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Preparation of Li Ion Conductive Ceramics via Liquid Process

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Abstract**—**$Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$(LATP) has received much attention as a solid electrolyte for lithium batteries. In this study, the LATP solid electrolyte is prepared by the co-precipitation method using Li_3PO_4 as a Li source. The LATP is successfully prepared and the Li ion conductivities of bulk (inner crystal) and total (inner crystal and grain boundary) are 1.1×10^{-3} and 1.1×10^{-4} S cm^{-1}, respectively. These values are comparable to the reported values, in which $Li_2C_2O_4$ is used as the Li source. It is conclude that the LATP solid electrolyte can be prepared by the co-precipitation method using Li_3PO_4 as the Li source and this procedure has an advantage in mass production over previous procedure using $Li_2C_2O_4$ because Li_3PO_4 is lower price reagent compared with $Li_2C_2O_4$.

Keywords**—**Co-precipitation method, lithium battery, NASICON-type electrolyte, solid electrolyte.

I. INTRODUCTION

RECHARGEABLE batteries have played a key role in our information-rich world [1]. Many types of rechargeable batteries have been developed thus far.

Among them the rechargeable Li ion battery has been recognized as the most suitable battery for information devices due to its high energy and power densities.

However, the Li ion batteries have safety issues caused by flammable organic solvents contained in the electrolytes. In order to solve the safety issues, the all-solid-stat batteries using inflammable ceramics electrolytes have been suggested [2]. The all-solid-state batteries do not contain any flammable components; thus, the safety issues would be solved.

Many kinds of Li ion conductive ceramics which mean solid electrolytes for the all-solid-state batteries have been reported so far. NASION (Na Super Ion Conductor) structure phosphates $Li_{1-x}M'_xM''_{2-x}(PO_4)_3$ (M'=Al, Y, Fe, etc., M''=Ti, Ge, Hf, etc.) have been accepted promising candidates for the all-solid-state batteries [3]-[5]. Among them, $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$(LATP) is especially expected for the application of all-solid-state batteries because of its high lithium ion conductivity (~ 10^{-3} S cm^{-1}) [6]. Hoshina et al. fabricated the all-solid-state thin film battery composed of LATP solid electrolyte and $LiNi_{0.5}Mn_{1.5}O_4$ cathode. They operated the thin film battery successfully [7]. Kotobuki et al. also fabricated the all-solid-state battery with three dimensionally ordered structure using LATP solid electrolyte and confirmed charge and discharge behaviors [8]. One of the problems of LATP for practical application is the difficulty in mass production. Most studies on LATP have adopted solid state reaction and melt-quenching methods for the LATP preparation [9], [10]. These methods cannot be easily applied to the mass production due to its high energy consumption and contamination of impurities in the final products.

The co-precipitation method allows the materials react uniformly at molecular level and has the advantages lower polycrystalline synthesized temperature and shorter sintering time [11]. By the lowering synthesized temperature and shorter sintering time, reduction of process cost for the LATP preparation can be possible. Therefore, it is expected that the mass production of LATP solid electrolyte would be possible by application of the co-precipitation method for the LATP preparation. We applied the co-precipitation method for the LATP preparation using $Li_2C_2O_4$ as a Li source [12]. The LATP was successfully prepared by the co-precipitation method. However, $Li_2C_2O_4$ is not low-price reagent; it may cause a problem if our co-precipitation procedure would be applied for the mass production.

In this study, the application of co-precipitation method for the LATP preparation using Li_3PO_4, which is the low-price reagent, as the Li source was attempted. The LATP solid electrolyte was successfully prepared by the co-precipitation method and Li ion conductivity of obtained LATP was comparable with reported value.

II. EXPERIMENTAL

The LATP solid electrolyte was prepared by the co-precipitation method.Li_3PO_4 and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved into purified water and dropped into NH_4HCO_3 solution under vigorous stirring at 80°C. 10% of excessive amount of Li was added into the solution to compensate evaporation of Li during heat treatment and calcination. After that, $Ti(C_3H_7O)_4$ and $NH_4H_2PO_4$ solution were dropped into the solution containing co-precipitant. The mixture was dried at 100°C to remove the solvent. The dried mixture was heated at 800°C for 30 min. Obtained precursor powder was ground by a ball-mill at 650 rpm for 1hin iso-propanol (Pulver Risette 7 Fritsch) with ϕ 0.5 mm Zirconia ball.

The ball-milled powder was supplied for a sintered pellet preparation. The powder was pelletized in diameter of 20 mm and then calcined at 1050°C for 6 h in air. All reagents were purchased from Wako Chemical Co. Ltd., Tokyo, Japan and used without further purification.

The as-prepared and boll-milled powder and the sintered

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Pellet were subjected to X-ray diffraction (XRD, Rigaku Ultima IV) measurement using Cu Kα radiation to identify crystal phases of them. Scanning electron microscope (SEM, JEOL-6300LA) was used to observe the morphologies of the powder and pellet cross section.

Li ion conductivity of the calcined pellet was measured by the AC impedance method. Both surfaces of the sintered pellet were polished to obtain flat surface and control its thickness before measuring Li ion conductivity. Prior to measurement, Au was sputtered onto both sides of the pellet to prepare Li blocking electrodes and to ensure electrical contact with Cu current collector. The AC impedance data were collected at ±10mV voltage signal in a frequency range of 100 ~ 1MHz using chemical impedance meter (HIOKI Chemical Impedance Meter 3352-80). The AC impedance measurement was performed at 30 ~200°C.

III. RESULTS

Fig. 1 shows the XRD patterns of precursor powders before and after ball-milling. Comparing the standard peaks of $LiTi_2(PO_4)_3$ (LTP) having NASICON structure (Fig. 1 (c)), all diffraction peaks of the precursor powder before ball-milling (Fig. 1 (a)), were well matched with the standard peaks, representing that the LATP was formed after heating the precursor participant. Lower diffraction intensities in the powder after ball-milling were attributed to reduce the particle size of power by the ball-milling (Fig. 1 (b)).The standard peaks of $AlPO_4$ which is the most possible impurity phase, is depicted in Fig. 1 (d). No diffraction peaks from impurity phases were confirmed in the powder before and after ball-milling.

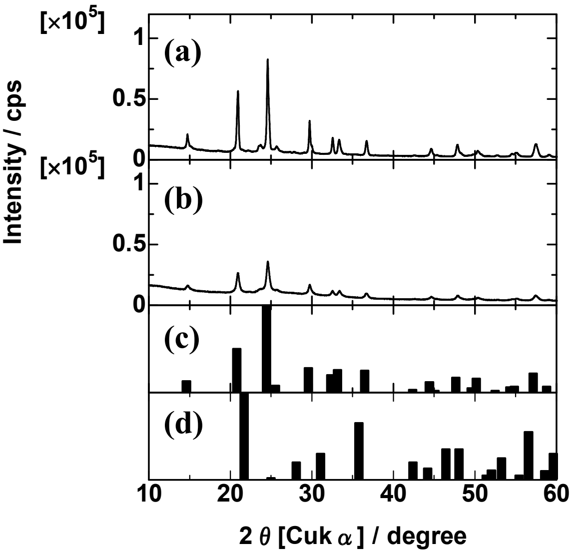

Fig. 1 XRD patterns of precursor powder heated at 800◦C for 30 min before and after the ball-milling (a) Before the ball-milling, (b) After the ball-milling, (c) Standard pattern of $LiTi_2(PO_4)_3$, (d) Standard pattern of $AlPO_4$

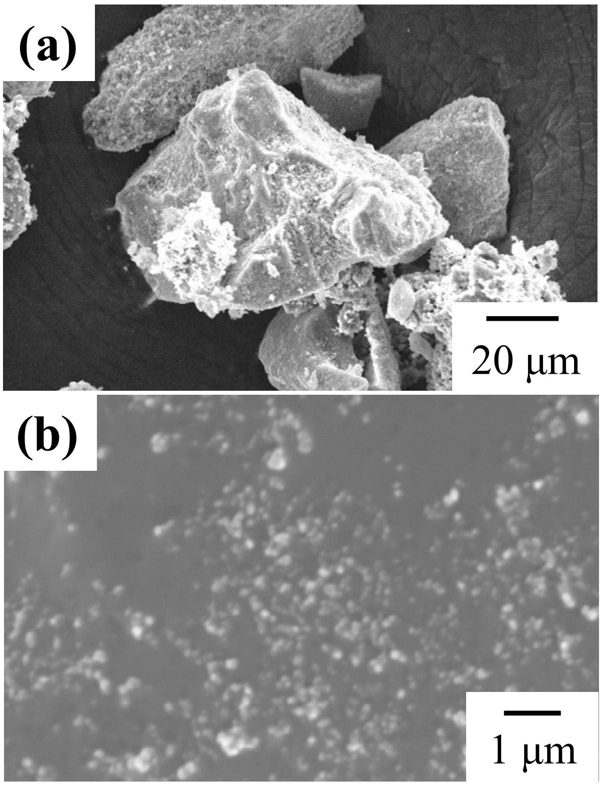

Fig. 2 SEM images of precursor powder heated at 800◦C for 30 min before and after the ball-milling (a) Before the ball-milling, (b) After the ball-milling

SEM images of the precursor powder before and after ball-milling are revealed in Fig. 2 (a) and (b), respectively. Notably, both powders have completely different morphologies. Before the ball-milling, large powder with a particle size of approximately 40 ~ 60 μm was observed. The powder was crushed well by the ball-milling. The particle size was reduced to ~ 100 nm after the milling (Fig. 2 (b)).

The milled powder was supplied to form the pellet, which was then calcined at 1050°C for 6h. The XRD pattern of the calcined pellet is depicted in Fig. 3 with the standard pattern of LTP. All diffraction peaks can be attributed to the LTP with NASICON structure, indicating that the LATP solid electrolyte was successfully prepared by the co-precipitation method. No impurity phase formation was confirmed after the calcination.

The cross-sectional SEM images of the calcined pellet are displayed in Fig. 4. The pellet is thought to be sintered well because no void space was observed in its cross-section. Many crystal grains were existed, however, the grains were well contacted each other.

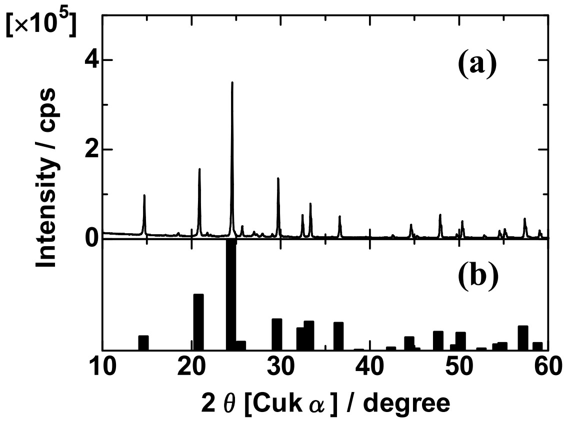

Fig. 3 XRD pattern of LATP pellet sintered at 1050°C for 6 h (a) LATP pellet, (b) Standard pattern of $LiTi_2(PO_4)_3$

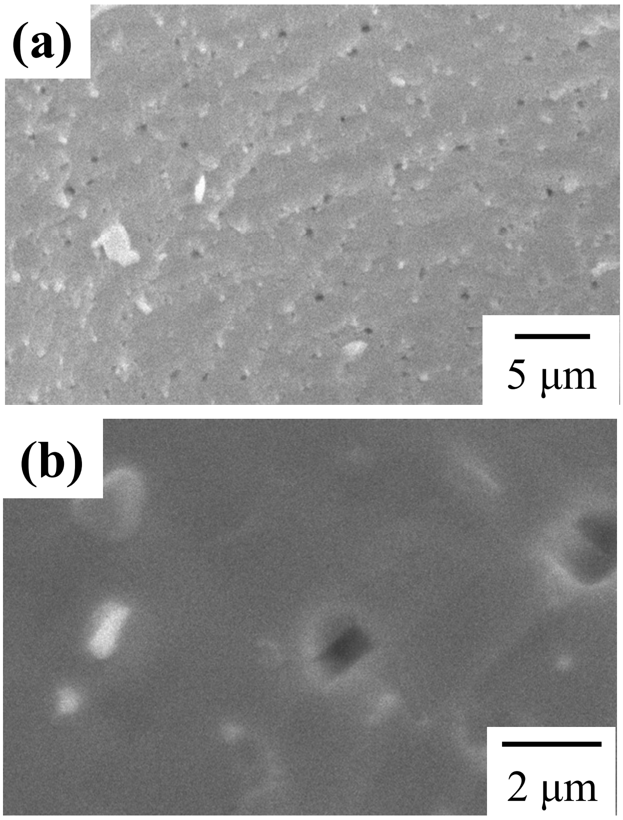

Fig. 4 SEM images of LATP pellet sintered at 1050°C for 6 h

Complex impedance plot of the LATP pellet using Aublocking electrodes measured at 30°C is shown in Fig. 5. A semicircle at high frequency and a tail at low frequency were observed. This characteristic profile of the impedance plot appears often in Li ion conductive ceramics [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 the high- and low-frequency sides were ascribed to inner crystal and total (inner crystal and grain boundary) impedances, respectively [15]. The bulk (inner crystal) and total Li ion conductivities were estimated to 1.1 × 10^{-3} and 1.1 × 10^{-4} S cm^{-1}, respectively. These values are comparable to prepare previously reported values [12], [15], [16].

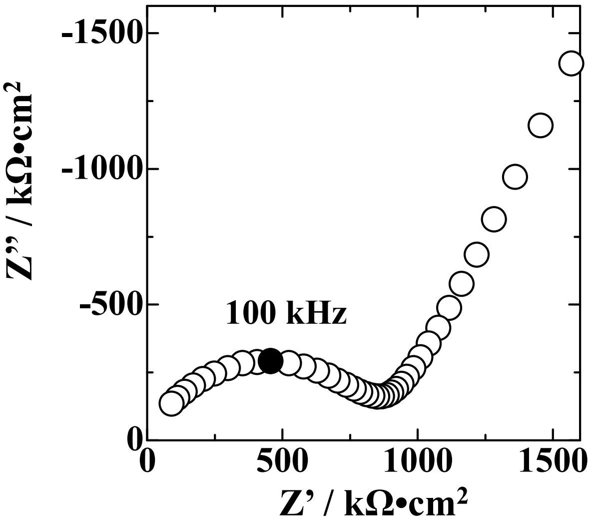

Fig. 5 Complex impedance plot at 30◦C of LATP pellet sintered at 1050◦C for 6 h

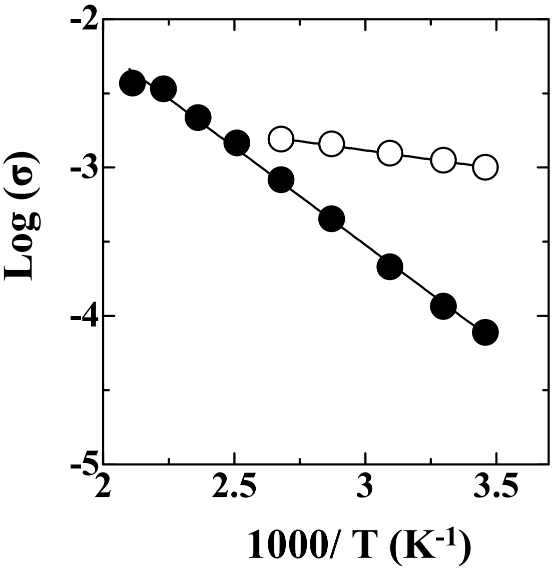

Fig. 6 Arrhenius plot of the LATP pellet sintered at 1050°C for 6h

The AC impedance measurement was performed under various temperatures to depict the Arrhenius plot (Fig. 6).Both Li ion conductivities increased with decrease of temperature. The bulk Li ion conductivity was not able to estimate over 150◦C because the semicircle disappeared. Both plots were well fit by the Arrehnius equation. The fitting accuracies (R^2 factor) were greater than 0.99 in both plots, implying that the Li ion conduction mechanism does not change in this temperature range. The activation energies of bulk and total ion conduction were 0.05 and 0.11 eV, respectively.

IV. DISCUSSION

In this study, Li_3PO_4 was used as the Li source to prepare the LATP solid electrolyte by the co-precipitation method.

The precursor powders prepared by the heated at 800°C was composed of LATP as shown in Fig. 1. The powder was crushed easily by the ball-milling (Fig. 2). These behaviors were observed in the powder prepared by same procedure using $Li_2C_2O_4$ [12].

Well-sintered pellets could be obtained by the calcination at 1050°C. The conventional solid state reaction and melt-quenching methods have required the calcination temperature as high as 1200°C to prepare bulk LATP. The co-precipitation allows us to recuce the calcination temperature more than 150°C [12].

The bulk and total conductivities were estimated to 1.1×10^{-3} and 1.1×10^{-4} S cm^{-1}, respectively. These values were comparable to reported values, which were obtained from the LATP prepared using $Li_2C_2O_4$ [12]. Therefore, it is conclude that the LATP solid electrolyte can be prepared by the co-precipitation method using Li_3PO_4 as the Li source.

The Li ion conductivity of practical liquid electrolyte soaked in separator is approximately $\sim 10^{-3}$ S cm^{-1} [17]. The total conductivity of the prepared LATP was lower than present liquid electrolyte and not high enough for application to the all-solid-state batteries. This was attributed to low grain boundary conductivity because the bulk (inner crystal) conductivity was comparable to the liquid electrolyte. This was supported by SEM images in Fig. 4, which revealed many grain boundaries in the cross section. Therefore, higher total conductivity would be obtained by improvement of the grain boundary conductivity. In our previous study, which investigated a preparation of LATP using sol-gel method, an amorphous LATP powder was used to form pellet and calcined at 1,000°C. The bulk and total conductivities of sintered LATP pellet were 3.1×10^{-3} and 4.5×10^{-4} S cm^{-1}, respectively, higher than this study [18]. This makes an image that the grain boundary conductivity can be improved by using the amorphous powder. In this study, crystallized LATP powder was supplied for pellet formation. Therefore, the grain boundary and total conductivities could be improved if the amorphous powder, which was prepared by heating precipitant at low temperature, was used.

It is verified that the LATP solid electrolyte can be prepared by the co-precipitation method using Li_3PO_4 as the Li source and improvement of grain boundary conductivity is needed.

V. SUMMARY

The co-precipitation method using Li_3PO_4 as the Li source was applied to prepare the LATP solid electrolyte. The bulk and total conductivities were estimated to 1.1×10^{-3} and 1.1×10^{-4} S cm^{-1}, respectively. These values were comparable to reported values, which were obtained from the LATP using $Li_2C_2O_4$. Therefore, it is conclude that the LATP solid electrolyte can be prepared by the co-precipitation method using Li_3PO_4 as the Li source. However, the total conductivity was still lower than that of practical liquid electrolyte. The reason for a difference in the conductivity could be attributed to the grain boundary conductivity.

REFERENCES

[1] J. M. Tarascon, and M. Armand, “Issues and challenges facing rechargeable lithium batteries”, Nature vol. 414 pp.359-367, 2001.

[2] J. W. Fergus, “Ceramics and polymeric solid electrolytes for lithium-ion batteries”, J. Power Sources vol. 195 pp.4554-4569, 2010.

[3] H. Aono, E. Sugimoto, and Y.Sadaoka, “Ionic conductivity and sinterability of lithium titanium phosphate system”, Solid State Ionics, vol. 40/41, pp.38-42, 1990.

[4] H. Aono, E. Sugimoto, and Y. Sadaoka, “Ionic Conductivity of Solid Electrolytes Based on Lithium Titanium Phosphate”, J. Electrochem. Soc., vol. 137 pp. 1023-1027, 1990.

[5] C. J. Leo, B. V. R. Chowdari, and C. V. R. Subba, “Lithium conducting glass ceramic with Nasicon structure”, Mater. Res. Bull, vol. 37, pp.1419-1430, 2002.

[6] J. Fu, “Superionic conductivity of glass-ceramics in the system Li_2O-Al_2O_3-TiO_2-P_2O_5”, Solid State Ionics, vol. 96, pp.195-200, 1997.

[7] K. Hoshina, K. Yoshima ,M. Kotobuki, and K. Kanamura, “Fabrication of $LiNi_{0.5}Mn_{1.5}O_4$ thin film cathode by PVP sol–gel process and its application of all-solid-state lithium ion batteries using $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ solid electrolyte”, Soli State Ionics, vol. 209/210, pp. 30-35, 2012.

[8] M. Kotobuki, Y. Isshiki, H. Munakata, and K. Kanamura, “All-solid-state lithium battery with a three-dimensionally ordered$Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ electrode”, ElectrochimicaActa, vo.55, pp. 6892-6896, 2010.

[9] J. S. Thokchom, and B. Kumar, “The effects of crystallization parameters on the ionic conductivity of a lithium aluminum germanium phosphate glass–ceramic”, J. Power Sources, vol. 195, pp. 2870-2876, 2010.

[10] J. K. Feng, L. Lu, and M. O. Kai, “Lithium storage capability of lithium ion conductor $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$”, J. Alloy. Compd., vol. 501, pp. 255-258, 2010.

[11] J. G. Li, T. Ikegami, J. H. Lee, and T. Mori, “Well-sinterable $Y_3Al_5O_{12}$ Powder from Carbonate Precursor”, J. Mater. Res., vol. 15, pp.1514-1523, 2000.

[12] M. Kotobuki, and M. Koishi, “Preparation of $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ solid electrolyte via a co-precipitation method”, Ionics, vol. 19, pp. 1945-1948, 2013.

[13] J. T. S. Irvine, D. C. Sinclair, and A. R. West, “Electroceramics: characterization by impedance spectroscopy”, Advance Materials vol. 2, pp.132-138, 1990.

[14] V. Thangadurai, and W. Weppner, “Investigations on electrical conductivity and chemical compatibility between fast lithium ion conducting garnet-like $Li_6BaLa_2Ta_2O_{12}$and lithium battery cathodes”, J. Power Sources, Vol. 142, pp.-339-, 2005.

[15] J. Fu, “Fast Li^+ ion conduction in Li_2O-(Al_2O_3-Ga_2O_3)-TiO_2-P_2O_5 glass ceramics”, J. Materials Science vol. 33, pp.1549-, 1998.

[16] J. L. Naraez-Scmanate, and A. C. M. Rodrigues, “Microstructure and ionic conductivity of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$NASICON glass-ceramics”,Solid State Ionics vol.181 pp.1197-, 2010.

[17] Y. Liang, S. Cheng, J. Zhao, C. Zhang, S. Sun, N. Zhou, Y. Qui, and X. Zhang, “Heat treatment of electrospunPolyvinylidene fluoride fibrous membrane separators for rechargeable lithium-ion batteries”, J. Power Sources, vol. 240, pp. 204-211, 2013.

[18] M. Kotobuki, and M. Koishi, “Preparation of $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ solid electrolyte via a sol-gel route using various Al sources”, Ceramics International, vol. 29, pp. 4645-4649, 2013.