

Two-dimensional X-ray Absorption Analysis of Discharged LiFePO₄ Electrode In-plane Direction

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Demands for large-scale lithium-ion batteries for electric vehicles and grids have increased in order to reduce CO₂ emissions in consideration of the global environment. To improve the reliability for practical large-scale batteries, further improvements in safety, rate capability, and cycle life are required. One of the unique behaviors occurring in lithium-ion battery composite electrodes is an inhomogeneous reaction of active materials[1]. Since the heterogeneous reaction behavior induces overcharging and degradation of local active materials, the homogeneous charge–discharge reaction should be required. Ouvrard et al. reported that an inhomogeneous electrode reaction was caused during the charge–discharge process in LiFePO₄ lithium-ion battery cathode, which was detected using X-ray absorption spectroscopy[2]. The study concluded that the ionic and electronic connectivity influenced by applied pressure is a crucial parameter for reaction distribution in composite electrodes. In this study, we examine the commercially used composite electrodes. We compare the electrochemical characteristics using the commercial electrodes with self-made composite electrodes prepared in the laboratory and then measured the reaction distribution in-plane direction by imaging XAS.

Two types of composite electrodes using LiFePO₄ as the active material were used, and their thickness and mass loading were almost similar. Two electrode cells were assembled using 1 M LiPF₆ in a solvent mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a volume ratio of 3:7, and lithium counter electrode. Charge–discharge measurements were performed with an upper limit voltage of 3.8 V and a lower limit voltage of 2.0 V at rates of 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 C. Imaging XAS measurements using the half-discharged electrodes at 2.0 C were performed at beamline BL-4 in Ritsumeikan University SR Center. Fe K-edge XAS was measured in a transmission mode using a two-dimensional detector[3].

The discharge rate capability test indicated that the capacity retention of 5 C was 81% for the commercial electrode and 21% for the self-made electrode, compared with the discharge capacity at 0.05 C, and the self-made electrode showed a remarkable decrease in capacity at high

rates. The imaging XAS of the self-made electrodes implies a lack of inhomogeneous reaction after discharging at 2 C. This is due to the inhomogeneity of the composite, especially the distribution of the active materials.

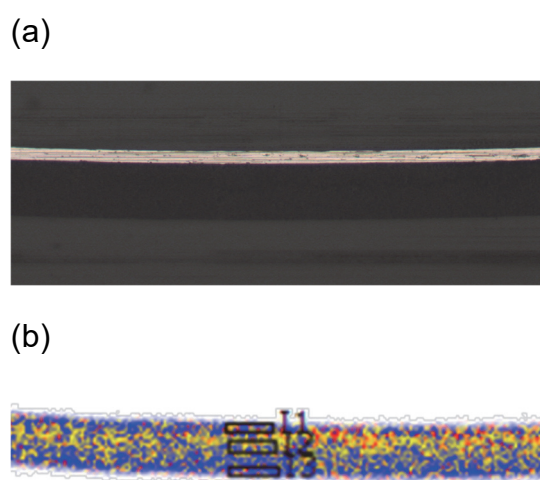


Fig. 1 (a) Scanning electron microscopic image in-plane direction of the self-made composite electrode half-discharged at 2 C. The thickness of the electrode is approximately 100 μm. The upper side is aluminum current collector. (b) Two-dimensional discharged state mapping of the self-made composite electrode in-plane direction. The blue corresponds to the discharged state.

References

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