

Reaction Distribution Analysis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in a Perpendicular Direction by Two-dimensional XAFS

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Thick composite electrodes may potentially increase the capacity and energy density of practical lithium-ion batteries. However, in a thick electrode, the charge and discharge capacity per active material is relatively small. This is due to the large number of inactive regions resulting from the low lithium-ion conductivity in composite electrodes, which causes reaction distributions in the direction from current collector side to separator sides to occur. In a previous study on composite electrodes with varying porosity of the LiFePO_4 electrode, the reaction distribution in the thickness direction was analyzed by imaging X-ray absorption fine structure (XAFS) [1,2]. In the vicinity of the current collector inside the electrode, the charge–discharge reaction proceeds with a delay, implying that the reaction distribution becomes heavier in thick electrodes. In this study, we measured the Ti K-edge imaging XAFS of a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative electrode in a direction perpendicular to the current collector.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (which was used as the active material), acetylene black, and PVDF were mixed at a weight ratio of 80:5:15 and coated on aluminum foil. The dried electrodes were roll-pressed at 9.0 kN. Electrode thicknesses of 44 and 189 μm with porosity of 32% were examined. Electrochemical measurements were performed using a two-electrode cell with a lithium counter electrode. 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a volume ratio of 3:7 was used as an electrolyte. To observe the inhomogeneity of the state of charge (SOC) perpendicular to the current collector, thin cross-sectional electrodes were prepared. After charging (lithium-inserting) to 60 mA h g^{-1} at a rate of 0.5 C, the cells were disassembled, washed, and the electrodes were dried. The electrodes were fixed with epoxy-resin and thinned by diamond wire saw. Ti K-edge imaging XAFS of the electrodes were measured at the beamline BL-4 in Ritsumeikan University SR center.

The theoretical capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is 175 mA h g^{-1} , which we observed for the charge–discharge at a low rate. As for the rate capability test, the capacities of the 44 and 189 μm electrodes at a rate of 5 C were 20 and 0 mA h g^{-1} , respectively. The decrease in capacity at a higher rate was notable as the electrode thickness increased.

Figure 1 maps the absorption edge energy

obtained from two-dimensional imaging XAFS for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes. In $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes, since titanium is reduced by lithium intercalation, the absorption edge energy at the Ti K-edge is shifted towards the low energy side. Therefore, the mapping of the absorption edge energy corresponds to the mapping of SOC. Although we expected to observe distribution for the 189 μm electrode due to the poor rate capability, we did not observe this. This result does not agree with a previous study where the cutting procedure did not include a wet process [3].

In order to investigate why the inhomogeneous reaction was not observed, we measured the XAFS of the electrodes for the planer direction with different SOC. The electrodes were charged for 0, 117, and 145 mA h g^{-1} and were then disassembled and air dried. The edge energy of the samples handled in the atmosphere did not change. We presume that this is because Ti^{3+} was not preserved but was oxidized from Ti^{3+} to Ti^{4+} by humidity in the air. The redox potential of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is approximately 1.5 V vs. Li/Li^+ , which is converted to -1.48 V vs. the standard hydrogen electrode. The charged state easily reacts with moisture in the atmosphere and is not maintained. Therefore, the XAFS measurement of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ without exposure to air is required for the analysis of the reaction distribution.

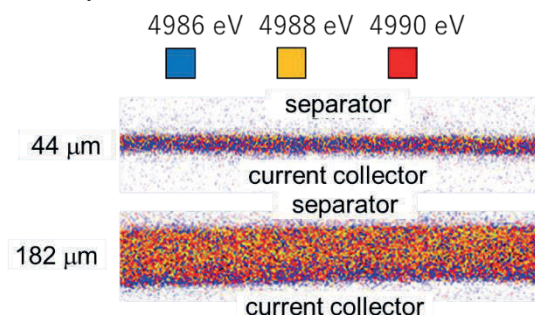


Fig. 1 Mapping of X-ray absorption edge energy at Ti K-edge of the charged $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes.

References

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