formation of the large grains would be caused by the small particle size of the precursor powder. Small particles possess high surface energy, leading to the rapid growth of grains and improved sinterability during sintering [24]. Therefore, high conductivity and low activation energy of Pellet-Li$_3$PO$_4$ would be caused by the high crystallinity of LATP and its low grain-boundary resistance due to the large size of LATP grains.

Li$_3$PO$_4$ provided soft, low-crystallinity precursor particles, which could be easily crushed and reduced in particle size by ball-milling. Due to the small particles, the sintered pellets possessed large grains with high crystallinity, resulting in high Li ion conductivity. It is concluded that the Li source for co-precipitate formation greatly influences the properties of sintered LATP pellets. The Li source is one of the keys to obtain LATP with high Li ion conductivity.

5. Conclusion

In this study, LATP solid electrolyte was prepared through co-precipitation using Li$_3$PO$_4$ and Li$_2$C$_2$O$_4$ salts. The co-precipitates were heated at 800°C to prepare the precursor powders. The particles in the precursor powder from Li$_3$PO$_4$ were smaller than those from Li$_2$C$_2$O$_4$. XRD results showed moreover that the precursor powder from Li$_3$PO$_4$ had a low crystallinity. The soft, low-crystallinity powder was crushed efficiently by ball-milling and small particles were easily obtained. The small precursor particles promoted sintering in the LATP pellet preparation. As a result, well-sintered LATP pellets with large grains were obtained by sintering the precursor powder from Li$_3$PO$_4$ due to the high surface energy of the small particles. The large grains improved the crystallinity of LATP and reduced the grain-boundary resistance, resulting in high Li ion conductivity and low activation energy. Therefore, the LATP pellets from Li$_3$PO$_4$ showed higher Li ion conductivity and lower activation energy than those from Li$_2$C$_2$O$_4$. The highest total Li ion conductivity of LATP pellets from Li$_3$PO$_4$ was $2.0 \times 10^{-11}$ S cm$^{-1}$ and the activation energy was 0.28 eV.

Disclosure statement

No potential conflict of interest was reported by the authors.

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