

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

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### 1 Introduction

Hollandite-type oxides have a tunnel structure comprising double chains of  $MO_6$  ( $M$ =metal) octahedra forming  $(2 \times 2)$  tunnels, as depicted in Fig. 1. These large  $(2 \times 2)$  tunnels are privileged pathways for  $Li^+$  ion diffusion. Therefore, several oxides with hollandite-type structure work as electrode materials for lithium ion batteries [1,2]. We have recently succeeded in the synthesis of the  $K^+$ -extracted hollandite-type  $K_xTi_{0.9}Nb_{0.1}O_2$  specimens for the first time. In this work, we examined the  $K$  extraction and  $Li$  intercalation mechanisms by X-ray absorption spectroscopy (XAS).

### 2 Experiment

The hollandite-type specimens were prepared by the solid state reaction. Mixtures of  $K_2CO_3$ ,  $TiO_2$ , and  $Nb_2O_5$  powders were calcined at 1200 °C for 1 h under  $H_2$  atmosphere. To extract  $K^+$  ions from the tunnel structure, the resultant specimens were then treated by piranha solution at 80 °C for 4 h.

Composite working electrodes consisted of 80 wt % hollandite-type specimen, 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>  $LiPF_6$  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, which 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 and Nb K-edge X-ray absorption near-edge structure (XANES) spectra of the  $K_xTi_{0.9}Nb_{0.1}O_2$  powders before and after  $K^+$  extraction. As Fig. 2 presents, XANES spectra were slightly shifted after  $K^+$  extraction. This finding shows that  $K^+$  ions in the tunnel space were extracted by oxidation of both Ti and Nb rather than ion-exchange mechanism.

Figure 3 presents Ti and Nb K-edge XANES spectra of the  $K_{0.03}Ti_{0.9}Nb_{0.1}O_2$  electrode under initial  $Li^+$  insertion-deinsertion. As Fig. 3 shows, evidence of reduction to lower valent Ti and Nb ions after  $Li^+$  insertion was

detected by the XANES spectra. The mean valence state of Ti at 1.0 V is between 3+ and 4+. On the other hand, the valence state of Nb at 1.0 V is about 4+ because the chemical shift of the spectrum was close to  $NbO_2$ . After  $Li^+$  deinsertion up to 3.0 V, the XANES spectra agreed fairly well with initial spectra at OCV, which were consistent with the excellent charge-discharge property of the hollandite-type  $TiO_2$  electrode.

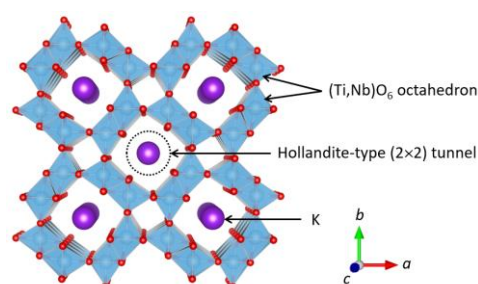


Fig. 1: Crystal structure of the hollandite-type  $K_xTiO_2$ .

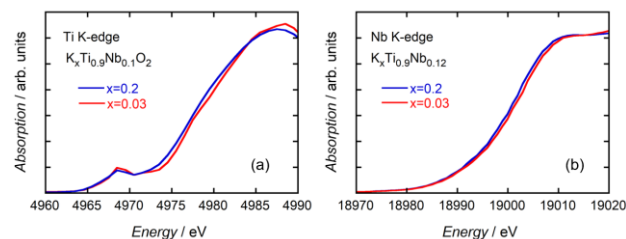


Fig. 2: (a) Ti K-edge and (b) Nb K-edge XANES spectra of the  $K_xTi_{0.9}Nb_{0.1}O_2$  ( $x=0.2$  and  $0.03$ ) powders before and after  $K^+$  extraction.

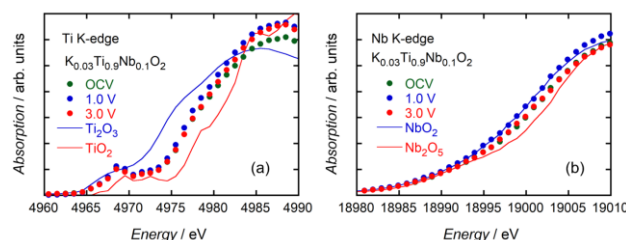


Fig. 3: (a) Ti K-edge and (b) Nb K-edge XANES spectra of the  $K_{0.03}Ti_{0.9}Nb_{0.1}O_2$  electrode during the initial  $Li^+$  insertion-deinsertion.

### References

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