Discharge Condition Dependence of Reaction Distribution of Lithium Iron Phosphate Cathode

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In composite electrodes of lithium-ion batteries (LIBs), charge/discharge reaction proceeds with spatial inhomogeneity. The inhomogeneous reaction distribution is caused by electronic conduction pathways in the $LiFePO_4$ (LFP) cathode because of its poor electronic conductivity [1]. In this study, *in-situ* XAFS imaging analysis has been carried out under various conditions of temperature, electrolyte concentration, and discharge rate for the LIB cell with the LFP cathode. We have clarified the dependence of the discharge conditions on the reaction inhomogeneity.

Three Al-laminated LIB cells were prepared using LFP as the cathode active material and $LiPF_6$ solutions having different concentrations (1.0 M, 0.5 M, and 0.1 M) as the electrolyte solution. *In-situ* XAFS imaging measurements for the discharge process were carried out at some temperatures (28 °C, 40 °C, and 60 °C) and the discharge rates (0.2 C and 2 C) at BL-4 of the SR Center.

The K-edge energy (E_0) of Fe was determined using the XANES spectrum obtained at each pixel of the 2D detector, and the E_0 values were used to depict the chemical state map for the cathode at every discharge state. The effects of electrolyte concentration, temperature, and discharge rate on the reaction distribution were evaluated using the variation statistics of the E_0 values. The histograms for the 10 % discharged state were compared under 18 discharge conditions. In order to quantitatively evaluate the inhomogeneity of the reaction distribution, the variance of E_0 was calculated from the histogram Figure 1 shows the variance of E_0 for the 10 % discharged state at various conditions compared with that at fully charged state.

It was clarified that the variance of 2 C discharge was larger than that of 0.2 C discharge. The inhomogeneity of cathode reaction increases at the higher discharge rate for any temperatures and the electrolyte concentrations. It is considered that the inhomogeneity appears more prominently for the high-rate discharge process, because the electric current concentrates at the reaction channels with lower electrical resistance in the cathode composite.

Comparing the results of the 2 C discharge, it was clarified that the inhomogeneity becomes large at the higher temperature and the higher electrolyte concentration. The ion diffusion rates in the electrolyte solution are faster at higher temperature. The concentration gradient in the electrolyte solution, which contributes to prevent local reaction, quickly eliminates at higher temperature. As the result, the reaction inhomogeneity is considered to be emphasized. Similarly, at the higher electrolyte concentration, there are enough Li ions around the reaction channel supplied from the electrolyte solution, and it is thus considered that the discharge reaction proceeds continuously near the reaction channel. The remarkably inhomogeneous pattern appeared at higher temperature, the higher rate, and the higher concentration is ascribed by the electron and the ion conductivities.

We have evaluated quantitatively the inhomogeneous reaction distribution of the LIB cathode under various conditions by using the statistics of E_0 values obtained from XAFS imaging experiments. This approach succeeded in clarifying the effects of temperature, electrolyte concentration, and discharge rate to the reaction distributions

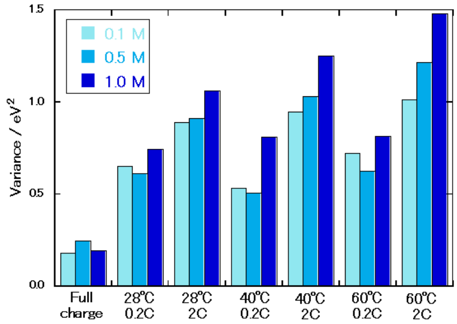

Fig. 1 Variance of E_0 for 10 % discharged states.

Reference

[1] M. Katayama, K. Sumiwaka, R. Miyahara, H. Yamashige, H. Arai, Y. Uchimoto, T. Ohta, Y. Inada, and Z. Ogumi, *J. Power Sources*, **2014**, *269*, 994.