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Ionic Conductivity of $LiTi_2(PO_4)_3$ Mixed with Lithium Salts

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$LiTi_2(PO_4)_3$-lithium salt systems have been investigated in order to obtain a high lithium ion conductor. The salts acted as binder for sintering. The porosity decreased considerably and the conductivity of the pellets increased by the binder utilization. The maximum conductivity was 3×10^{-4} $S\cdot cm^{-1}$ for the $LiTi_2(PO_4)_3$ - $0.2Li_3BO_3$ system. The mixed binder was found to exist as a glassy or a thin coating second phase.

A high lithium conductive solid electrolyte for a high energy batteries has been requested. Recently, lithium titanium phosphate mixed with various metal ions, $Li_{1+X}M_XTi_{2-X}(PO_4)_3$ (M=Cr, Ga, Sc, or In),[1-5] has been found to show high conductivities even at room temperature. We reported that the conductivity was greatly enhanced by a partial replacement of the Ti^{4+} site with the M^{3+} ion such as Al^{3+}, Sc^{3+}, Y^{3+}, or La^{3+}.[6] The enhancement of the conductivity was attributed to the increase in lithium ion concentration and in the pellet density.[7] In this study, various lithium salts Li_3PO_4, Li_3BO_3, Li_2SO_4, LiCl, or $LiNO_3$ were mixed with $LiTi_2(PO_4)_3$ as a binder for the purpose of obtaining a high dense pellet, and their ionic conductivities and porosities were investigated.

The $LiTi_2(PO_4)_3$ was first synthesized by heat (stoichiometric mixtures of Li_2CO_3, TiO_2, $(NH_4)_2HPO_4$) at 1173 K for 2 h, and then were mixed with the lithium salts by a wet process. The mixed materials were heated at 1173 K at 2 h and then ball-milled for 12 h by the wet process. The dried mixture was pressed into pellets at the pressure of 1×10^{8} Pa. The pellets were sintered at 1073-1273 K for 2 h. The sintering temperature was chosen in such a way that the highest conductivity was obtained. In the case of the $LiTi_2(PO_4)_3$ sample, sintering was performed at 1433 K. The pellet was heated up to 573 K once in a dry N_2 gas atmosphere before a conductivity measurement in order to eliminate adsorbed water. The electrical conductivity was measured by means of the complex impedance method. The porosity of the sintered pellets was determined by the Archimedes' method. Lithium content for the sintered pellets maintained during the heating process, which was confirmed by means of the atomic adsorption analysis.

The $LiTi_2(PO_4)_3$ (X=0) pellet was poor in ionic conductivity and high in porosity. Many cracks appeared in the sample when sintering was conducted at 1483 K. The δT-1/T relation for $LiTi_2(PO_4)_3$ mixed with various salts is shown in Fig.

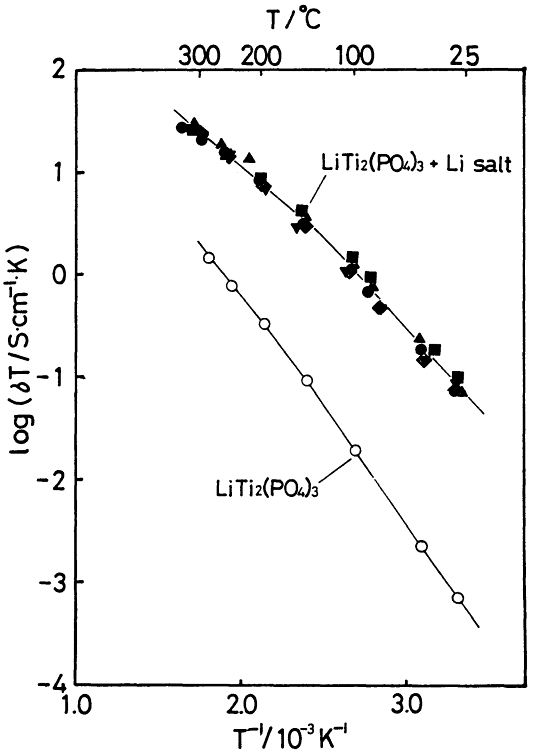

Fig. 1. Temperature dependence of the electrical conductivity.

$LiTi_2(PO_4)_3$ - $0.2Li_3PO_4$ (●)
$LiTi_2(PO_4)_3$ - $0.2Li_3BO_3$ (■)
$LiTi_2(PO_4)_3$ - $0.2Li_2SO_4$ (▲)
$LiTi_2(PO_4)_3$ - 0.8LiCl (▼)
$LiTi_2(PO_4)_3$ - $0.8LiNO_3$ (◆)

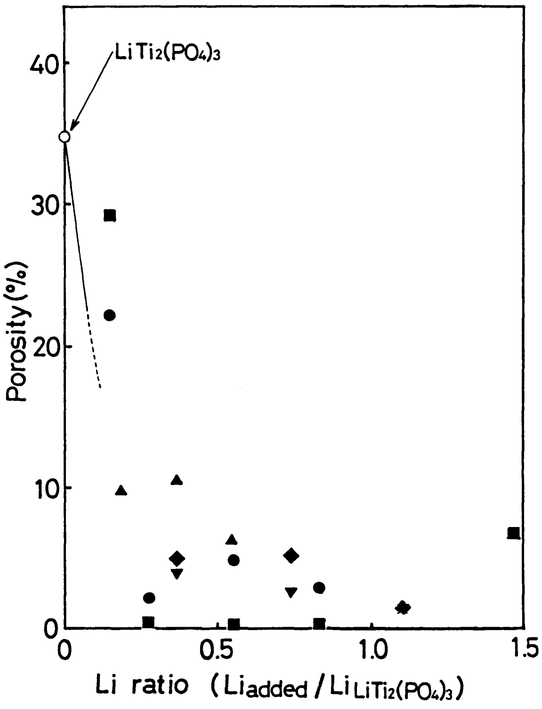

Fig. 2. The variation of the pellet porosity for $LiTi_2(PO_4)_3$ mixed with various lithium salts.

$LiTi_2(PO_4)_3$-Li_3PO_4 (●)
$LiTi_2(PO_4)_3$-Li_3BO_3 (■)
$LiTi_2(PO_4)_3$-Li_2SO_4 (▲)
$LiTi_2(PO_4)_3$-LiCl (▼)
$LiTi_2(PO_4)_3$-$LiNO_3$ (◆)

1. The conductivity was greatly enhanced by the lithium salt addition as a binder. A gently curved relation appears over the entire temperature range for the $LiTi_2(PO_4)_3$-lithium salt system. The activation energy at room temperature is about 35 kJ/mol for all the lithium salt mixed samples. The relation between the porosity of the sintered pellets and the lithium atomic ratio of the added lithium salt to $LiTi_2(PO_4)_3$ is plotted in Fig. 2. High dense pellets were obtained by the lithium salt addition for all the systems examined. These binders decomposed during sintering and resulted in a glassy or a thin coating second phase because few peaks except for the $LiTi_2(PO_4)_3$ phase were confirmed by the X-ray diffraction analysis. Grains was bound by the second phase, which might fill pores in the sintered $LiTi_2(PO_4)_3$ phase. The porosity for the Li_3BO_3 added system is particularly low, since Li_3BO_3 easily becomes a glassy phase.[8] Figure 3 presents the dependence of the lithium ratio of the added lithium salt to $LiTi_2(PO_4)_3$ on the electrical conductivity at 298 K. The conductivity is enhanced by the binder

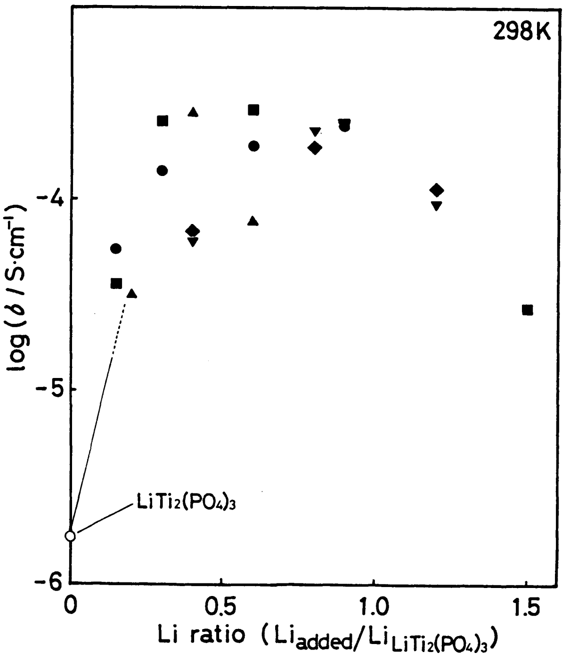

Fig. 3. The variation of the electrical conductivity at 298 K for lithium salt added systems.

$LiTi_2(PO_4)_3$-Li_3PO_4 (●)
$LiTi_2(PO_4)_3$-Li_3BO_3 (■)
$LiTi_2(PO_4)_3$-Li_2SO_4 (▲)
$LiTi_2(PO_4)_3$-LiCl (▼)
$LiTi_2(PO_4)_3$-$LiNO_3$ (◆)

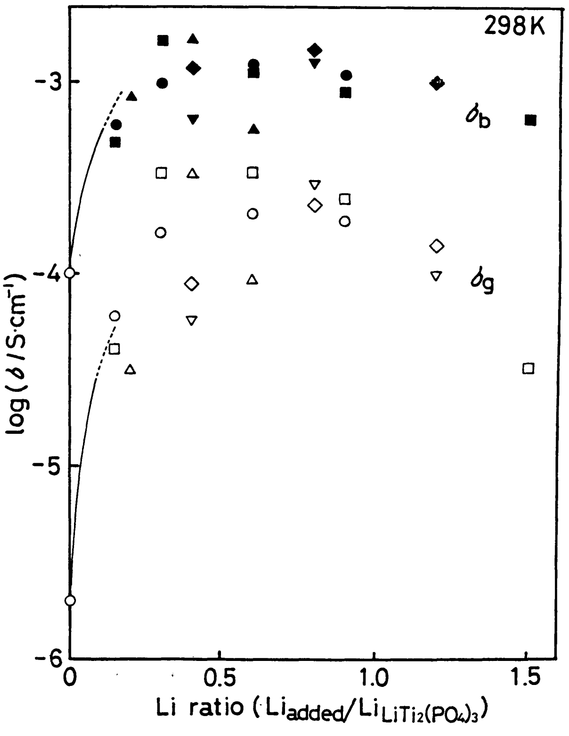

Fig. 4. The conductivities of a bulk and a grain boundary at 298 K.

-Li_3PO_4: bulk (●), grain boundary (○)
-Li_3BO_3: bulk (■), grain boundary (□)
-Li_2SO_4: bulk (▲), grain boundary (△)
-LiCl : bulk (▼), grain boundary (▽)
-$LiNO_3$: bulk (◆), grain boundary (◇)

utilization, and main reason for the enhancement was attributed to the increase of the pellet density. The maximum conductivity was $3x10^{-4}$ $S \cdot cm^{-1}$ for the $LiTi_2(PO_4)_3$ - $0.2Li_3BO_3$ system. The Li_3BO_3 mixed system showed the higher conductivity compared with the other systems. The lower porosity for this sample might be responsible for the conductivity enhancement. In addition, glassy Li_3BO_3 has been known to be a lithium ionic conductor.9) This would be also effective to improve the conductivity at grain boundaries. Figure 4 shows the conductivity of a bulk and a grain boundary at 298K obtained from the complex impedance method. Although the conductive bulk phase is only the $LiTi_2(PO_4)_3$ phase for all the samples, the conductivity is enhanced about by one order of magnitude by the binder addition. The bulk conductivity is approximately $1x10^{-3}$ $S \cdot cm^{-1}$ for all the binder added systems. The new conductive phase might be formed by the addition of the lithium salts. The conductivity at the grain boundary is greatly enhanced by the binder addition. The total conductivity in Fig. 3 is dependent on the σ_g.

The $LiTi_2(PO_4)_3$ sample mixed with various lithium salts is proved to be a considerably effective lithium solid electrolyte for its high conductivity at room temperature and the easy preparation.

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