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Ionic Conductivity of β-$Fe_2(SO_4)_3$ Type $Li_3Cr_2(PO_4)_3$ Based Electrolyte

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The electrical properties were studied for the $(1-y)Li_3Cr_2(PO_4)_3$-$yLi_5Mg_2(PO_4)_3$ system. The Mg^{2+} ion can not replace the Cr^{3+} site. The crystal structure for $Li_3Cr_2(PO_4)_3$ in this system is the β-$Fe_2(SO_4)_3$ type monoclinic phase. The conductivity and the sinterability improve with the increase in y for the phosphate system. The maximum conductivity was 4.6×10^{-5} $S \cdot cm^{-1}$ at 298 K for y=0.2. The activation energy for a Li^+ ion migration at the bulk component was ca. 0.43 eV for all the samples.

Lithium ionic conductors are promising materials for high energy density batteries. High Li^+ conducting solid electrolytes at room temperature have been eagerly investigated for the utilization of the all solid-state lithium battery.

NASICON-type1) Li^+ ion conductive electrolytes have been reported to show a high conductivity even at room temperature.2-8) The solid electrolytes based on $LiTi_2(PO_4)_3$ (cell volume ca. 1309 $Å^3$) show a maximum conductivity and a minimum activation energy for Li^+ migration.8) $LiTi_2(PO_4)_3$-based solid electrolytes have the most suitable lattice size for Li^+ migration. F.d'Yvoire et al. reported that the NASICON-type structure was obtained by quenching $Li_3Cr_2(PO_4)_3$ from 1703 K to room temperature.9) The cell volume of the NASICON-type $Li_3Cr_2(PO_4)_3$ reported is 1316 $Å^3$, which is very close to that of $LiTi_2(PO_4)_3$. This indicates that a $Li_3Cr_2(PO_4)_3$-based compound has the possibility for high conductivity. Furthermore, the conductivity enhancement can be also expected by the increase in mobile lithium ions, if the Cr^{3+} site is substituted for a divalent Mg^{2+} ion in

$Li_3Cr_2(PO_4)_3$.

In this study, the electrical properties and the crystal structure were examined for the polycrystalline $Li_{3+x}Mg_xCr_{2-x}(PO_4)_3$ system.

Li_2CO_3 (purity:99.99%), MgO (99.9%) Cr_2O_3 (99.9%), and $(NH_4)_2HPO_4$ (extra pure grade) were used as starting materials. The mixture was reacted in a platinum crucible at 1173 K for 2 h in the air atmosphere. The preheated material was ground into fine powder by a ball-mill method for 6 h (wet process: methanol). The dried powder was again reacted at 1173 K for 2 h in air. Then it was reground for 12 h by the same ball-mill method. A proper amount of 3 wt% PVA solution was mixed with the dried powder, and then pressed into a pellet at a pressure of $1x10^8$ Pa. The pellet was sintered for 2 h in air. Au electrodes were sputtered on the polished surfaces of the pellet by an Ion Coater (Shimadzu IC-50). The conductivity was determined by a complex impedance method (cole-cole plot) using Hewlett Packard LCZ meters (4276A and 4277A) with a frequency range from 10^2 to 10^6 Hz. Apparent porosity of the sintered pellets was determined by the Archimedes' method.

For $Li_3Cr_2(PO_4)_3$, a β-$Fe_2(SO_4)_3$ type ($P2_1/n$) phase was formed when the sintering was conducted at the temperature lower than 1473 K.[10,11] Monoclinic phase (C/2c) was obtained for the samples sintered above 1473 K. However, cracks appeared in the $Li_3Cr_2(PO_4)_3$ pellets by the phase transition from $P2_1/n$ to C/2c. In the case of the $Li_{3+x}Mg_xCr_{2-x}(PO_4)_3$ system ($x>0$), β-$Fe_2(SO_4)_3$ type $P2_1/n$ phase was formed when the sintering was conducted above 1473 K. We tried to obtain the NASICON-type rhombohedral ($R\overline{3}c$) phase by quenching the molten samples by pressing them between two iron plates. However only the $P2_1/n$ monoclinic phase was formed by the quenching for the samples of $x>0$. We could not succeed in obtaining the NASICON-type $Li_3Cr_2(PO_4)_3$-based electrolyte. The electrical properties were determined for the sintered samples of the β-$Fe_2(SO_4)_3$ type monoclinic ($P2_1/n$) phase.

We presumed that the lattice constants increase with the x value, because the ionic radius of Mg^{2+} (0.720 Å) ion is larger than that of Cr^{3+} (0.615 Å) ion.[12] However, the lattice constants did not increase. The $Li_5Mg_2(PO_4)_3$ phase was observed as a second phase when Mg^{2+} is mixed with $Li_3Cr_2(PO_4)_3$. In the present $Li_{3+x}Mg_xCr_{2-x}(PO_4)_3$ system, the Mg^{2+} ions could not substitute the Cr^{3+} sites at all, and resulted in the mixed phase of $Li_3Cr_2(PO_4)_3$ and $Li_5Mg_2(PO_4)_3$. The $Li_{3+x}Mg_xCr_{2-x}(PO_4)_3$ system should be described as the $(1-y)Li_3Cr_2(PO_4)_3$-$yLi_5Mg_2(PO_4)_3$ system ($y=x/2$).

The total conductivity (bulk plus grain boundary) at 298 K and the porosity of the sintered pellet for the $(1-y)Li_3Cr_2(PO_4)_3$-$yLi_5Mg_2(PO_4)_3$ system are plotted in Fig. 1. The conductivity was greatly enhanced with

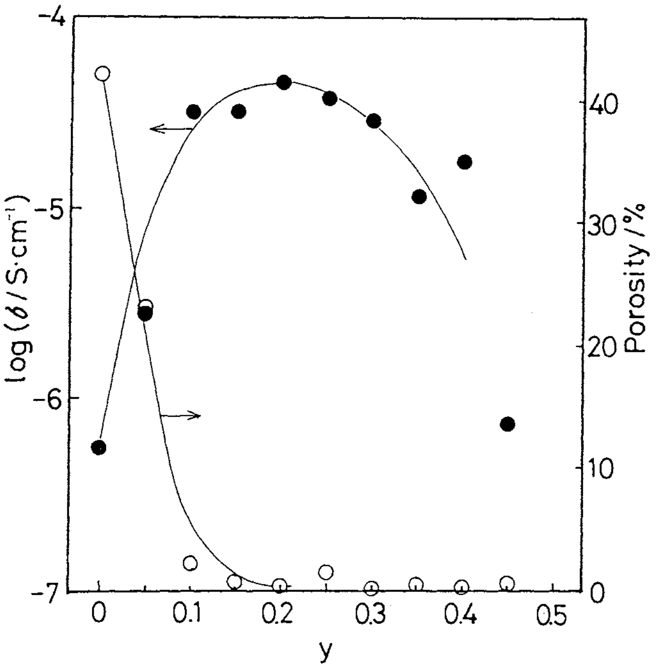

Fig. 1. The conductivity at 298 K and the porosity of the sintered pellet of (1-y)$Li_3Cr_2(PO_4)_3$-y$Li_5Mg_2(PO_4)_3$ system: (●) conductivity, (○) porosity.

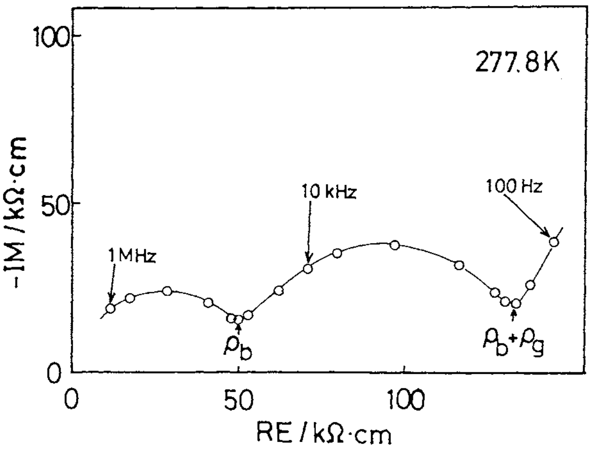

Fig. 2. Cole-cole plot for 0.8$Li_3Cr_2(PO_4)_3$-0.2$Li_5Mg_2(PO_4)_3$ at 277.8 K.

the y increase, and a maximum conductivity of $4.6x10^{-5}$ S·cm^{-1} was obtained for y=0.2. Although the high density pellet could not be obtained for $Li_3Cr_2(PO_4)_3$ (y=0), the porosity decreased by increasing y. The second phase of $Li_5Mg_2(PO_4)_3$ would contribute to obtain high density pellets. $Li_5Mg_2(PO_4)_3$ (y=1.0) itself showed a low conductivity, which was made clear in this study. The conductivity decreased for the system above y=0.2. The lithium migration was blocked by the excessive formation of the low conductive $Li_5Mg_2(PO_4)_3$ phase.

Figure 2 presents the cole-cole plot for the 0.8$Li_3Cr_2(PO_4)_3$-0.2$Li_5Mg_2(PO_4)_3$ sample at 277.8 K. Two semicircles are ascribed to the resistance for the bulk and the grain boundary components. The total resistance (bulk plus grain boundary) was obtained from the minimum point of a lower-frequency region. The bulk resistance (ρ_b) was determined from the minimum point between the two semicircles in a higher-frequency region. By the cole-cole plot method, the conductivities for the bulk and the grain boundary were separately estimated. The activation energies of the conductivity of the bulk and the grain boundary components are shown in Fig. 3. The activation energy was determined in the temperature range from 273 K to

373 K. The activation energy for the bulk component is constant. The activation energy for Li^+ migration in $Li_3Cr_2(PO_4)_3$ bulk was determined to be 0.43 eV. The addition of $Li_5Mg_2(PO_4)_3$ phase in $Li_3Cr_2(PO_4)_3$ did not influence the activation energy for the bulk component. The activation energy for the grain boundary decreased by the increase in y value. This indicates that the total conductivity enhancement (in Fig. 1) resulted from the decrease in the activation energy of the Li^+ ion conduction at the grain boundary.

In conclusion, $Li_3Cr_2(PO_4)_3$-based ceramics were investigated to obtain a high Li^+ ionic conductor at room temperature. The $0.8Li_3Cr_2(PO_4)_3$-$0.2Li_5Mg_2(PO_4)_3$ sample shows a maximum conductivity of 4.6×10^{-5} $S \cdot cm^{-1}$ at 298 K. This conductivity was about one order of magnitude lower than that of the NASICON-type Li^+ ion conductors reported by us.[5,6] However, the obtained conductivity is considerable high in the oxide-based electrolytes. The β-$Fe_2(PO_4)_3$ type electrolyte would be another candidate for the promising high Li^+ conducting material.

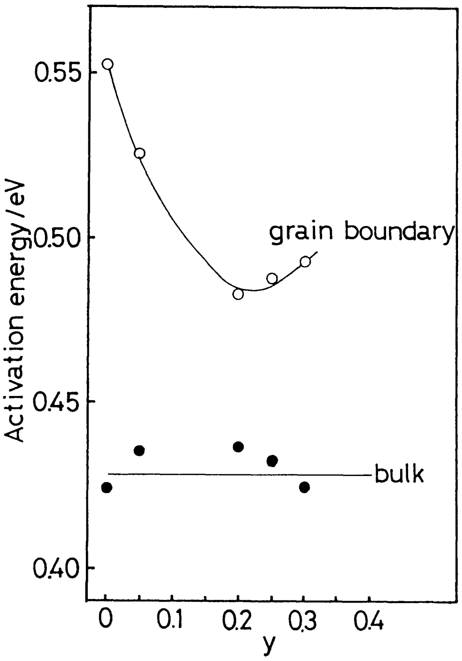

Fig. 3. The activation energies for the bulk and the grain boundary for $(1-y)Li_3Cr_2(PO_4)_3$-$yLi_5Mg_2(PO_4)_3$ system: (●) bulk, (○) grain boundary.

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