Ion transfer between lithium-ion conductive electrolytes under DC polarization

Fumihiro Sagane, Takeshi Abe, Yasutoshi Iriyama, and Zempachi Ogumi

Department of Energy & Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510

Lithium-ion batteries have high energy densities, and are widely used for portable devices, such as cellular phones, notebooks, and so on. And recently, a lot of studies have been made for their use in hybrid electric vehicle (HEV). For the use in HEV, lithium-ion batteries must possess high power densities, and therefore, fast charge and discharge reactions should be required. To enhance the reaction rates of lithium-ion batteries, lithium-ion diffusion in the electrodes and the electrolyte, and further the ion transfer at the electrode/ electrolyte interfaces are required to take place rapidly. Among them, we have focused on the lithium-ion transfer at the interface.

To understand the lithium-ion kinetics at the interface, we have fabricated the electrolyte/electrolyte interfaces, where only ion transfer occurs, and have found that the lithium-ion suffers large activation barrier to transfer at the interface[1)]. Here we report lithium-ion transfer at lithium-ion conductive solid/liquid interface under DC polarization to elucidate the ion transfer in more detail.

Li_2O-Al_2O_3-TiO_2-P_2O_5 based glass (supplied by OHARA Inc.) was used as the lithium-ion conductive electrolyte. Electrolyte solution was dimethyl sulfoxide (DMSO) containing 0.1 mol dm^{-3} LiI and I_2. The asymmetrical four-electrode-cell was fabricated and electrochemical impedance spectroscopy (EIS) under DC polarization was employed. The four-electrode-measurement was employed after obtaining steady state at each DC voltage.

Figure 1 shows the complex impedance plots of Pt / 0.1 mol dm^{-3} LiI+I_2-DMSO/glass electrolyte/0.1 mol dm^{-3} LiI+I_2-DMSO/Pt under OCV and ±50 mV polarization. Only one semi-circle appeared. In this system, the four impedance due to the ion transfer will appear, i.e., 1) the lithium-ion transport in the glass electrolyte, 2) the ion transport in the DMSO-based electrolyte, 3) the I^-/I redox impedance at the Pt/DMSO-based electrolyte interface, and 4) the lithium-ion transfer at the glass/DMSO interface. The first two components were identified by the impedance spectra obtained by the cell of Au/glass electrolyte/Au and Pt/LiI+I_2-DMSO/Pt, and the transport was sufficiently fast that no semi-circles but only spike appeared in the measuring frequency ranges. The I^-/I redox impedance doesn't appear because of the four-electrode measurements. Therefore, the semi-circle in Fig.1 was ascribed to the lithium-ion transfer at the glass/DMSO interface.

As is clear from Fig. 1, the radii of the semi-circles are changed by applied DC voltages, in the order of -50 mV > OCV (DC=0) > +50 mV. The potential was applied to glass electrolyte with reference to DMSO-based electrolyte. Accordingly, when the positive voltage is applied, lithium-ion transfers from the glass electrolyte to DMSO-based electrolyte, and for the negative voltage, the transfers from DMSO to the glass electrolyte occurs. Note that the lithium-ion transfer from the solid electrolyte to the electrolyte solution requires solvation, while the transfer from the electrolyte solution to the solid electrolyte involves de-solvation process. Based on these results and consideration, the charge transfer reaction of lithium-ion at the solid/liquid interface gives the larger resistances in the de-solvation process than those in the solvation process.

Acknowledgement

This work was supported by Grant-in-Aid for 21th century COE program - COE for a United Approach to New Material Science - from the Ministry of Education, Culture, Sports, Science and Technology.

References

1) T. Abe, M. Ohtsuka, F. Sagane, Y. Iriyama, and Z. Ogumi *J.Electrochem.Soc.* in press.

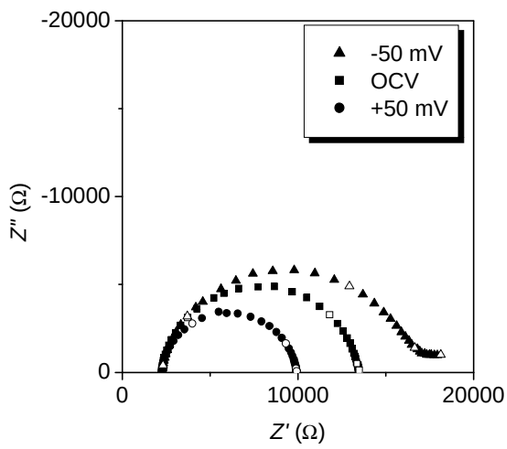

Fig.1 Complex impedance plots of Pt/LiI+I2-DMSO/glass electrolyte/LiI+I2-DMSO/Pt (4-electrode, 30 ^oC)