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An In Situ Synchrotron X-ray Diffraction Study of TiO_2(B) Electrode upon Lithium Insertion

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1 Introduction

We have reported that the mesoporous carbon-titania composite materials produced by a tri-constituent coassemble sol-gel method have very good rate performance as Li ion anode materials [1]. It was found recently that the composites include a considerable amount of TiO_2 (B) phase and thereby it is indicated that the TiO_2 (B) phase is a key material for the good rate performance. However, the detailed Li ion storage mechanism of the TiO_2 (B) phase is not understood well. Then we performed in situ X-ray diffraction experiment of TiO_2 (B) phase during Li ion insertion and extraction in order to know the structural change of TiO_2 (B) phase with Li ion content.

2 Experiment

TiO_2 (B) phase sample was prepared by dehydration of $H_2Ti_4O_9$. The electrochemical cell having diamond windows specially designed for the in situ synchrotron XRD measurement was used. The TiO_2 (B) phase sample was mixed with polyvinylidene difluoride (PVDF) and the mixture coated on a Cu wire mesh was used as a working electrode. Li metals were used as a reference and counter electrode. Charge-discharge experiments were done in a potential range of 3.0-1.3 V with constant current density of 30-50 mA/g. In situ synchrotron XRD measurement was performed at a beam line BL-18C of KEK. High energy X-ray of 20 keV was used as an incident beam and an imaging plate was used as a detector.

3 Results and Discussion

We could observe more than 20 XRD patterns during one charge-discharge process (XRD data were observed at the potentials marked in Fig. 1). The qualities of the obtained XRD data are good enough for us to perform Rietveld analysis. Fig. 2 shows the determined lattice parameter *a* as a function of capacity (i.e. as a function of the inserted Li ions). Other lattice parameters were also determined in the same manner. The length of the *a*-axis and *b*-axis gradually increased with lithium insertion, while that of the *c*-axis and angle-β were almost constant during lithium storage. Observing the figure carefully, we find that the changes in the cell parameters were not monotonous. In case of the *a*-axis, step-like changes were observed at around 120 mAh g^{-1} (~1.57 V vs. Li/Li^+) and 160 mAh g^{-1} (~1.52 V vs. Li/Li^+). Similarly, in case of *b*-axis, the expansion slopes also changed at those points. These points were approximately matched with the plateau potentials in Fig. 1.

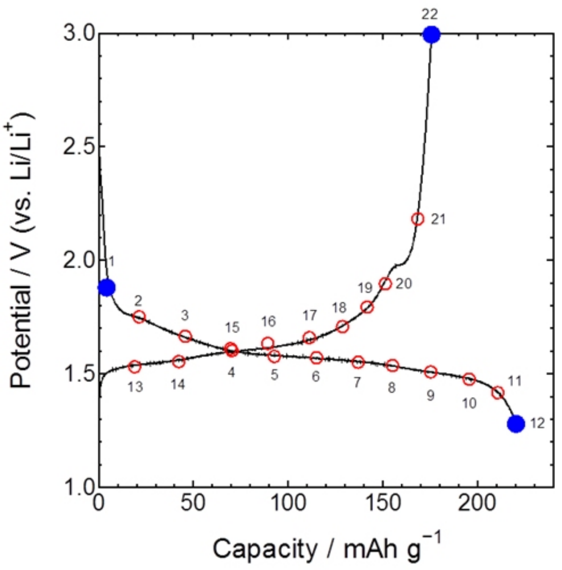

Fig. 1: Galvanostatic charge-discharge curves of the bulk TiO_2(B) electrode in the first cycle. The current density was set to 50 mA g^{-1}.

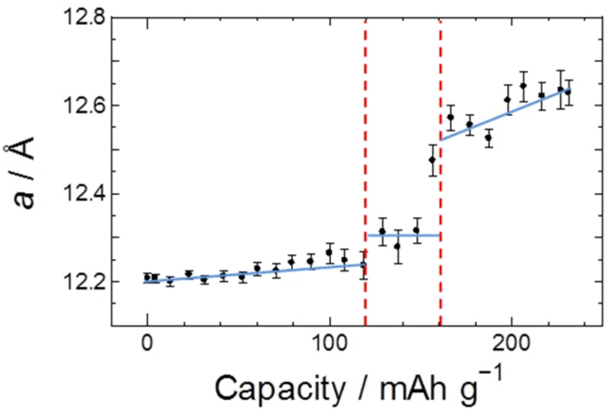

Fig. 2: Changes in lattice parameter *a* of TiO_2(B) upon lithium insertion.

Reference
[1] Y. Ishii, *et al.*, J. Phys. Chem. Solids, **71**, 511, (2010).

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