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DC Conductivity of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ Ceramic with Li Electrodes

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The ionic conductivity of a solid electrolyte, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, was measured with Li and Li-Al alloy electrodes. The contact resistance between the Li electrode and the electrolyte was a dominant factor for the DC conductivity. A higher DC conductivity was obtained by an utilization of the Li_4Al alloy electrodes.

A high lithium conductive solid electrolyte has been becoming a promising candidate for a separator of a solid lithium battery. A NASICON-skeleton type solid electrolyte, $Na_{1+X}M_XZr_{2-X}(PO_4)_3$ (M=Cr,In,Yb,etc.)[1)] and $Na_{1+X}Zr_2Si_XP_{3-X}O_{12}$,[2)] have been reported to show a high Na^+ ionic conductivity. Recently, analogous Li^+ conductors, i.e. $Li_{1+X}M_XTi_{2-X}(PO_4)_3$[3-11)] and $Li_{1+X}Ti_2Si_XP_{3-X}O_{12}$,[9)] were prepared and their conductivities were found to be remarkably high even at room temperature. A maximum conductivity of $7x10^{-4}$ $S\cdot cm^{-1}$ at 298 K was obtained for the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ electrolyte as described in our preceding papers.[9,10)] The conductivities were determined by a complex impedance plot with Au blocking electrodes, but not with Li electrodes.

In this paper, DC conductivity for $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ electrolyte was measured with Li or Li-Al alloy electrodes for the purpose of determining what carrier migrates and interfacial properties between the electrolyte and the electrodes.

A stoichiometric mixture of Li_2CO_3 (99.99%), Al_2O_3 (99.9%), TiO_2 (99.9%), and $(NH_4)_2HPO_4$ (extra pure grade) was used as a starting material for the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ preparation. The detail of the sample preparation is described in Ref. 9. The sintered pellet was cut into rodshaped samples (14 mm, 7 mm x 2 mm) for the DC conductivity measurement. The DC conductivity was determined by a two probe method with a Potentiostats-Galvanostats HA-301 from Hokuto Denko Co. and an Electrometer TR-8652 from Advantest Co. Gold leads (dia. 0.05 mm) for the measurement were previously mounted to the sample with an Au paste (Fig. 1). The rod sample was settled in a vacuum evaporator (HUS-5, Tokyo Vacuum Machinery Co.) and one end of two Au leads was placed outside of the chamber. Li or Li-Al alloy electrodes were deposited by a vacuum evaporation ($<10^{-5}$ Torr) on both cross sections of the sample (Fig. 1). In order to prevent a short-circuit between the electrodes by the evaporated metal, the sample surface was beforehandly covered. The measurement of the DC conductivity was conducted in the vacuum evaporator ($<10^{-5}$ Torr) after the sample heated by the electrode evaporation was adequately cooled down to room temperature (ca. 1 h). A four probe method and a complex impedance method were also carried out for the determination of the conductivity. The complex impedance method (100-1M Hz) was conducted with LCZ meters 4276A and 4277A from Hewlett Packard Co.

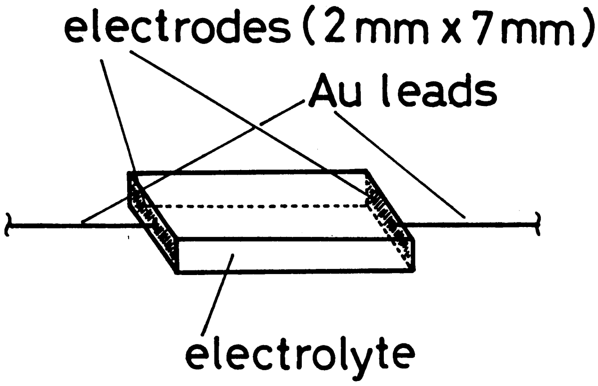

Fig. 1. The conductivity measurement.

The conductivity determined by the complex impedance method with an Au blocking electrodes is $1.2x10^{-3}$ S·cm at 298 K in this study. The DC conductivity variation vs. time at 298 K with the Li or Li-Al alloy electrodes by a two probe method is presented in Fig. 2. The results for the four probe method with the Li electrodes are also plotted in the same figure. The conductivity with the Li electrodes by the four probe did not change with the time span measured and is almost the same as that by the complex impedance method. This behavior indicates that lithium ions migrate in the sample. The DC conductivity by the two probe method kept constant value of about $3x10^{-4}$ $S·cm^{-1}$ for 2 min after the current flow, and the value is lower than the value of $1.2x10^{-3}$ $S·cm^{-1}$ determined by the complex impedance method. However, the DC conductivity decreased with the further current flow.

Figure 3 presents the variation of the Cole-Cole plots with the Li electrodes. The complex impedance was measured after the DC current was applied for the determined time (0, 20, 40, 80, 180 min.). Before the DC application (0 min), a smaller semicircle was observed. The DC resistance

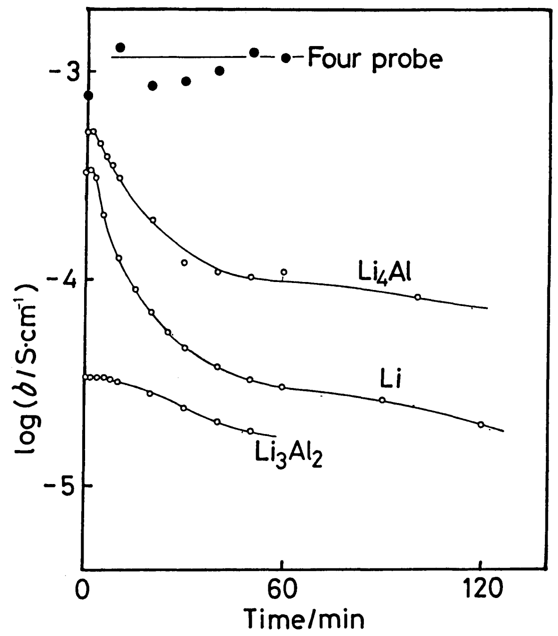

Fig. 2. The DC conductivity variation by the two probe method at 298 K with Li and Li-Al alloy electrodes under 0.07 mA/cm^2.
(●) : the conductivity by the four probe method with Li electrodes.

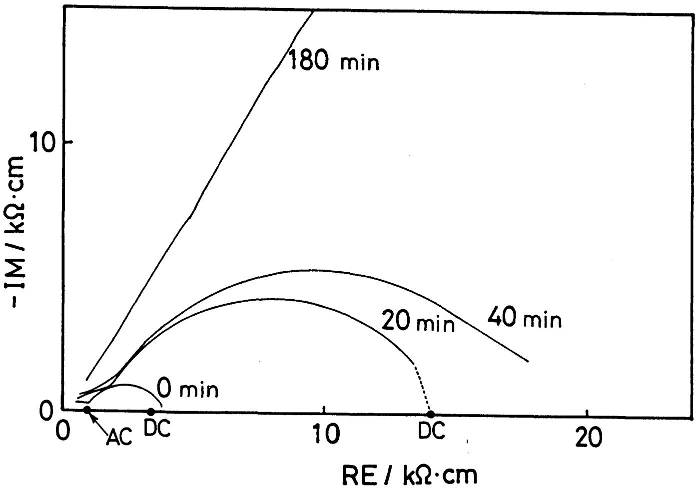

Fig. 3. The variation of the Cole-Cole plots at 298 K using Li electrodes.

with Li electrodes and the AC resistance from the Cole-Cole plot with the blocking electrodes are also indicated on the abscissa. AC and DC resistances are close to the each intersected point of the semicircle to the abscissa. The DC resistance with the Li electrodes is a total value for bulk, grain boundary, and the electrolyte-electrode interface. The AC resistance with blocking electrodes does not include the interface resistance. The semicircle presented in the figure is ascribed to the contact resistance between the electrodes and the electrolyte, and became progressively greater with the measuring time. The decrement of the DC conductivity using Li electrodes is mainly resulted from the increase in the contact resistance. The decreased DC conductivity did not return to its initial value when an applied potential was reversed. We may enumerate two possibilities for the increase of the contact resistance: (1) the formation of the poor interfacial contact between the electrodes and the electrolyte by a heterogeneity of the Li deposition for the cathode or the Li shortage for the anode,[12)] (2) the formation of $Li_{1+x}Ti_2(PO_4)_3$ phase by Li^+ ion insertion in the $LiTi_2(PO_4)_3$ lattice.[13)] The conductivity using the Li-Al alloy electrodes was higher than that of Li electrodes(Fig.2). The initial conductivity with the Li_4Al alloy is $5x10^{-4}$ $S \cdot cm^{-1}$ at 298 K. This may be resulted from the easier lithium diffusion in the Li-Al alloy electrodes. Li_3Al_2, a lower Li content alloy gave a lower DC conductivity. We presume that a lithium-poor phase is formed by Li migration on the anode for the lower Li content alloy.

It is concluded that the carrier ion is found to be Li^+ ions for the $LiTi_2(PO_4)_3$ based solid electrolyte. A high interfacial resistance between the electrolyte and the Li electrodes was obtained in this material. The contact resistance was improved by the application of Li-Al alloy electrodes. The interfacial resistance might be reduced by the utilization of the more appropriate electrode.

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