

Surface Film Analysis of $\text{LiFePO}_4\text{-Li}_4\text{Ti}_5\text{O}_{12}$ Full Cell Showing Capacity Degradation

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For the academic research on lithium-ion batteries, charge–discharge measurements using half-cell configuration with lithium metal is generally used, whereas practical batteries adopt full-cell configuration without lithium metal. Full-cell test shows different degradation phenomena from half-cell because the limited lithium ions contained in the positive electrode [1,2]. In order to improve battery performance, it is important to understand the problems that occur in full-cell. In this study, as an extreme model case, reaction irreversibility proceeding to the initial cycle was examined in full-cell using lithium iron phosphate (LFP) and lithium titanate (LTO), which showed two-phase reaction in wide composition regions. We have already analyzed the charge/discharge state of each electrode in a full cell from X-ray absorption spectroscopy, which observed valence changes. Additionally, the electrochemical measurements using a three-electrode cell indicated that the irreversible reaction is caused in LTO under charge reaction [3]. In this study, to analyze the factors of side reactions of negative electrode, the difference in surface film was examined by F K-edge X-ray absorption fine structure (XAFS) of LTO negative electrode which carried out charge/discharge reaction.

For the electrode preparation, 80 wt% carbon-coated LiFePO_4 powder, 10 wt% acetylene black and 10 wt% Polyvinylidene-difluoride were mixed in 1-methyl-2-pyrrolidinone anhydrous solvent. These were then coated on an aluminum foil current collector at a thickness of about 20 μm . 1M LiPF_6 in a 3:7 volume ratio of ethylene carbonate (EC) and diethyl carbonate (EMC) was used as the electrolyte solution. In the full-cell, the capacity of the negative electrode was adjusted to be about 10 wt% excess compared with that of the positive electrode. In the positive electrode, LiCoO_2 (LCO) or LFP was used, and the half-cell using the lithium metal as the counter electrode was also examined. F K-edge XAFS of the charge-discharged LTO electrodes was measured by total electron yield mode and fluorescence mode at BL-11, Ritsumeikan University.

Fig. 1 shows F K-edge XAFS of the LTO-negative electrode after 10 cycles of charge-discharge reaction at 0.1 C by changing the combinations of the positive and negative electrodes. The observed structure contains the information from PVDF of the binder, LiPF_6 of the electrolyte salt, and the

contribution of LiF derived from the surface film. It is difficult to clearly distinguish them. However, the spectra after cycling did not show any change in the spectra with respect to the positive electrode in the total electron yield mode (Fig. 1(a)). The main peak coincided with the peak energy of LiF, and no difference in the positive electrode was seen in the spectrum of the fluorescence method (Fig. 1(b)). Therefore, it was suggested that the irreversible capacitance derived from the negative electrode caused only in LFP-LTO has a small contribution due to the film formation by the electrolyte decomposition.

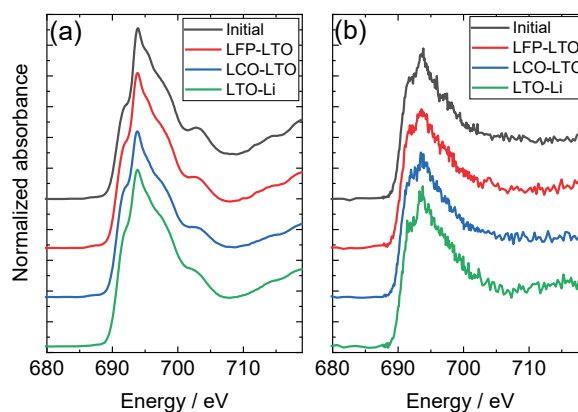


Fig. 1 F K-edge XAFS of LTO electrodes charged and discharged using various positive electrodes.

References

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