Analysis of Lithium-ion Diffusion in Silicon Single Crystal using Si K-edge X-ray Absorption Spectroscopy

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Diffusion phenomena of lithium ion in silicon negative electrode of lithium-ion battery are one of the fundamental properties, which have not been fully understood at this moment. In this study, using silicon single crystal electrodes, the diffusion behavior was investigated. Electrochemical method and Si K-edge X-ray absorption spectroscopy were applied to estimate the state of alloying in silicon-lithium system. The results of cyclic voltammetry measurements show larger reduction and oxidation current density in Si (100) than Si (111), indicating preferential diffusion into Si (100). X-ray absorption near edge structure (XANES) at Si K-edge depends on the state of alloying, which can be used for the estimation of alloying state. The apparent diffusion coefficient of lithium ion in single crystal electrodes of (100) calculated from the analysis of XANES is higher than that of (111).

1. Introduction

Lithium-ion battery is utilized for the large-scale energy storage in electric vehicles, renewable energy system, and it is required to improve the theoretical energy density. The theoretical energy density of silicon negative electrode is 4200 mA h g^{-1}, which is approximately ten times higher than that of graphite currently used as negative electrodes[1]. In addition, there are other advantages for the low cost due to the high abundance[2], and the high safety due to the stable structure of the lithiated silicon[3]. From these reasons, silicon is one of the promising candidates for the next generation lithium-ion battery negative electrode material. However, the poor cycle stability is a severe problem to realize the practical use of silicon negative electrode[4]. This is because the volume expansion of silicon crystal with lithium insertion is approximately 280% which is quite large compared with the other negative electrode[5], inducing the formation of crack and breaking solid electrolyte interface[6]. In recent years, various attempts such as nanosizing silicon[7], wire formation[6], and using plane-like structure[8] to reduce distortion in silicon crystals have been performed. For the further development of silicon negative electrode, the fundamental information about lithium ion diffusion phenomena in the silicon crystal structure should be fully understood.

The silicon negative electrode can accommodate lithium ions by forming an alloy with lithium[9]. The initial lithiation (charge) reactions of the silicon negative electrode at room temperature are shown in the following formulas:

$$\mathrm{Si\ (crystalline)} + 3.75\mathrm{Li}^+ + 3.75\mathrm{e}^-$$
$$\rightarrow \mathrm{Li}_x\mathrm{Si\ (amorphous)} + (3.75-x)\mathrm{Li}^+ + (3.75-x)\mathrm{e}^-$$
$$\rightarrow \mathrm{Li}_{15}\mathrm{Si}_4\ \mathrm{(crystalline)}. \quad (1)$$

In the initial charge reaction, a two-phase reaction occurs, in which crystalline silicon reacts with lithium ions to form an amorphous Li-Si alloy, and then the crystalline $Li_{15}Si_4$ is formed[10]. In delithiation reaction, lithium is extracted from the crystal $Li_{15}Si_4$, and amorphous silicon is formed[11]. Although the phase transition behavior in silicon electrodes, the diffusion phenomena of lithium-ion in silicon crystals have not been investigated so well. In this study, we aimed to reveal lithium ion diffusion phenomena in silicon negative electrode by using silicon single crystal which is the simplest model, which has been used by other research gropus[12, 13]. To investigate the detailed mechanism, we performed X-ray absorption spectroscopy (XAS), and cyclic voltammetry measurement. The diffusion of lithium ion in silicon is assumed to be different between each crystal plane due to the size of vacancy. Therefore, we investigated the anisotropy of lithium-alloying reaction by using two crystal planes of (100) and (111) silicon single crystals.

2. Experimental

Silicon (100) and (111) single crystals used in this research were purchased from Crystal Base, Limited Company. The size is 10 mm square, and the thickness is 0.525 mm, and the one side is mirror polished. The resistance is from 0.0018 to 0.020 Ω cm for Si (100) and from 0.010 to 0.020 Ω cm for Si (111). The silicon single crystals were dipped in 5 wt% HF aqueous solution for 5 minutes and washed with high purity purified water to remove the surface oxide film.

For the assemble of three-electrode electrochemical cells, the pretreated silicon (100) single crystals were used as a working electrode, and Li metal foils (t = 200 μm, purity 99.9%) purchased from Honjo Metal Co., Ltd. was used as a counter electrode and a reference electrode. The electrolyte used in this study was a solution of 1 M $LiPF_6$ dissolved in EC/EMC (3:7 (v/v)) where EC and EMC stand for ethylene carbonate ethyl methyl carbonate, which was purchased from Kishida Chemical Co., Ltd. The cells were assembled in a glove box filled with an argon atmosphere, and electrochemical measurements were carried out at room temperature. The single crystal samples after the electrochemical measurements were washed with ethylene carbonate in a glove box.

Another measurement samples were prepared by just contacting with Li foil. The pretreated silicon (100) and (111) single crystal was brought into the glove box and contacted with Li metal foil as shown in Fig. 1. Samples were pressed by using a torque driver set at ten cN m. They were maintained for 1-5 days and disassembled after that.

The samples made by two methods were put in a transfer vessel in a glove box and brought into BL-10 of Ritsumeikan University SR Center. Si K-edge X-ray absorption spectroscopy (XAS) measurements were performed in a fluorescence mode.

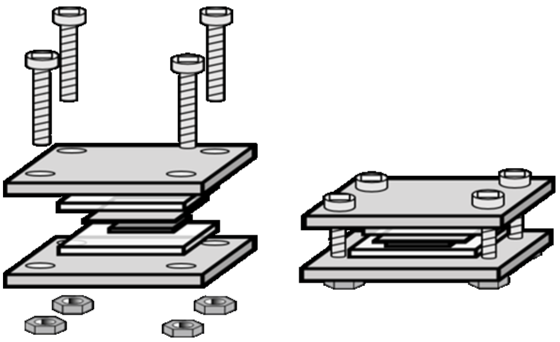

Fig. 1 Schematic image of contacting silicon single crystal with Li metal foil.

3. Results and Discussion

3.1 Cyclic voltammetry measurements

The results of cyclic voltammetry measurements using Si (100) and Si (111) are shown in Fig. 2. In both voltammograms, the significant reduction peak at 0.01 V is observed in the scanning towards low potential. It is presumed that a significant reduction current is caused by the alloying of lithium with silicon single crystal. Also, the two large oxidation peaks at about 0.31 V and 0.51 V are observed in the positive scan. It is presumed that they are involved in the two de-alloying process. These results are consistent with results of cyclic voltammograms reported previously[13]. Comparing with the current densities of Si (100) and Si (111), the current density of Si (100) is about twice as large as that of Si (111). From these results, the amount of lithium ion reacted with Si (100) is estimated much larger than Si (111).

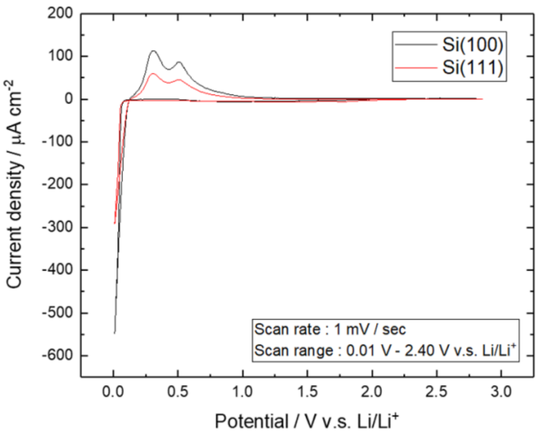

Fig. 2 Cyclic voltammogram of Si (100) and Si (111) single crystals.

3.2 XAS measurements of silicon single crystals after electrochemical measurement

Si K-edge X-ray absorption near edge structures (XANES) of Si (100) kept at 0.25 and 0.01 V v.s. Li/Li$^+$ for five hours are shown in Figure 3. The features are interpreted from the view of the transition of core electrons into the Si 3p empty states. The edge position of Si (100) at 0.01 V is shifted towards lower energy, and the peak intensity at 1842 eV is decreased. This change reflects the change of the density of states in silicon. The first principles calculation in the case of Li-Si alloying showed the density of state is changed due to the alloying with lithium and the shape changes like metals [14]. There is no shift in Si (100) at 0.25 V compared with the initial state, which is consistent with the little reduction current above 0.25 V shown in Fig. 2. Therefore, Si K-edge XANES corresponds to the state of alloying between lithium and silicon.

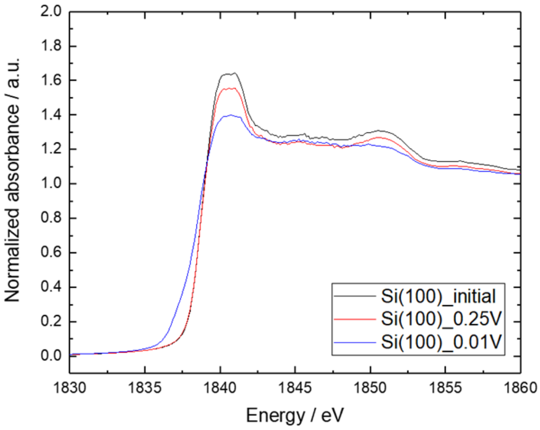

Fig. 3 Si K-edge XANES spectra of Si (100) kept at 0.25 and 0.01 V v.s. Li/Li$^+$.

Figure 4 shows the radial distribution function obtained by extracting the vibration of Si K-edge extended X-ray absorption fine structure (EXAFS) of Si (100) at each scanned potential. The nearest bond distance of Si-Si is 2.35 Å and the second distance is 3.83 Å, which correspond to the first and the second peaks of the radial distribution function. The intensity of the first peak is decreased after the scan to 0.01 V. Figure 5 shows the simulated radial distribution function of $Li_{15}Si_4$, $Li_{13}Si_4$, Li_7Si_3 and Si, which is expected to form as a stable phase in the Li-Si alloy system. This simulated result shows the drastically decrease of the first peak intensity after alloying reaction, which is not consistent with the experimental data in Fig. 4. This is because the reaction in electrochemical measurements occurs only on the surface of the single crystals electrode and the unreacted inner part contributes to the EXAFS data. Unfortunately, the local structure analysis of the alloyed state is difficult due to the quite small peak of the first coordination and the multiphase state is not preferred to the EXAFS analysis. Therefore, we will focus on the analysis of the reaction state for the alloying process in Li-Si using Si K-edge XANES.

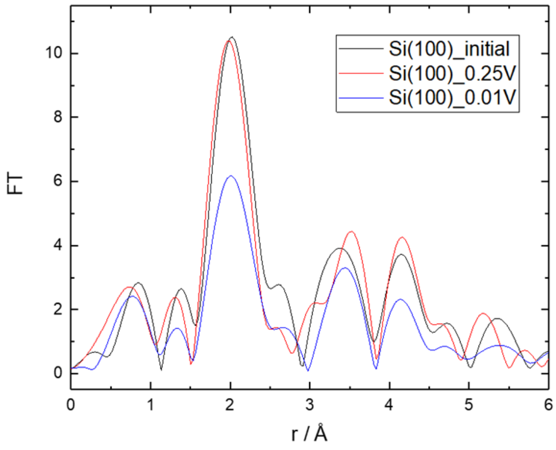

Fig. 4 Radial distribution function extracted from Si K-edge EXAFS of Si (100) kept at 0.25 and 0.01 V v.s. Li/Li$^+$.

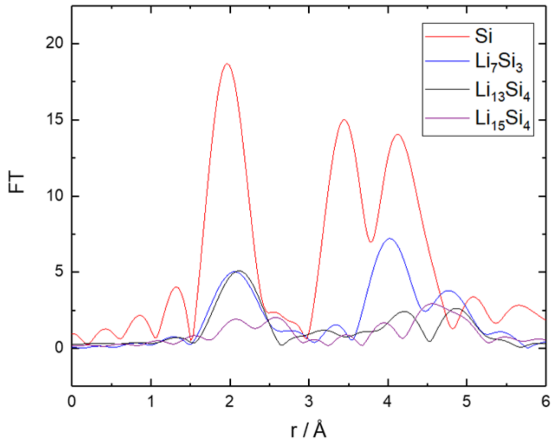

Fig. 5 Simulated radial distribution function of Li-Si alloy system.

3.3 XAS measurement of silicon single crystal after contacting with Li metal foil

Figure 6 (a) shows Si K-edge XANES of Si (100) directly contacted with Li metal foil for 1-5 days. The edge energy is gradually shifted towards lower energy with increasing contacted time, and after 4 days, the spectra show almost no change. This change reflects the alloying process of lithium into Si single crystal as observed in Fig. 3. Figure 6 (b) shows the comparison between Si (100) and Si (111). The lower energy shift of the absorption edge is also observed in Si (111); however, the energy shift is smaller than that of Si (100).

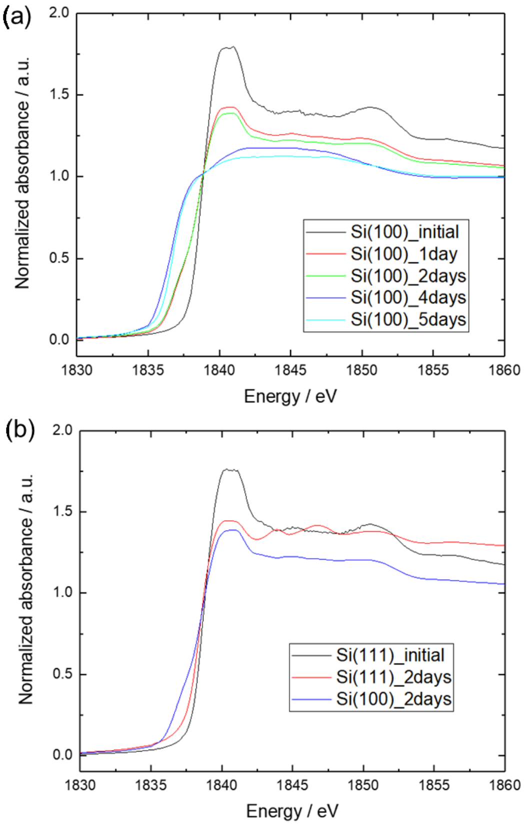

Fig. 6 Si K-edge XANES of (a) Si (100) directly contacted with Li metal foil for 1-5 days and (b) Si (100) and Si (111) for 2 days.

To quantify the state of the alloying reaction of silicon and lithium, the two-component analysis was performed using the initial state, and Si (100) reacted for 5 days as the unreacted Si and the fully alloyed Li-Si, respectively. The relationship between the state of alloying and the square root of the reaction time is plotted in Fig. 7. The state of alloying increases with the reaction time and the higher alloying state is observed in Si (100).

In this experiment, the lithium diffusion into the silicon single crystal can be considered as semi-infinite diffusion. The amount of lithium ion diffused into the inside of silicon single crystal (M_t) is expressed by the following equation (2):

$$M_t = 2C_0\left(\frac{Dt}{\pi}\right)^{1/2} \qquad (2),$$

where C_0 is the surface lithium concentration at the moment of contacting with lithium metal foil, D is the diffusion coefficient of lithium to the silicon single crystal, and t is the reaction time. Using this equation and the data in Fig. 7, the diffusion coefficient of lithium can be calculated.

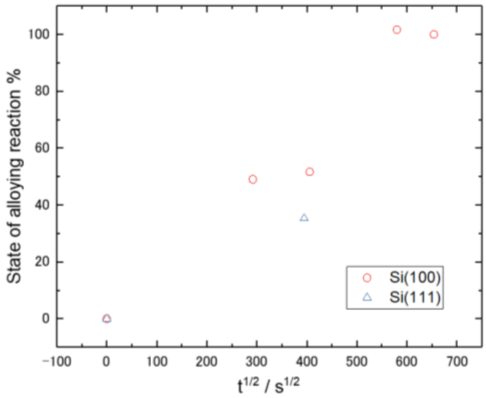

Fig. 7 Relationship between the square root of connecting time and the state of allying in silicon single crystal.

The diffusion coefficient of Si (100) is calculated as 2.03 × 10^{-6} cm^2 s^{-1} and that of Si (111) is calculated as 6.28 × 10^{-7} cm^2 s^{-1}. From this result, it can be confirmed that Si (100) has a larger diffusion coefficient than Si (111). The relationship is consistent with the results of cyclic voltammetry measurements. However, the plotting points in these measurements were very few. We have to measure more points and improve the quality of the data. The reported diffusion coefficient of lithium-ion on nano-silicon estimated by cyclic voltammetry, electrochemical impedance spectroscopy or galvanostatic intermittent titration technique are approximately 10^{-12} cm^2 s^{-1}, which is a large divergence from our study[15]. This is because the value by the electrochemical measurements can be influenced by the solid electrolyte interface. The further study including increasing the measurement points, discussion of the method of background subtraction and the self-absorption effect is necessary to discuss the quantification of the diffusion coefficients.

3.4 Discussion

The diffusion of lithium into silicon will be discussed using the vacant size in each lattice plane as shown in Fig. 8. To quantitatively calculate the area of the vacancy in each silicon crystal plane, two parameters are defined; 1.17 Å is the covalent bond radius of silicon atoms and 3.83 Å is the shortest distance between two silicon atoms on the crystal plane. The calculated areas of the vacancy formed by four silicon atoms in Si (100) and Si (111) are 10.4 and 8.4 $Å^2$, respectively. It is presumed that the diffusion of lithium into Si (100) plane is more accessible than Si (111), which results in the higher diffusion coefficient of Si (100) estimated by Si K-edge XANES.

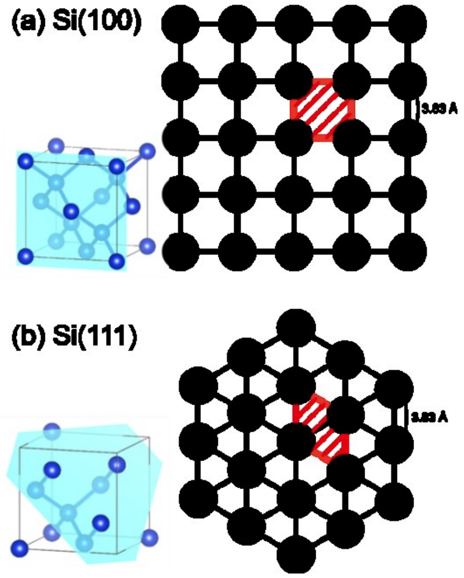

Fig. 8 Cross-section of a unit cell of (a) Si (100) and (b) Si (111).

4. Conclusions

Diffusion phenomenon of lithium ion in silicon single crystals was investigated by Si K-edge X-ray absorption spectroscopy. The results of cyclic voltammetry measurements show larger reduction and oxidation current density in Si (100) than Si (111), indicating preferential diffusion into Si (100). Si K-edge X-ray absorption near edge structure depends on the state of alloying of Li-Si, which can be used for the analysis of the reaction state in silicon single crystals. Extended X-ray absorption fine structure analysis at Si K-edge indicates the quite low intensity of the first coordination shell. The two-component analysis of Si K-edge XANES using the silicon contacted with Li foil provide the alloying state. When following the semi-infinite diffusion, the apparent diffusion coefficient of Si (100) and Si (111) can be estimated. The diffusion coefficient of Si (100) is approximately 3.2 times higher than that of Si (111). Si K-edge X-ray absorption spectroscopy is one of the useful techniques to analyze the diffusion behavior of lithium ion in silicon negative electrodes.

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