Operando Analysis of Silicon Anode for Lithium Ion Battery Using Soft X-ray Absorption Spectroscopy

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Abstract:

Operando soft X-ray absorption structure (XAS) measurement has been developed to observe Li-Si alloying process under battery charge. An electrochemical cell was fabricated for XAS study and a series of XAS spectra of the Si negative electrode during charge process were observed. Changes in Si K-edge XAS spectra indicated that Si was lithiated by the step reaction via the intermediate phase $Li_{1.6}Si$ rather than the gradual lithiation. This is the first evidence on the direct visualization of the chemical variation of Si.

1. Introduction

Since lithium ion batteries have a high energy density per unit weight, they are widely used not only in mobile phones, laptop computers and other mobile devices, but also in machinery in which a large scale and high energy density are required, such as electric vehicles (EVs). Research and development are currently being carried out targeting higher capacity, higher output, higher durability and lower cost, focusing on the active materials of the cathode and anode, separators, electrolytes, additives and other battery components[2]. Against graphite as a common active material for anodes, Si-based anode active materials (hereinafter, silicon electrodes) have attracted attention from the viewpoint of realizing higher capacities (roughly 10 times larger than graphite) in the next-generation lith-

ium ion batteries. However, since Si particles are refined by the expansion and contraction that occur during Li insertion/extraction in the charging/discharging process, deconstruction of the conductive structure in the anode and a resulting decrease in capacity is an issue which causes in limited applications of Si.

Among silicon electrodes, crystalline Si has attracted considerable attention, and various techniques have been adopted to cope with expansion/contraction of crystalline Si to enable use as an anode material. These include addition of an additive to the electrolyte to form a stable film (solid electrolyte interphase: SEI) on the refined Si surface[3], or the use of nanoparticles of crystalline Si as the anode to minimize the refinement caused by expansion/contraction.

A number of methods have been applied to understand the mechanism of the charge/discharge process of Si electrodes. However, most of analyses have been based on the technique of dismantling batteries in designated charged and discharged states and removing and analyzing the electrodes. Thus, the discussion of the nonequilibrium states during operation as a storage device is inadequate. Crystal structure during battery operation can be analyzed by the X-ray diffraction method[4], but because crystalline Si changes to amorphous during charging, this method is not available to the Si in the amorphous condition. The chemical state of Si can be investigated by using EELS (Electron Energy Loss Spectroscopy) and/or XAS (X-ray

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Absorption Spectroscopy) with regardless of its crystallinity. In particular, the chemical state of the anode during battery operation can be investigated directly by XAS by utilizing the penetrating power of X-rays. However, in acquiring XAS spectra of light elements such as Si, it is essential to use soft X-rays below 2 keV. Unlike the hard X-rays used in K-edge XAS measurements of transition elements, the penetrating power of soft X-rays in substances is significantly reduced, and consequently, *operando* measurement is difficult, but worthwhile challenging.

Therefore, the authors developed an *operando* charge-discharge cell which makes it possible to acquire the Si K-edge XAS spectrum from a Si anode during the charge/discharge process. This paper reports the results of observation of the Si-Li alloying reaction during the first charge by using the developed *operando* charge-discharge cell.

2. Experimental Method

2.1 Electrochemical Cell

Figure 1 shows a schematic diagram of the electrochemical cell for *operando* SX-XAS (hereinafter, electrochemical cell), and **Photo 1** shows the cell inside the XAS chamber. 7.5 μm thick polyimide (PI) film was used as a window material to separate the electrochemical cell from vacuum, on which a metallic thin film was sputtered and used as the collector. The structure is similar to that published by Nakanishi et al[5]. A Si anode film was prepared by coating and baking a slurry on the PI film, using a slurry consisting of a mixture of Si single crystal powder as the active material, PI as the binder and acetylene black (AB) as a conductive agent at a ratio of Si : PI : AB = 76 : 12 : 12 wt%. Metallic Li foil with a diameter of φ 8 mm was placed as the counter electrode. The electrolyte used here consisted of LiPF$_6$ with a concentration of 1 mol/l and ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of EC : DEC = 1 : 1.

2.2 *Operando* Si K-edge XAS Measurement

The Si K-edge XAS measurements were performed at the BL-10 soft X-ray beamline in the Ritsumeikan University Synchrotron Radiation (SR) Center. This experiment was carried out under so-called *operando* conditions, in which the XAS spectra were collected continuously during charging. As the charging speed, the CC (Constant Current) mode of the 0.3 C charge rate was used, and a cell voltage was applied up to 5 mV. XAS spectra were taken in the energy range from 1 820 eV to 1 900 eV repeatedly by the PFY (Partial Fluorescence Yield) method using an SDD (Silicon
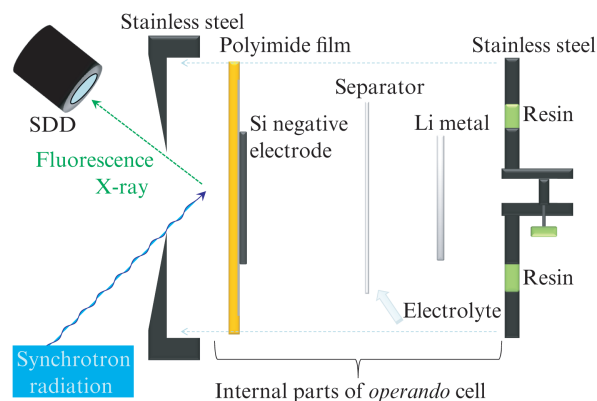

Fig. 1 Schematic diagram of electrochemical cell for *Operando* SX-XAS
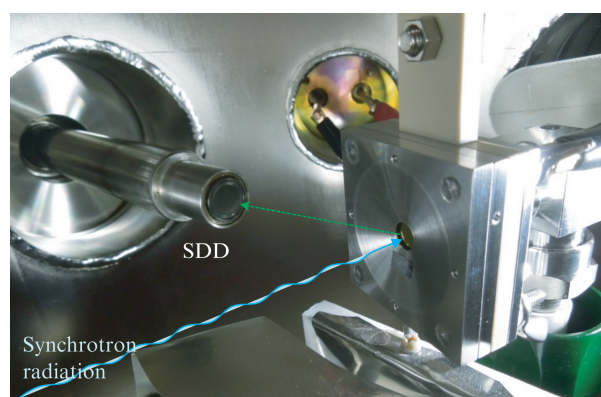

Photo 1 Appearance of the *Operando* SX-XAS cell

Drift Detector). Each spectrum was taken in approximately 244 s.

For comparison, Si K-edge XAS spectra were also acquired by the PFY method for a silicon wafer (Crystal Si) and quartz powder (SiO$_2$) and fully charged Li$_x$Si (hereinafter, Full charged Li$_x$Si) which was made by electrochemical charging to 0.5 mV of a laminated cell using the same composition with a copper foil collector, as reference compounds.

3. Experimental Results

Figure 2 shows the charging curve obtained during the first charge in the *operando* Si K-edge XAS measurement, and **Fig. 3** shows the XAS spectrum taken at every 4 min. The spectrum gradually changed by charging. In particular, an extra band appears and grows in the pre-edge region.

Figure 4 shows the Si K-edge XAS spectra of the reference compounds, which were measured separately. Since the peaks (white line) of the Full charged Li$_x$Si and Crystal Si are broad and difficult to analyze in detail, their first derivatives were shown in **Fig. 5**.
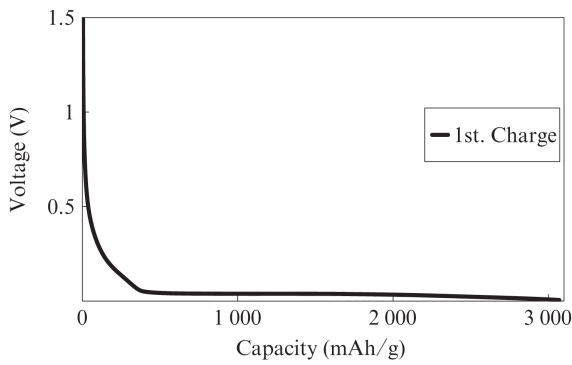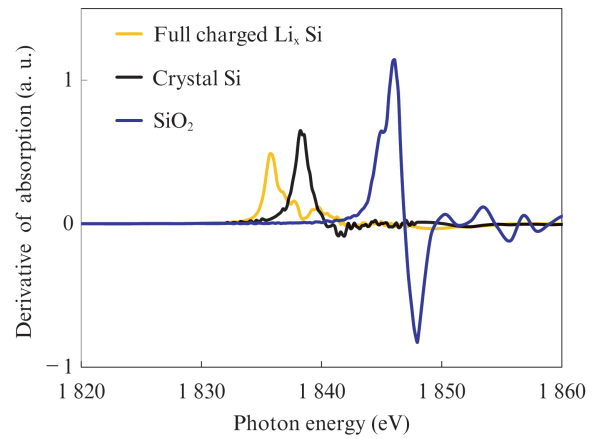
Fig. 2 Charging curve on first charge

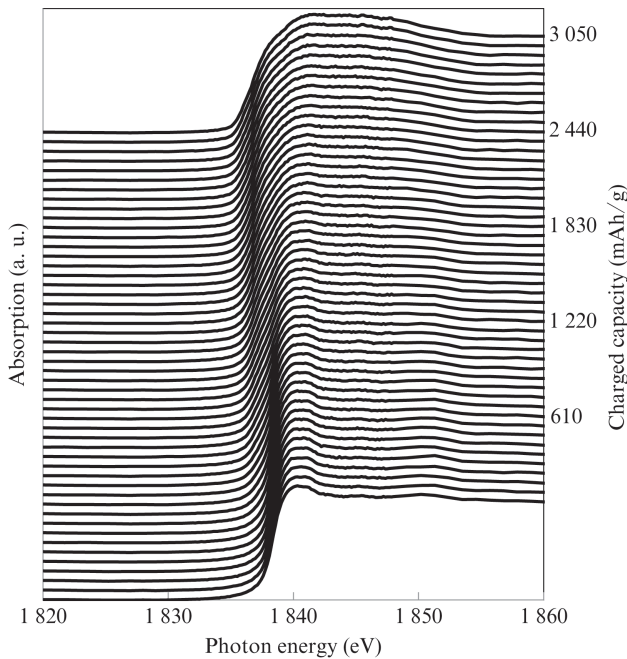Fig. 5 First derivative Si K-edge XAS spectra of reference compounds

Table 1 First derivative XAS spectral peak of reference compounds

Reference compounds	Crystal Si	SiO$_2$	Full charged LixSi
Peak (eV)	1 838.2	1 846.0	1 835.7

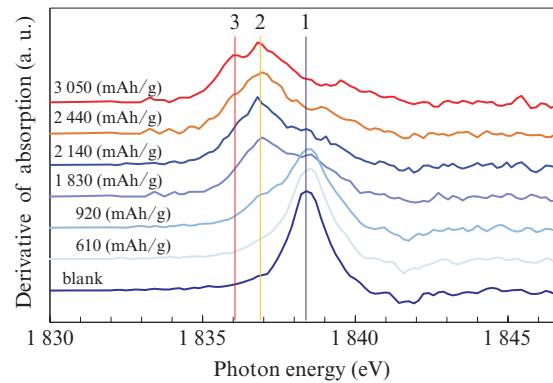Fig. 3 *Operando* Si K-edge XAS spectra on first charge

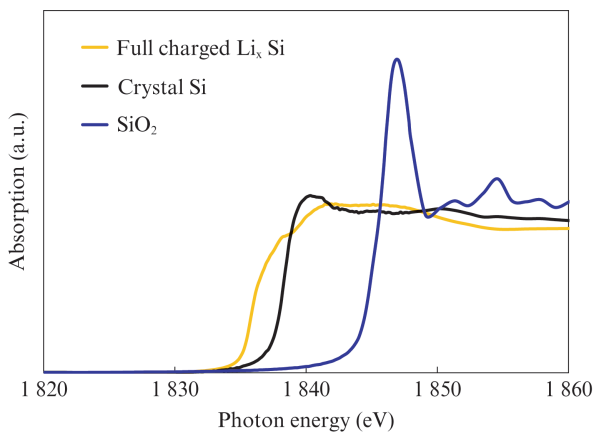Fig. 6 First derivative Si K-edge XAS spectra on first charge

Fig. 4 Si K-edge XAS spectra of reference compounds

Table 1 shows the first derivatives of the reference compounds, whose peak energies are regarded as the absorption edge. The edge shift can be a measure of the chemical state. The edge of SiO$_2$ shifts to higher energy from that of Crystal Si by 8 eV, and conversely, the edge of the lithiated Full charged Li$_x$Si shifts to lower energy by 2 eV.

Figure 6 shows the first derivatives for the charged states of 0, 610, 920, 1 830, 2 140, 2 440 and 3 050 (mAh/g) from the spectra acquired by *operando* Si K-edge XAS of the first charge, and their peak energies are listed in **Table 2**. Mainly three edges were observed from the first derivative spectra. Here, let the three peaks in the first derivatives Peak 1, Peak 2 and Peak 3. Comparing the peaks of the first derivatives for the

Table 2　Operando Si K-edge first derivative XAS spectral peaks on first charge

Charged capacity (mAh/g)	0	610	920	1 830	2 140	2 440	3 050
Peak1 (eV)	1 838.2	1 838.6	1 838.6	1 838.4	—	—	—
Peak2 (eV)	—	—	(shoulder peak)	1 836.8	1 836.8	1 837.0	1 836.8
Peak3 (eV)	—	—	—	—	—	(shoulder peak)	1 836.0

first charge of the Si anode with those of the reference compounds, any of the peaks for the first charge did not match the peak for SiO_2. Peak 1 is assigned to that of Crystal Si, and Peak 3 to that of the Full charged Li_xSi. However, Peak 2 did not match any of the reference compounds.

At the charged capacities of 0 and 610 mAh/g, the observed peak was only Peak 1, which matches that of the reference compound Crystal Si, and at the charged capacity of 920 mAh/g, an additional shoulder peak appeared at the position of Peak 2. At the charged capacity of 1 830 mAh/g, Peak 2 became dominant and Peak 1 decreased, and at 2 140 mAh/g, only Peak 2 was observed. Then, at the charged capacity of 2 440 mAh/g, Peak 3 appeared as a shoulder. Finally, at 3 050 mAh/g, Peak 3 became comparable with Peak 2. Thus, the *operando* Si K-edge XAS measurement has made clear the chemical state changes of Si during the first charge.

4.　Discussion

In lithium ion batteries in which crystalline Si is used as the active material, it is known that a decomposition reaction of the electrolyte proceeds preferentially in the surface region of the crystalline Si during the first charge, and a solid electrolyte interphase (SEI) is formed. According to this *operando* Si K-edge XAS experiment of the first charge of the crystalline Si anode, the chemical state of the crystalline Si did not change until the battery was charged to 610 mAh/g. This means that the charging current is consumed in some reaction other than storage of Li in Si (lithiation of Si), suggesting that the SEI formation proceeds in this period.

As charging proceeded over 920 mAh/g, the chemical state of the Si anode changed from crystalline Si to an intermediate phase, different from the final Si-Li alloyed phase. It has been reported that amorphous Si includes $Li_{2.5}Si$ as an intermediate phase during charging, and the alloying reaction finally progresses to $Li_{3.75}Si$[6]. Thus, it is possible that the intermediate phase also appeared in the crystalline Si system in this experiment. In the process of charging from 920 mAh/g to 2 140 mAh/g, this intermediate phase increased and the initial crystalline Si phase decreased, while in the further charging process up to 3 050 mAh/g, the
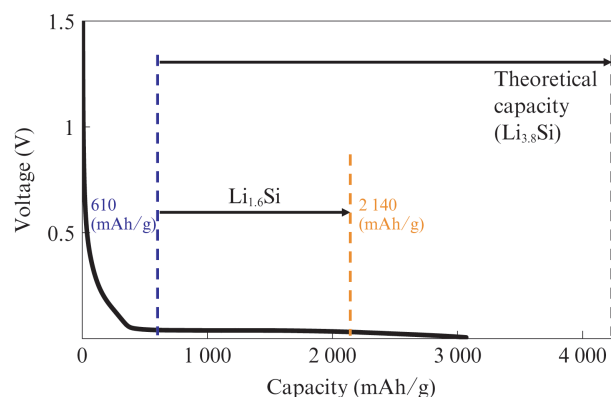

Fig. 7　Schematic diagram of the amount of Li inserted into crystalline Si in this experiment

initial state crystalline Si disappeared, the intermediate phase decreased and the final chemical state increased. Based on these facts, it was found that the Li-Si alloying reaction during the first charge of crystalline Si does not proceed continuously with an arbitrary composition, but rather, with a two-step reaction, via an intermediate Li-Si alloy phase.

Finally, based on the charging behavior of the crystalline Si, we estimated the composition of the Li-Si alloy in the intermediate phase. A battery can be charged up to 4 210 mAh/g, where the alloy phase, $Li_{3.75}Si$ is formed. In this experiment, the first charge was performed until the charged capacity of the electrochemical cell reached approximately 3 050 mAh/g. However, the chemical state did not change up to 610 mAh/g. Accordingly, we assumed that the lithiation of Li of the crystalline Si started at 610 mAh/g, and formed the alloy phase of $Li_{3.75}Si$ at the charge capacity of 4 210 mAh/g. Since the intermediate phase (Peak 2 in Fig. 6) was dominant at the charged capacity of 2 140 mAh/g, the Li-Si alloy state of the intermediate phase was estimated to be $Li_{1.6}Si$. **Figure 7** shows a schematic diagram of the amount of Li inserted into crystalline Si. The composition and structure of this Si intermediate phase are issues for future research.

5.　Conclusion

JFE Techno-Research have developed an electrochemical cell which enables Si K-edge XAS experiment under *operando* conditions. Using this cell, the Si-Li

alloying reaction (lithiation reaction) during the first charge was observed. An analysis of the continuously-acquired XAS spectra confirmed that the preferential formation of the SEI in the first charge process of a crystalline Si anode takes place under a nonequilibrium condition, and clarified spectroscopically that a two-step Li-Si lithiation reaction occurs at the Si single-crystal anode. In the future, the authors will continue to clarify the physical properties of Si anodes, which are expected to become next-generation anode materials, and will promote the development of novel analysis techniques in order to contribute to higher capacity in batteries for EVs.

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