Ionic conductivity enhancement in $LiTi_2(PO_4)_3$-based composite electrolyte by the addition of lithium nitrate

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Abstract

The electrical and thermal properties of $LiTi_2(PO_4)_3$ (LTP) and LTP composite electrolytes were investigated. LTP-LiNO₃ composite electrolyte sintered at 900 °C revealed high conductivity (approximately 10^{-5} S cm^{-1} at 25 °C), compared with pure LTP sintered at the same temperature. The thermal behavior in the sintering process of pure LTP and LTP composite electrolytes was examined. Consequently, we found that the conductivity of the composite electrolyte was enhanced by partial melting and subsequent solidification of the pellet at around 800 °C. This phenomenon was attributed to the coexistence of $Li_4P_2O_7$ which was a byproduct of the decomposition of LiNO₃ and LTP. © 1997 Published by Elsevier Science S.A.

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1. Introduction

$LiTi_2(PO_4)_3$ (LTP) with a NASICON-type [1] structure is one of the promising lithium-ion conductive solid electrolytes. Among the series of $LiM_2(PO_4)_3$ (M = Ge [2], Ti [3], Sn, Hf, Zr [4]), $LiTi_2(PO_4)_3$ has achieved the optimum bottleneck size for Li$^+$ ionic conduction in the bulk structure [4]. The ionic conductivity of pure LTP is low (10^{-7} S cm^{-1} at 25 °C), however it is enhanced by M^{3+} substitution for Ti^{4+} or by the addition of lithium salts [4,5]. The enhancement by M^{3+} (M = Al, Cr, Ga, Fe, Sc [6]) substitution is explained as an improvement of the bulk conductivity by the increase of the mobile lithium-ion concentration in a three-dimensional framework structure. On the other hand, the role of additional lithium salts on the enhancement is not fully clarified.

Some mechanisms of the ionic conductivity enhancement in composite electrolytes have been proposed and classified roughly into two theories. One is the improvement of the ionic conductivity at grain boundaries, for example, by sintering of the powder or control of the particle size [5,7]. The other is the increase of the bulk ionic conductivity in the crystal structure which is due to Li$^+$-ion insertion into the cavities in the framework [8]. The latter involves microscopic control. In this work, we examined the sintering proc-

ess of LTP composite electrolytes by thermal analysis. Then we compared the ionic conductivity of samples which were calcined at various temperatures, and characterized the microstructures. We discussed the correlation between partial melting in the LTP composites and the enhancement of ionic conductivity.

2. Experimental

Pure LTP was obtained by heating a stoichiometric mixture of Li_2CO_3, TiO_2 and $(NH_4)_2HPO_4$ at 900 °C for 2 h. The obtained LTP powder was crushed and pressed using a pellet in a 10 mm diameter steel die, and the pellet was sintered at 700 and 900 °C for 2 h. The composite electrolyte was obtained by subsequent sintering of the pellets containing a mixture of LTP and LiNO₃ (mole fraction 1:1) powders at 700 and 900 °C for 2 h. Gold electrodes made of Engelhard A-3360 paste were formed on the surface of the pellets by decomposing and solidifying the paste by increasing the temperature to 600 °C over a period of 20 min. The cell constant was determined from the area of the electrodes and the pellet thickness.

X-ray powder diffraction analysis was conducted using a Mac Science MPX 18 X-ray diffractometer. Silicon powder was used as an internal standard for the correction of 2θ angle. Ionic conductivity measurements were performed in the fre-

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quency range of 1 Hz to 50 kHz with a Solatron 1250/1286 frequency analyzer. Thermogravimetric (TG) measurements and differential thermal analysis (DTA) were performed using a Rigaku-TG8101D thermal analyzer. Samples of approximately 15 mg placed in Pt or Al_2O_3 crucibles, were heated up to $T_{max} = 1000$ °C in dry air flow at a scan rate of 10 °C/min. Scanning electron microscope observations were performed with NIKON E-SEM 2700L in air at 500 Pa.

3. Results and discussion

3.1. Synthesis and characterization of LTP–LiNO₃ composite calcination

3.1.1. Temperature dependence of ionic conductivity

The ionic conductivity dependence on the calcination temperature for pure LTP and LTP composite electrolytes is shown in Fig. 1. The composite sintered at 900 °C (curve (a)) revealed high ionic conductivity (approximately 10^{-5} S cm^{-1} at 25 °C), compared with that of pure LTP sintered at the same temperature (curve 1(b)). σ values of the composite sintered at 700 °C (curve (c)) were 3 to 4 orders of magnitude lower than those of composite (curve (a)), although the difference in σ values between the two pure LTPs (curves (b) and (d)) was negligible. X-ray powder diffraction patterns of the composites (curves (a) and (c)) and pure LTP (curve (b)) are shown in Fig. 2. No significant difference in crystal lattice size between LTP in the composite and pure LTP was observed. The enhancement of the ionic conductivity without change of the crystal lattice size was observed previously [5]. The byproducts of LTP composite were $LiTiPO_5$ and $Li_4P_2O_7$, the ionic conductivity of which were lower than those of pure LTP [9]. Since simple mixing would cause a decrease in ionic conductivity. information on microstructure and bulk density was needed to explain the
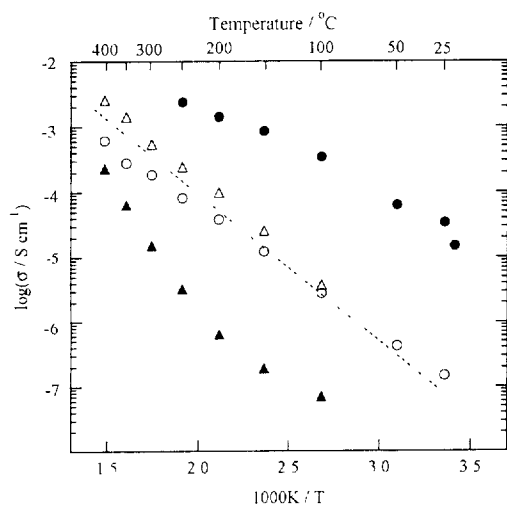
Fig. 1. Temperature dependence of the ionic conductivity (●) LTP + LiNO₃ 900 °C (a); (○) LTP 900 °C (b); (▲) LTP + LiNO₃ 700 °C (c), and (△) LTP 700 °C (d).
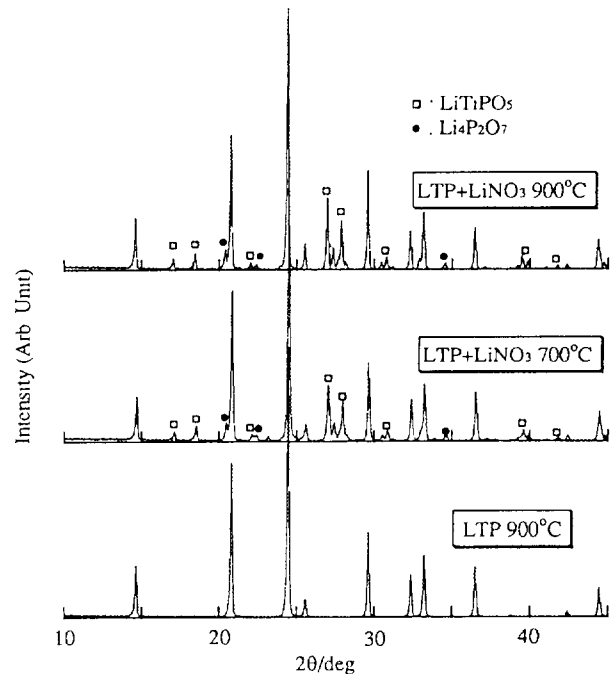
Fig. 2. Powder X-ray diffraction patterns of LTP and LTP composites

enhancement of the ionic conductivity for the composite (curve (a)). We observed the fracture surface of pure LTP and composites by SEM, as shown in Fig. 3. The cubic LTP grain size of composite (curve (a)) was larger than that of the other composites. This suggests that the densification of the pellet increased in the preparation condition of the composite (curve (a)). On the other hand, some pure LTP and LTP composites were calcined from 700 to 900 °C and the bulk densities were compared. As a result, the bulk density of the composite pellets increased abruptly between 780 and 830 °C while that of pure LTP increased linearly with the calcination temperature. These suggest that the densification of the composite pellet increased under calcination conditions of over 800 °C.

3.1.2. Calcination process of LTP–LiNO₃ composite

Thermal analysis of the calcination process of LTP–LiNO₃ composite was accomplished by TG/DTA measurement as shown in Fig. 4. $LiNO_3$ was decomposed into Li_2O at temperatures over 400 °C and no weight loss was observed above 440 °C. A small exothermic peak over 700 °C was observed only in the first heating cycle of the composite (Fig. 5). From the result of XRD analysis, this exothermic peak was assigned to the formation of $Li_4P_2O_7$ and $LiTiPO_5$ from LTP and Li_2O which was decomposed from $LiNO_3$. On cooling, a small exothermic peak at around 620 °C corresponded to the structural transition of $Li_4P_2O_7$ reported previously [10]. No endothermic peak which corresponded to the same transition was observed on heating at around 620 °C. However, it was reasonable that $Li_4P_2O_7$ was produced at temperatures over 700 °C. In the second heating cycle, an endothermic peak was observed at around 640 °C which was not shown in the figure. Finally, we could assign two peaks in the temperature
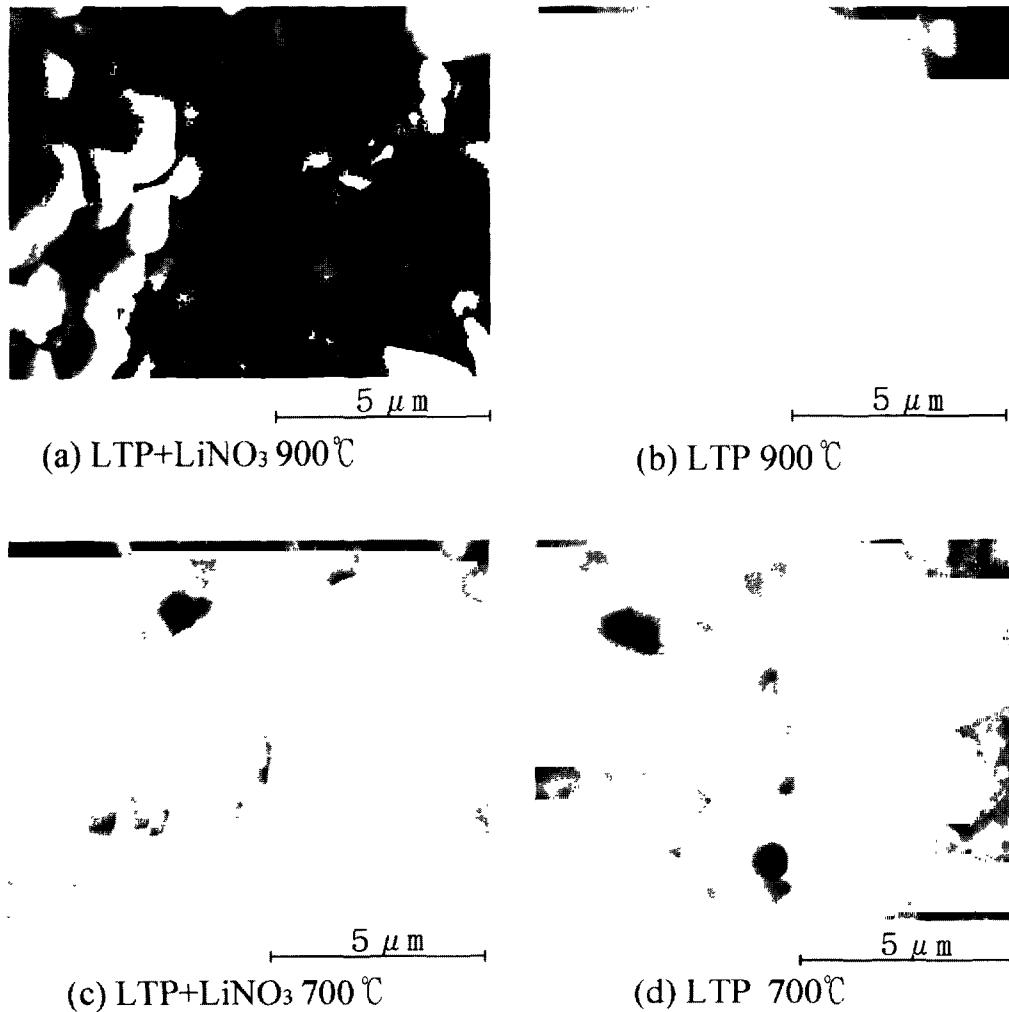
(a) LTP+LiNO₃ 900 ℃

(b) LTP 900 ℃

(c) LTP+LiNO₃ 700 ℃

(d) LTP 700 ℃

Fig. 3 Fracture surface of composite and LTP samples

750–820 °C range as the melting and subsequent solidification points of $Li_4P_2O_7$–$LiTiPO_5$–LTP mixture. These reversible peaks shifted to a lower temperature than that reported the melting point of $Li_4P_2O_7$ [10]. The small exothermic peak at around 755 °C on cooling was not identified yet. We concluded from XRD, SEM and TG/DTA observations that the enhancement of the ionic conductivity of LTP-based composite electrolytes could be improved by the densification of pellet and/or crystal growth of LTP during partial melting and solidification in the temperature 750–820 °C range.

3.2. Effect of $Li_4P_2O_7$ in composites

3.2.1. Elimination of $Li_4P_2O_7$ in ternary composite

In order to clarify the enhancement effect of ionic conductivity during melting and subsequent solidification, a binary composite of LTP and $LiTiPO_5$ was prepared by acid treatment of ternary $Li_4P_2O_7$–$LiTiPO_5$–LTP composite which had been prepared from LTP–$LiNO_3$ composite heated at 900 °C. The ternary composite was milled and immersed in 0.1 N HCl for about 10 min. Then $Li_4P_2O_7$ was eluted selectively by the immersion of HCl and completely removed from the ternary composite, as shown by the XRD pattern in Fig. 6. DTA traces of the binary composite are shown in Fig. 7. LTP–$LiTiPO_5$ binary composite showed no peak in the temperature 750 to 820 °C range in the DTA curve while LTP–$Li_4P_2O_7$ binary composite which was prepared from a mixture of LTP and $Li_4P_2O_7$ (mole fraction 10:1) showed melting and solidification peaks as shown in the same figure. The solidification
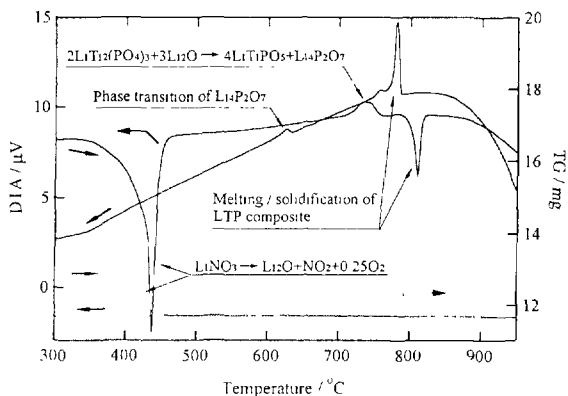

Fig. 4 TG/DTA curve between 300 and 950 °C. compounds were prepared from $LiTi_2(PO_4)_3$ and $LiNO_3$.

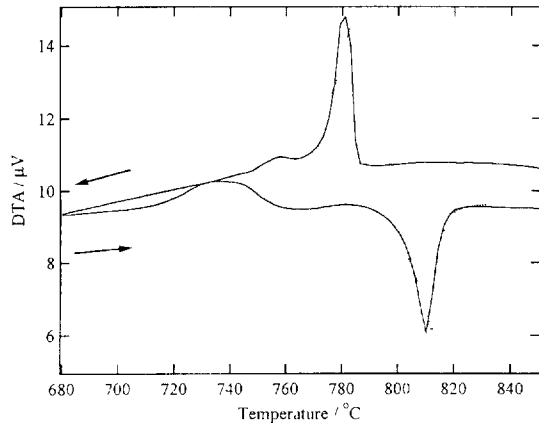Fig. 5 DTA curve between 680 and 850 °C. (————) under the composite formation from LiTi₂(PO₄)₃ and LiNO₃ and (· · ·) after composite formation.
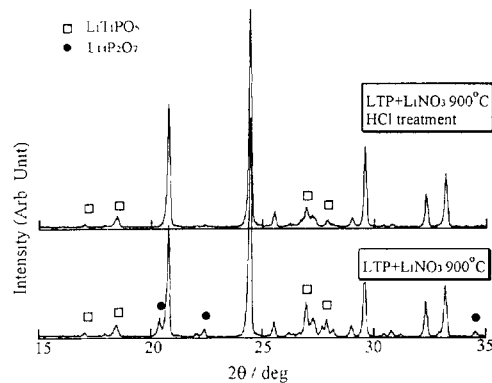

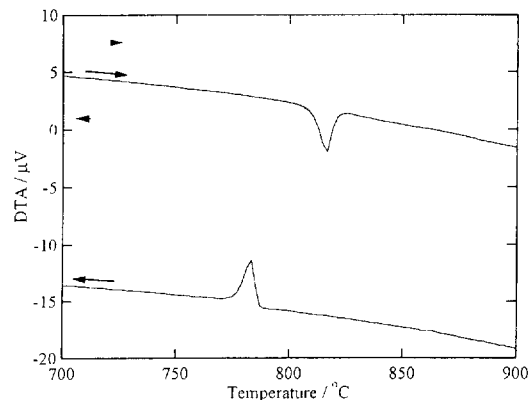Fig 6 Powder X-ray diffraction patterns of LTP + LiNO₃ composites treated by HCl

Fig 7 DTA curve between 700 and 900 °C (· ·) LiTi₂(PO₄)₃–LiTiPO₅ binary composite, and (————) LiTi₂(PO₄)₃–Li₄P₂O₇ binary composite

point of pure Li₄P₂O₇ was observed at around 875 °C [10]. This temperature decreased with the increase in amount of LTP. Namely, Li₄P₂O₇ acts as a solvent for LTP at temperatures over 800 °C and Li₄P₂O₇ does not react with LTP.

3.2.2. Effect on melting of Li₄P₂O₇

The temperature dependence of the ionic conductivity of binary composites is shown in Fig. 8. The ionic conductivity of LTP–Li₄P₂O₇ binary composite (curve (e)) was higher

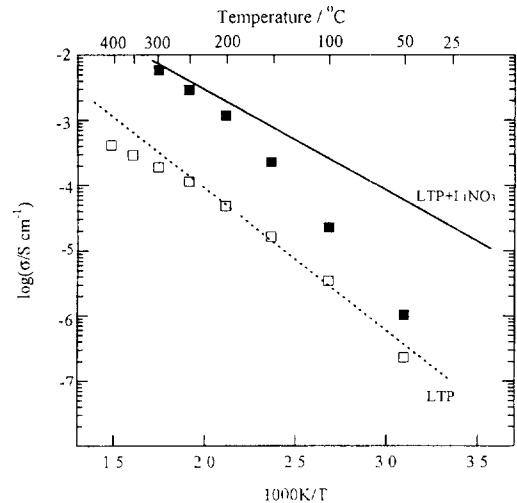Fig 8 Temperature dependence of the ionic conductivity (■) LTP + Li₄P₂O₇, 900 °C (e), and (□) LTP + LiTiPO₅, 900 °C (f) (————) LTP–LiNO₃ composite sinterd at 900 °C, and (· · ·) pure LTP.

than that of pure LTP, but the ionic conductivity of LTP–LiTiPO₅ binary composite (curve (f)) was similar to that of pure LTP. These results support the ionic conductivity enhancement by melting/solidification. Detailed investigation of the difference in ionic conductivity between LTP–Li₄P₂O₇–LiTiPO₅ which was prepared from LTP–LiNO₃ and LTP–Li₄P₂O₇ composite is required.

4. Conclusions

The ionic conductivity of LiTi₂(PO₄)₃ was enhanced by sintering at 900 °C with LiNO₃. Major factors of enhancement were considered as follows:

1. The addition of lithium salt such as LiNO₃ leads to partial melting/solidification of LTP composite around from 750 to 820 °C.
2. The conductivity enhancement of LTP-based composite electrolyte could be caused by the densification of pellet and/or the crystal growth of LTP in the melting and subsequent solidification process.
3. This phenomenon was observed in the coexistence of Li₄P₂O₇ which was produced from the reaction of LiNO₃ and LTP.

We now believe that the enhancement of conductivity by the control of microstructures will lead to the development of high lithium-ion conductive solid electrolytes for lithium batteries.

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