Mem. SR Center Ritsumeikan Univ. No. 22, 27 (2020)

Charge–discharge Irreversibility of a $LiFePO_4$–$Li_4Ti_5O_{12}$ Full-cell

Yuki Omote[1], Misaki Katayama[2], Yuki Orikasa[1]

1) *Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*
2) *Research Organization of Science & Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*

Configuration of a half-cell using lithium metal for the negative electrode is commonly used in laboratory research on lithium-ion batteries, where the anode supplies sufficient carrier ions. By contrast, lithium metal is not placed in lithium-ion batteries for practical use. Instead, the full-cell configuration, wherein the capacity of the negative electrode to the capacity of the positive electrode is substantially the same, is used. In the full-cell, only limited lithium ions that are supplied from the positive electrode are utilized as carrier ions to govern the actual charge and discharge capacities. Previous studies have reported the differences in degradation between the half-cell and full-cell configurations (1,2). In practical use, it is important to understand the problems that occur with the full-cell to improve the battery performance based on the mechanism. In this study, the irreversible charge–discharge reaction in the full-cell was observed using a lithium iron phosphate $LiFePO_4$ positive electrode and a lithium titanate $Li_4Ti_5O_{12}$ negative electrode, which both exhibit a two-phase reaction in almost compositional regions. In addition to electrochemical measurements, we analyzed the charge–discharge state from the X-ray absorption fine structure (XAFS), which can observe a valence change.

The active metals, the acetylene black, and PVDF were mixed to achieve a weight ratio of 8:1:1. They were then coated on the aluminum foil current collector. 1M $LiPF_6$ (EC: EMC = 3:7 v/v%) was used as the electrolyte. In the two-electrode cell, the capacity of the negative electrode was excessed by about 10% compared with the positive electrode. In addition, the half-cell and the three-electrode cell were also examined. Ti and Fe K-edge XAFS measurements were performed at the beamline BL-3 in the Ritsumeikan University SR center. The charged and discharged electrodes were washed and measured in a transmittance mode.

In the constant-current charge/discharge test of the half-cell at a 0.1 C rate, $LiFePO_4$ and $Li_4Ti_5O_{12}$ were reversibly charged and discharged with a capacity of about 150 mA h g^{-1}. However, in our full-cell experiment, we observed significant irreversible capacity, with the capacity decreasing at each cycle. It was proven that the potential of $Li_4Ti_5O_{12}$ negative increased in the middle of the discharge, and the cutoff voltage was reached when the three-electrode cell was used. The potential change of positive and negative electrodes was tracked. It is presumed that there is a difference in the charge–discharge states between $Li_4Ti_5O_{12}$ and $LiFePO_4$ due to side reactions during charging–discharging.

The charge states of $LiFePO_4$ and $Li_4Ti_5O_{12}$ were analyzed from Fe K-edge and Ti K-edge XAFS. The electrodes having the same chemical compositions that were prepared by charging or discharging were compared. For Fe K-edge XAFS in $Li_{0.3}FePO_4$, as shown in Fig. 1 (a), the charged and discharged states agree with the electrochemically expected composition. However, the different charged and discharged states are observed for the $Li_{5.8}Ti_5O_{12}$ electrode, as shown in Fig. 1 (b). This result indicates that the electrochemical current is consumed by some side reactions.

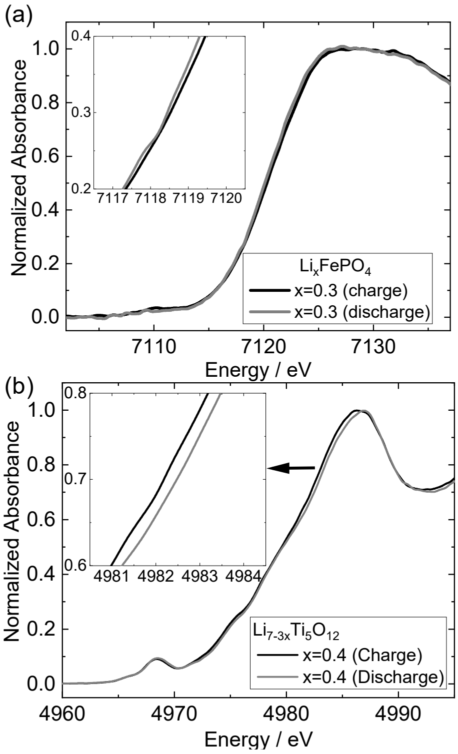

Fig.1 (a) Fe and (b) Ti K-edge X-ray absorption near the edge structure of charged and discharged electrodes using full-cell configurations.

References

(1) E. Bjorklund, et al., *J. Electrochem. Soc.*, **2017**, 164, A3054.
(2) J.H. Kim, et al., *Electrochem. Acta.*, **2013**, 90, 556.