The non-aqueous lithium electrolyte solution is a key material for the development of the Li batteries. The transport number of lithium ion is focused because the mobility of the lithium ion in the electrolyte is the important factor of the distribution of the lithium electrolyte in the cell and the reaction rate on the electrodes in the lithium batteries. Several techniques are employed or developed for the measurement of the transport number of lithium ion with the other ionic species; for example, the combination technique of ac impedance and dc polarization, cold neutron radiography, electrophoretic NMR, pulsed gradient spin-echo (PGSE) NMR, etc. The electrolyte solution is usually supported by a separator made of fibrous or porous membraneous 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 established the measurement of transport number of ionic species in lithium electrolyte solution using Hittorf’s cell(1). In this study, the transport number of the dissolved species in the lithium electrolyte with various solvent was measured and the influence of the solid phase to each dissolving species in the solution.

The transport number of lithium ion, $n_{Li^+}$, was measured by Hittorf’s method for the system LiClO$_4$-PC and GBL and their mixed solvent solution in the bulk system and the system coexisting with α-Al$_2$O$_3$ powder. The powder was dried by calcining at 500°C for 4 hours. Each 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 both electrode chambers were measured and the transport amount of the lithium ion was calculated. The potential probe was set between anode chamber and cathode chamber and the electrical conductivity was measured by four probe electrodes method. Apparent ionic mobilities were calculated from these results. The variation of transport number of lithium ion with the liquid content for α-Al$_2$O$_3$ powder/0.1M LiClO$_4$-GBL solution at 25°C are shown in Figure 1. The transport number of lithium ion decreased as the liquid content decreased and reached to the similar values for each systems and the difference among the systems for each solvent became smaller. It is suggested that the influence of the solid phase relatively increases with a decrease of the liquid content.

Since the transport number was calculated from the quantitative analysis of the ionic species in electrode chambers, the effect of the concentration gradient and electroosmosis. In the bulk system, the transport number increased with the measurement time; i.e., quantities of the electricity, because of the diffusion of ionic species. However, for the coexisting systems, the transport number showed the constant values.

Consequently, it is concluded that the transport number measurement using Hittorf’s method is available for the coexisting system containing powder and lithium electrolyte solution.

Reference