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Ionic Conductivity of Phospho-Olivine Compounds Measured by AC Impedance Spectroscopy

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Since the pioneering works by Padhi *et al.*$^{1)}$, mixed orthophosphates $LiMPO_4$ (M = Mn, Fe, Co, or Ni) with olivine structure have been extensively studied as lithium insertion compounds for rechargeable lithium batteries. Among them, $LiFePO_4$ (M = Fe) has been expected as a new positive electrode material because of its environmental benignity. It has been widely reported that the electrochemical lithium insertion/extraction properties of $LiFePO_4$ is limited by the intrinsic lower electronic conductivity in $LiFePO_4$. Hence, much effort has been devoted to overcome this problem, such as minimization of particle size, carbon coating, and aliovalent cation doping. In contrast to these studies focusing on the electronic conductivity of $LiFePO_4$, transport of lithium ion in the bulk have not been clearly understood, although they should play important roles for the rate capability and cycle ability of the charge and discharge reactions.

In this work, we measured the ionic conductivity of $LiMPO_4$ by AC impedance spectroscopy and also studied the contribution of its ionic conductivity to the total electric conductivity.

Sintered $LiMPO_4$ pellets were prepared by solid-state reaction. Platinum (Pt) electrodes were deposited on both sides of the pellets after polishing with emery paper. Resultant $Pt/LiMPO_4/Pt$ cell was heated in an argon-filled chamber and the temperature dependency of electric conductivity of $LiMPO_4$ was measured by AC impedance spectroscopy. This measurement was conducted in the temperature range from 385 to 573 K. All data were fitted by an equivalent circuit model of mixed conductor material followed by Thangadurai *et al*$^{2)}$.

Typical impedance plot of $Pt/LiFePO_4/Pt$ cell obtained at 420 K are shown in Fig. 1. This impedance spectrum consisted of three semicircles which can be assigned to ionic conductivity both in grain interior and at grain boundary and electronic conductivity. It should be noted that this impedance spectrum convergent on real axis at low frequency region, indicating that the $Pt/LiFePO_4$ was not blocking interface to this charge carrier. Because Pt electrode should be blocking interface for ion carrier, the semicircle at low frequency region can be assigned to electronic conduction in $LiFePO_4$. The semicircle observed at the highest frequencies could be attributed to dielectric polarization within the bulk of $LiFePO_4$. The semicircle appeared at intermediate frequencies could be influenced by the microstructure (grain size and second phase precipitation at grain boundaries) of $LiFePO_4$.

Arrhenius plots of these conductivities are summarized in Fig. 2. Activation energy of the ionic conduction in intergranular of $LiFePO_4$ was calculated to be 0.46 eV. The ionic conductivity and the electronic conductivity in $LiFePO_4$ at room temperature (298 K) was estimated to be 3.1×10^{-8} Scm^{-1} and 1.3×10^{-8} Scm^{-1}, respectively. Both the electronic conductivity at 298 K and activation energy of electronic conduction (0.50 eV) were in good agreement with previous reports $^{3)}$ $^{4)}$, supporting that the equivalent circuit applying in this study was appropriate for separating the ionic conductivity from total electric conductivity.

The ionic as well as electronic conductivity of other than M=Fe will be presented at the poster session.

References

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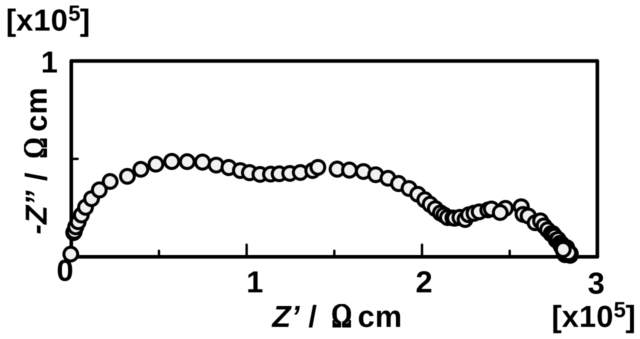

Fig. 1. Typical impedance plots of $Pt/LiFePO_4/Pt$ cell obtained at 420K.

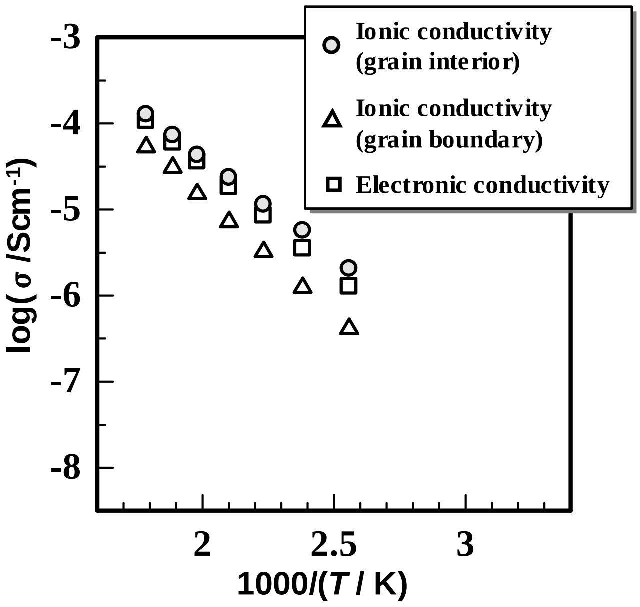

Fig.2. Arrhenius plots of ionic conductivity both in bulk (solid circles) and at grain boundary (open squares) and electronic conductivity (open triangles) of $LiFePO_4$.