Imaging XAFS analysis of high rate discharged $LiFePO_4$ Composite Electrode

Mayu Morimoto[1], Misaki Katayama[2], Yasuhiro Inada[1], Yuki Orikasa[1]
1) Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan
2) SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

As a cathode material of lithium-ion battery, lithium iron phosphate ($LiFePO_4$) exhibits high energy density with high structural stability for charge/discharge reaction. However, some reports have shown the inhomogeneous reaction during charge/discharge without homogenization [1-4], which can be observed in other typical cathode materials such as $LiCoO_2$. In the case of an inhomogeneous reaction, the charge/discharge current locally passes in the specific area, which generates the Joule heat, accelerates degradation, and affects the battery life. Therefore, it is extremely important in practical use to understand the mechanism of the inhomogeneous reaction. While the reaction distributions of $LiFePO_4$ electrodes have been reported to occur in the electrode plane direction [1-3], their experiments were performed at relatively slow rates, and the distribution phenomena during high rate charge/discharge have not been clarified. In this study, two-dimensional X-ray absorption (2D-XAS) study of the $LiFePO_4$ electrode which was charged/discharged at a high rate is reported.

Carbon-coated $LiFePO_4$ ($LiFePO_4$/C) was synthesized by the solid-state reaction method. Li_2CO_3, $Fe_2C_2O_4 \cdot 2H_2O$, and $(NH_4)_2HPO_4$ were mixed with the theoretical ratio in a planetary ball mill. Then 10wt% of acetylene black was added and further mixed. The obtained mixture was calcined at 800°C for 6 hours under 97%Ar-3%H_2. From XRD analysis, the main phase was LiFePO4 phase with a slight amount of FeO impurity.

For the charge/discharge measurements, $LiFePO_4$/C, acetylene black, and polyvinylidene fluoride were mixed at a ratio of 90:5:5 with 1-methyl-2-pyrrolidone. The slurry was coated onto an aluminum foil and dried in a vacuum oven at 80°C. The dried electrodes were roll-pressed at 4.7 kN. The prepared $LiFePO_4$ electrode, lithium metal, and electrolyte-soaked separator were constructed into a stainless steel flat cell. The electrolyte was a 1 mol dm^{-3} solution of $LiPF_6$ in ethylene carbonate/ethyl methyl carbonate (3:7 volume ratio). The cell construction process was performed in an Ar-atmosphere glove box. For 2D-XAS measurement, the $LiFePO_4$ electrodes were discharged at 5 C rate to the composition of $Li_{0.5}FePO_4$. As soon as the electrodes were discharged, they were removed from the cells, rinsed in dimethyl carbonate (DMC) and dried. 2D-XAS measurements were performed at the beam line BL-4 at SR center, Ritsumeikan University. The beam size was 4.4 (H) × 12.3 (W) mm^2. Fe *K*-edge XAS spectra of the $LiFePO_4$ electrodes were collected in transmission mode using a CMOS detector.

For charging to 3.8 V at 0.1 C, a capacity of 145 mA h g^{-1} was obtained. After that, the electrode was discharged for 75 mA h g^{-1} at 5 C. Figure 1 shows the 2D map of the absorption edge energy calculated from 2D-XAS measurement. In the previous report, it was shown that the reaction starts from the island-like point, however the result in this study shows the almost uniform reaction. The origin of this difference is currently under discussion. Further studies on the mechanism of reaction distribution are needed.

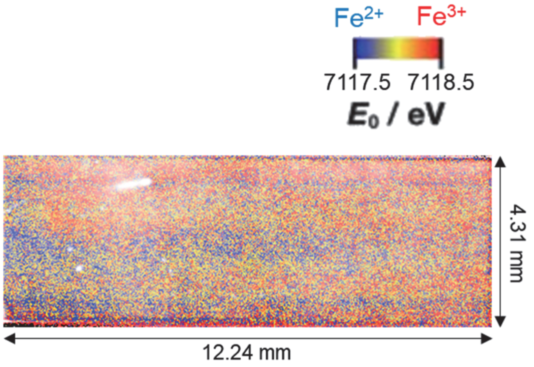

Fig. 1 2D-absorption energy map of $LiFePO_4$ electrode half-discharged at 5 C rate.

References

[1] G. Ouvrard et al, *J. Power Sources*., **2013**, *229*, 16-21.

[2] J. Liu, et al, *J. Phys. Chem. Lett.*, **2010**, *1*, 2120-2123.

[3] M. Katayama, et al, *J. Power Sources,* **2016***, 269*, 994-999.

[4] Y. Orikasa, et al, *Sci. Rep.*, **2016**, *6*, 26382.