

A new observation of reaction mechanism and structure analysis of mesoporous SnO₂ by using synchrotron X-ray techniques

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Abstract

Graphitic carbon is widely used as anode material due to its low cost, good cycle life, and very stable capacity in most commercial lithium-ion batteries (LIBs). However, capacity of carbon anode (372mAh/g and 830mAh/mL) is limited by the reversible electrochemical intercalation of lithium ions in its structure. So, the search of new anode material has been ongoing to achieve the higher capacity. SnO₂ has been widely studied in the last decade as one of the potential candidates for anode materials due to its higher specific lithium storage capacity (783mAh/g). But, its poor capacity retention over long-term charge-discharge cycling has prevented its use as commercial anode material in LIBs. This problem has been associated with its alloying reaction which results in large volume changes of electrode material during electrochemical cycling. SnO₂ reacts with lithium according to the two following reactions. (1) $\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O}$ (Conversion reaction; 711mAh/g), (2) $\text{Sn} + x\text{Li}^+ + x\text{e}^- \rightarrow \text{Li}_x\text{Sn}$ ($0 < x < 4.4$) (Alloying reaction; 993mAh/g of Sn or 783mAh/g of SnO₂). SnO₂ has a theoretical reversible capacity of 783mAh/g (eq.(2)). An irreversible conversion reaction occurs prior to the alloying reaction, which results in the reduction of SnO₂ to Sn and formation of a Li₂O matrix. Li₂O is not decomposable, so charge capacity of 711mAh/g (eq.(1)) associated with this reaction becomes irreversible.

We studied mesoporous SnO₂ electrode material because of its better electrochemical properties. Mesoporous SnO₂ was synthesized by sol-gel method by using the KIT-6 template. SEM & EDS were used to confirm the successful synthesis of this electrode material. Additionally, we performed diverse electrochemical tests such as EIS, GITT and cyclic voltammetry. In this work, we have tried to explain the electrochemical reaction mechanism of mesoporous SnO₂ by using *ex situ* X-ray Diffraction (XRD) and X-ray Absorption Spectroscopy (XAS) during cycles. Before the experiment, we were subdividing points in discharge/charge curves. Fig. 1 (a) shows *ex-situ* XRD patterns during 1st discharge of mesoporous SnO₂ which clearly show that SnO₂ structure changed into amorphous phase after point 4. Upon discharging below 0.2V amorphous SnO₂ phase converts into metallic phases which are indicated by broad peaks around 22 and 38 degree. To further study the mechanism we carried out *ex-*

situ XAS measurements on mesoporous SnO₂ anode samples (Fig. 1 (b)). The peaks at 1.59Å and 2.60Å in the Fourier transform spectrum of extended X-ray absorption fine structure (EXAFS) represent Sn-O bond and Li-Sn bonds, respectively. Irreversible capacity during first cycle of SnO₂ is related to conversion reaction and Li_{4.4}Sn is formed as a product of alloying reaction. Sn-O peak intensity was decreased gradually by progressing discharge and Li-Sn peak was revealed by alloying reaction after point 3. However, we can confirm new phase was appeared last region of discharge. Through this new phase, we can demonstrate that last region of discharge was not Li_{4.4}Sn phase.

Moreover, through the EXAFS data of the 1st charge, we can verify the existence of Sn-O bond of conversion reaction at the last region and conversion reaction is associated with capacity of mesoporous SnO₂ after initial discharge. These results were related to high performance of mesoporous SnO₂ and more detailed discussion will be presented at the time of meeting.

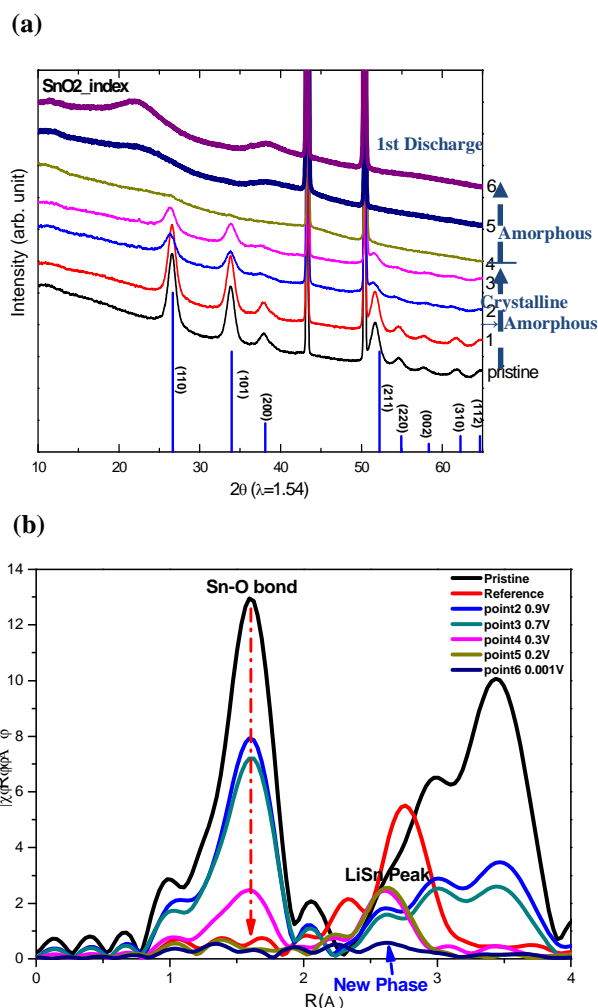


Fig.1 The *ex-situ* patterns of (a) X-ray Diffraction (XRD) (b) EXAFS (Fourier transforms (FTs) of the k^3 -weighted Sn K-edge EXAFS taken during the discharge. FT range is 2.0 – 13.8 Å⁻¹) of X-ray Absorption Spectroscopy (XAS) in subdivision of 1st discharge cycle.

Reference

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