

## XAS study of intercalation mechanism of electrode materials with the hollandite-type structure

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### 1 Introduction

Titanium dioxide with hollandite-type structure has been investigated as one of the negative electrode materials for secondary lithium batteries [1,2]. As Fig. 1 depicts, the hollandite-type  $\text{TiO}_2$  has a tunnel structure comprising double chains of  $\text{TiO}_6$  octahedra forming  $(2 \times 2)$  tunnels, which are privileged pathways for  $\text{Li}^+$  ion diffusion as well as large spaces for Li storage. The hollandite-type  $\text{TiO}_2$  samples include cationic residues such as  $\text{K}^+$  ions in their  $(2 \times 2)$  tunnels. The residual cations impede the insertion of  $\text{Li}^+$  ions in the tunnels during charge–discharge operation. We have recently succeeded in the synthesis of the sufficiently  $\text{K}^+$ -extracted hollandite-type  $\text{TiO}_2$  specimen by the ion extraction method using aqua regia [1,2]. The  $\text{K}^+$ -extracted hollandite-type  $\text{TiO}_2$  specimen worked as a rechargeable electrode material with a rechargeable capacity of about 150 mAh/g over the 50 cycles [1,2]. In this work, we examined the K extraction and Li intercalation mechanisms by X-ray absorption spectroscopy (XAS).

### 2 Experiment

The hollandite-type  $\text{K}_x\text{TiO}_2$  specimens were prepared by the solid state reaction. Mixtures of  $\text{K}_2\text{CO}_3$  and  $\text{TiO}_2$  powders were calcined at 1000 °C for 8 h under  $\text{H}_2/\text{Ar}$  atmosphere. To extract  $\text{K}^+$  ions from the tunnel structure, the resultant specimens were then treated by HCl or HCl/ $\text{HNO}_3$  solutions. Further details of the sample preparation of the specimens have been reported in previous works [1,2].

Composite working electrodes consisted of 80 wt % hollandite-type  $\text{TiO}_2$ , 15 wt % acetylene black, and 5 wt % polyvinylidene fluoride, pasted on Al foil as a current collector. The electrolyte solution used was 1 mol/dm<sup>3</sup>  $\text{LiPF}_6$  dissolved in blended ethylene carbonate (EC) and diethyl carbonate (DEC) at a volumetric ratio of 1:1. Electrochemical testing was conducted using coin cells with Li foils as counter electrodes. The coin cells were assembled in an Ar-filled glovebox and cycled at a rate of 10 mA/g. After the electrochemical tests, composite electrodes were taken out from the cell, and were then rinsed with DEC and sealed in a gas barrier film in the Ar-filled glovebox.

The XAS spectra of powder specimens and hermetically-sealed electrodes were measured by transmission mode using synchrotron radiation at beamline BL-9C of Photon Factory in KEK. The computer program, ATHENA, [3] was used for the analysis of the XAS data.

### 3 Results and Discussion

Figure 2 shows Ti K-edge X-ray absorption near-edge structure (XANES) spectra of the  $\text{K}_x\text{TiO}_2$  powders after  $\text{K}^+$  extraction and the  $\text{TiO}_2$  electrodes under initial  $\text{Li}^+$  insertion-deinsertion. As Fig. 2(b) presents, XANES spectra were slightly shifted after  $\text{K}^+$  extraction. This finding shows that  $\text{K}^+$  ions in the tunnel space were extracted by oxidation of Ti rather than ion-exchange mechanism. As Fig. 2(b) shows, evidence of reduction to lower valent Ti ions after  $\text{Li}^+$  insertion was detected by the XANES spectra. The mean valence state of Ti at 1.0 V is above 3+ because the chemical shift of the spectrum was between those of  $\text{TiO}_2$  and  $\text{Ti}_2\text{O}_3$ . After  $\text{Li}^+$  deinsertion up to 3.0 V, the XANES spectrum agreed fairly well with initial spectrum at OCV. These findings were consistent with the excellent charge-discharge property of the hollandite-type  $\text{TiO}_2$  electrode [1,2].

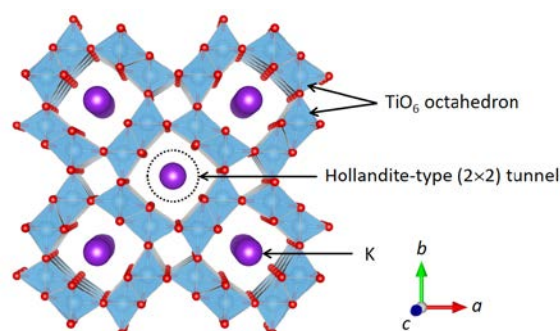


Fig. 1: Crystal structure of the hollandite-type  $\text{K}_x\text{TiO}_2$ .

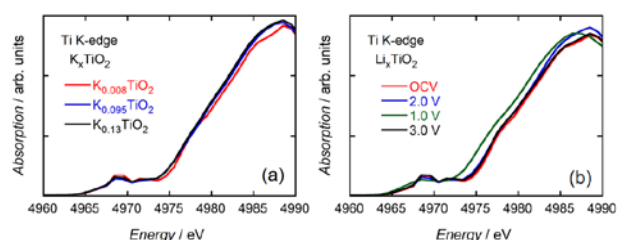


Fig. 2: Ti K-edge XANES spectra of (a) the  $\text{K}_x\text{TiO}_2$  powders after  $\text{K}^+$  extraction and (b) the  $\text{TiO}_2$  electrodes under initial  $\text{Li}^+$  insertion-deinsertion.

### References

- [1] M. Sakao et al., *Solid State Ionics* **225** (2012) 502.
- [2] M. Sakao et al., *Solid State Ionics* **243** (2013) 22.
- [3] B. Ravel and M. Newville, *J. Synchrotron Radiat.* **12** (2005) 537.

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