

## The Transport Properties of Lithium Electrolyte Solution Coexisting with Porous Solid Materials

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The non-aqueous lithium electrolyte solution was key materials for the development of the Li batteries. Numerous studies of the lithium electrolyte solution have been done such as ionic mobility, conductivity, stability, etc. In the practical system applied to batteries, the electrolyte is coexisting with various kinds of the materials, such as active materials as electrodes, separators, and several additives. The electrolyte solution is usually supported by a separator made of fibrous or porous membranous materials between the active materials for the electrodes and most part of the electrolyte penetrated into the porous site of the separator. Nevertheless the interaction and influence of the solid phase are rarely considered. We have been studying the physicochemical properties of the electrolyte solution coexisting with the porous solid phase. Previously, we studied the electrical conductivity of heterogeneous systems consisting of  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\text{LiClO}_4$  solution was measured using various kinds of organic solvents and the composition dependence and temperature dependence were measured and the influence of the solid phase was discussed (1). In this study, the transport number of the dissolved species in the lithium electrolyte solutions was measured and the influence of the solid phase to the each dissolving species in the solution.

The transport number of lithium ion,  $t_{\text{Li}^+}$ , was measured by Hittorf's method for the system  $\text{LiClO}_4$ -PC solution in the bulk system and the system coexisting with the  $\alpha$ - $\text{Al}_2\text{O}_3$  powder. The powder was dried by calcining at  $500^\circ\text{C}$  for 4 hours. Each  $\text{LiClO}_4$  solution was dehydrated and mixed thoroughly and molded into alumina press in the dry box. In the Hittorf's cell, the Ni wire was used as the cathode where the reduced Li metal deposited and Li foil was used as the anode. The sample of solid/liquid coexisting system was kept into the middle chamber. The electrolysis was carried out for several hours at constant current. The weight change of Ni wire and the change of the concentration in the both electrode chambers were measured and the transport amount of the lithium ion was calculated. The electrical conductivity was measured by the same method described at Ref .1. Apparent ionic motilities were calculated from these results.

The temperature dependence of  $t_{\text{Li}^+}$  is shown in Figure 1. The value of  $t_{\text{Li}^+}$  increases at the temperature range above  $35^\circ\text{C}$ . The ionic mobility calculated from these values showed that activation energy of  $\text{Li}^+$  was larger than  $\text{ClO}_4^-$  ion, due to the large solvation structure. Above  $35^\circ\text{C}$ , thermal effect to the structure seems to be available, and the increase of  $t_{\text{Li}^+}$  was hindered. Therefore, the transport number measurement for the solid/liquid coexisting system was carried out from  $25^\circ\text{C}$  to  $35^\circ\text{C}$ . The transport number of lithium ion decreased with an increase of the specific surface area and a decrease of the liquid content. Therefore, the variation of  $t_{\text{Li}^+}$  with apparent average thickness of the liquid phase at various temperature is shown in Figure 2. The transport number

decreased as the apparent average thickness of the liquid phase decreased. It is suggested that the  $\text{Li}^+$  ion is influenced from the solid phase more intensively than anions. The apparent ionic mobilities decreased with the thickness of the liquid phase for both ions as shown Figure 3, however, the  $\text{Li}^+$  ion was influenced more than  $\text{ClO}_4^-$  ion. Consequently, The solid phase influences to each dissolving species separately.

### Reference

1) M. Mizuhata, G-J. Cha, Y. Harada, H. Kimura, A. Kajinami, and S. Deki, *International Symposium on Lithium Batteries*, 463-470 (1999).

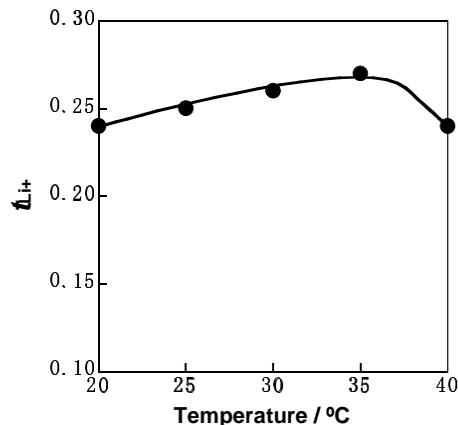


Figure 1. Temperature dependence of transport number of lithium ion. Concentration of  $\text{LiClO}_4$ : 0.1 M.

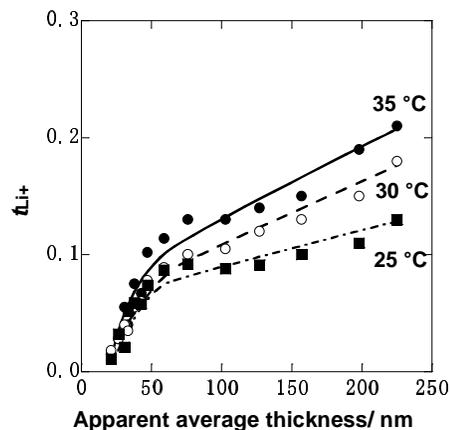


Figure 2. Variation of  $t_{\text{Li}^+}$  with apparent average thickness of the liquid phase. Concentration of  $\text{LiClO}_4$ : 0.1 M.

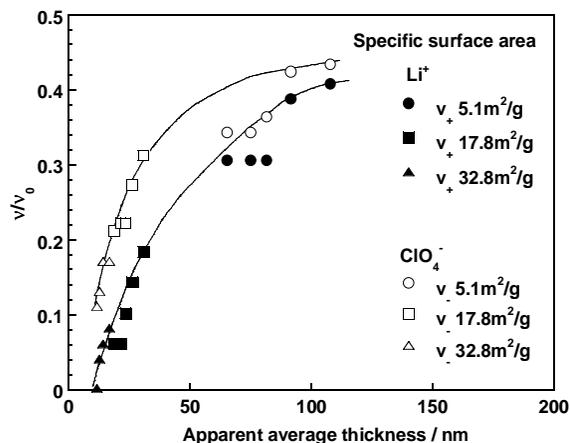


Figure 3. Variation of normalized apparent ionic motilities,  $v/v_0$ , with apparent average thickness of the liquid phase. Concentration of  $\text{LiClO}_4$ : 0.1 M.