

EELS characterization of Li-inserted spinel lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$

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Introduction

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is one of the most important ceramics as an anode material for the Lithium ion battery, due to its excellent properties such as long life cycle and high rate charge-discharge performance. These properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are explained from the crystal stability during Li intercalated/de-intercalated processes [1]. Thus the crystal structure changes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by the Li insertion have been studied intensively, and it has been revealed that Li moves from 8a site to 16c site of spinel during electrochemical Li insertion, and that spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is transformed into $\text{Li}_7\text{Ti}_5\text{O}_{12}$ with ordered rock-salt structure. However, the details of electronic structure and chemical states of Li-inserted $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are not yet clear, and it is important to reveal the mechanism of the electrochemical reaction. In this study, we perform electron energy-loss spectroscopy (EELS) characterization of Li-inserted $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and investigate the difference between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li-inserted one from Li-K, Ti-L and O-K edge spectra.

Experiment

Li-inserted $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared by Li-doping method as follows: $\text{Li}_4\text{Ti}_5\text{O}_{12}$ wafer was contacted with a Li metal in electrolyte solution (1M LiPF₆, EC/DMC = 1.0) and the sample was rinsed by DMC to wash away the electrolyte composition. After the Li doping, the color of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was turned from white to black as done by the electrochemical reaction. All the EEL spectra were acquired by TEM (JEM-3000F) equipped with GIF at 100kV. The energy spectrum resolution was 0.6eV, evaluated by a half-wide value of zero-loss peak.

Result and discussion

Figure 1 (a) shows Ti-L edge EEL spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li-inserted sample. In the spectrum of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, we can see clearly four main peaks derived from Ti^{4+} L_3 and L_2 edges [2], while the spectrum of the Li-inserted sample shows only two main peaks derived from Ti^{3+} . This result indicates the reduction of $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ by the electrochemical reaction. Figure 1 (b) shows the EEL spectra of Li-K edge region. Both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li-inserted sample show a clear peak at 58.5 eV, identified as the Li-K edge. However, the intensity of these two peaks was not equal. Here, we estimated the intensity ratio of these two spectrum peaks by normalized Ti-M peak intensity. The intensity ratio is about 1.9, which is similar to the ideal ratio of the Li contents in the two materials before and after the Li-inserted reaction as $\text{Li}_7\text{Ti}_5\text{O}_{12}/\text{Li}_4\text{Ti}_5\text{O}_{12} = 1.75$. This indicates that the Li-insertion reaction certainly occurred and that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was transformed into $\text{Li}_7\text{Ti}_5\text{O}_{12}$ phase by the present Li doping. On the O-K edge spectra in figure 1 (c), both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li-inserted sample similarly show two pronounced peaks at 532 eV and 534 eV, which reflect the O 2p contributions, hybridized with the Ti 3d states with the $t_{2g}-e_g$ splitting [3]. On the other hand, the peaks in the higher

energy region, originated from the mixing between the O p orbitals and Li s orbital, are quite different for the two materials. This suggests that the Li-inserted sample should have different Li-O bonding structures from original $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

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References

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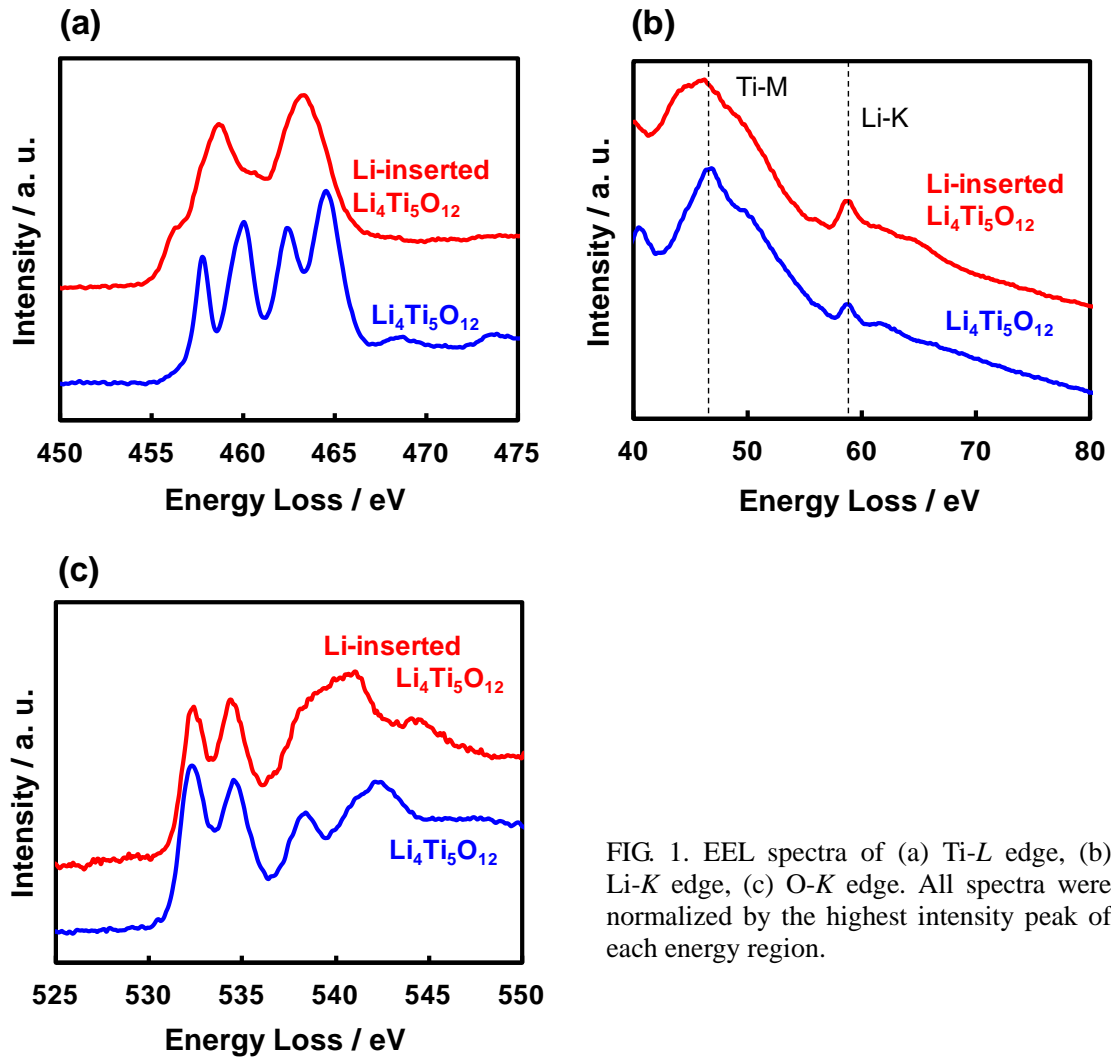


FIG. 1. EEL spectra of (a) Ti-L edge, (b) Li-K edge, (c) O-K edge. All spectra were normalized by the highest intensity peak of each energy region.