

# Charge Compensation Analysis of $\text{TiTe}_2$ Electrode for All-Solid-State Silver Secondary Batteries Using X-ray Absorption Fine Structure Measurement

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All-solid-state secondary batteries have one of the candidates for post lithium-ion batteries. For the further development, it is necessary to analyze the diffusion behavior of the carrier ions during charge-discharge. However, the detection of lithium-ion is challenge by X-ray technique due to light-element. In contrast, silver-ion conductors which contain heavy elements are known as superionic conductors that exhibit high ionic conductivity at room temperature. For the X-ray analysis, the behavior of silver ions can be easily detected. Therefore, as a model case of an all-solid-state secondary battery, the analysis of silver secondary battery can provide useful information. For the operation and analysis of the all-solid-state silver battery, the positive electrode active materials which exhibit stable charge-discharge properties is needed. Although the  $\text{TiTe}_2$  active material has been reported as the electrode for an all-solid-state silver battery<sup>1</sup>, the charge compensation mechanism is not understood when silver ions insert into  $\text{TiTe}_2$  and extract from  $\text{Ag}_x\text{TiTe}_2$ . In this study, we investigate the charge compensation mechanism of  $\text{TiTe}_2$  electrode using XAFS measurement.

For the assembly of the all-solid-state silver battery cell,  $\text{Ag}_6\text{I}_4\text{WO}_4$  was used as a solid electrolyte. A mixture of Ag and the electrolyte (1:1 wt%) was used as a negative electrode, and a mixture of  $\text{TiTe}_2$  active material, acetylene black and electrolyte (10:10:1 wt%) was used as a positive electrode. The insertion and extraction reaction of  $\text{Ag}^+$  into  $\text{TiTe}_2$  was performed by charge and discharge at a constant current of 0.2C. The lower and upper cutoff voltages were 0 V and 0.35 V, and three samples; after 1st discharge, 1st charge and 2nd discharge were prepared. The cells were disassembled promptly after charging and discharging in an Ar-filled glove box. As a comparison, a pristine positive electrode powder was also investigated. For these four samples, the XANES measurements at a total electron yield mode were carried out at the Ti  $L_{3-}$ ,  $L_{2-}$ edge at BL-2 in SR Center, Ritsumeikan University.

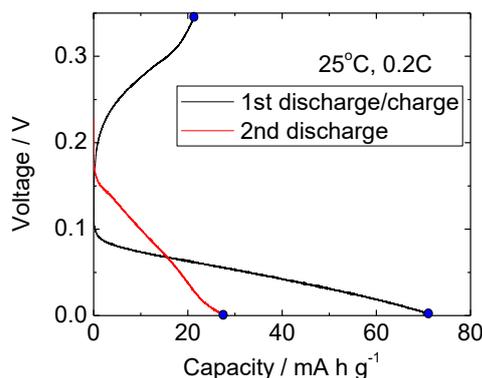
Fig. 1 shows charge and discharge curves of  $\text{Ag}|\text{Ag}_6\text{I}_4\text{WO}_4|\text{TiTe}_2$  cell at 25°C. In the first cycle of discharge, about 0.8 moles of Ag is inserted in  $\text{TiTe}_2$ , but only 0.3 moles of Ag is extracted in charging. Therefore, about 0.3 moles of Ag is

reversibly inserted and extracted with  $\text{TiTe}_2$ .

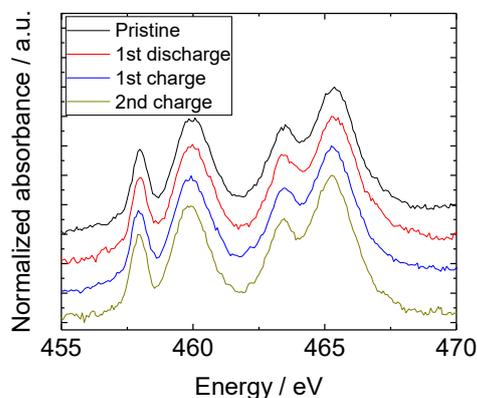
Ti L-edge XANES spectra of each sample is shown in Fig. 2. When the charge compensation is carried out by using Ti-3d orbital, the significant change should be observed in Ti L-edge XANES. However, no change is observed among these four samples, implying no contribution of Ti-3d orbital of charge-discharge reaction in  $\text{TiTe}_2$ . Therefore, the charge compensation accompanying intercalation of Ag to  $\text{TiTe}_2$  occurs with transferring electrons into Te orbital. Unfortunately, in Te  $M_{5-}$ edge XANES measurements, no clear peak was observed. The utilization of hard X-ray measurement should be considered.

## References

(1) Y. G. Guo, Y. Hu, J. Lee, J. Maier, *Electrochem. Comm.*, **2015**,8, 1179.



**Fig. 1** Voltage profile of  $\text{Ag}|\text{Ag}_6\text{I}_4\text{WO}_4|\text{TiTe}_2$  cell at 25°C. The blue circle shows the state of each sample on which XANES measurement was performed.



**Fig. 2** The Ti L-edge XANES spectra of charged-discharged  $\text{TiTe}_2$ .