

Two-dimensional X-ray Absorption Analysis of Inhomogeneous Charge-discharge Behavior in $\text{Li}_4\text{Ti}_5\text{O}_{12}$

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For the improvement of the practical energy density of the lithium-ion battery, the utilization of thick composite electrodes is one of the choices in the research and development. However, it is a challenge to realize the practical charge-discharge operation using thick electrodes, because the charge-discharge capacity per active material is not improved. This is because the increased inactive region of active materials in composite electrodes due to low effective lithium-ion conductivity in the composite electrodes [1]. Although many researchers recognize the fact that such a reaction distribution is one of the factors governing battery performance, the reaction distribution analysis is still challenging, especially during battery operation. While the reaction distribution of composite electrodes showing sloping voltage profile is relaxed, the electrode exhibiting flat profile holds the reaction distribution along the depth direction². In this study, we investigate the reaction distribution in thick $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite electrode where two-phase reaction proceeds by using two-dimensional X-ray absorption spectroscopy.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ was synthesized by solid-state reaction. Li_2CO_3 and TiO_2 were mixed in a ball mill with acetylene black, and then the mixture was calcined at 800°C in an argon atmosphere. For electrode preparation, 80 wt% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder, 5 wt% acetylene black and 15 wt% PVDF were mixed in 1-methyl-2-pyrrolidinone anhydrous solvent, which was coated on an aluminum foil and dried in a vacuum oven. The thickness of the pressed electrode was from 56 micrometers to 119 micrometers. 1 M LiPF_6 in EC: EMC (3: 7 vol%) solution was used as the electrolyte. The galvanostatic charge-discharge measurements between 1.0 and 2.5 V at room temperature were performed. To analyze the reaction distribution of the composite electrodes in the depth direction, two-dimensional X-ray absorption measurements were performed at the beamline BL-4 in SR center, Ritsumeikan University³. Ti K-edge XAS spectra of the cross-sectional electrodes were measured in a transmission mode using a CMOS detector.

We investigated the thickness dependency on the rate capability of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode. The charge capacity at 5C rate of the 119-micrometer electrode is less than 30% of the theoretical capacity. However, for the 56-micrometer electrode, 80% of the theoretical charge capacity exhibits even at 5C rate.

Using the half charged composite electrodes at 2C rate, the reaction distribution analysis was performed. The previous study reported the Ti K-edge X-ray absorption edge of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is shifted during charge-discharge reaction⁴. Figure 1 shows the mapping of the absorption edge energy, corresponding to the state of charge in $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The state of charge in the depth direction at the 56-micrometer electrode is almost uniform. On the other hand, the unreacted part near current collector side reaction is observed. The inactive part of the thick electrode caused by poor ion supplying contributes the decreased rate capability.

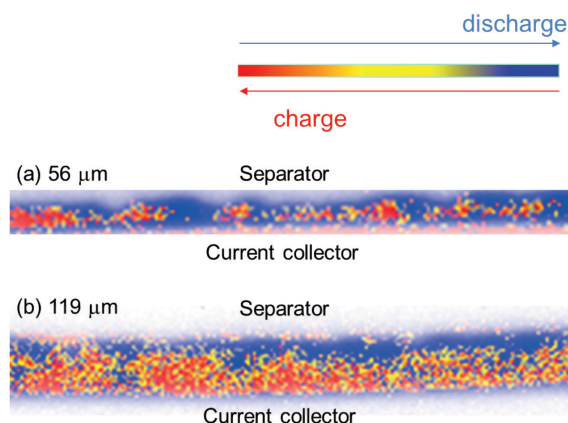


Fig. 1 Two-dimensional chemical state map of (a) 56 mm and (b) 119 mm $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite electrodes after 50% charge at 2C rate.

References

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