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Microscopic Structural Analysis of Advanced Anode Material for Lithium Battery†

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Abstract:

JFE Techno-Research analyzed the microstructure of silicon anodes in the charging/discharging reaction by electron microscopy measurements. Observation of the morphology of the Si anode in the initial charging reaction showed that the lithium absorption reaction into Si particles is inhomogeneous, and electron backscatter diffraction measurements revealed that the Li insertion route into Si crystals is the [101] direction. JFE Techno-Research also developed a novel ex-situ observation technique for analyzing the formation of the solid electrolyte interphase (SEI) on the Si anode in the charging state. From electron diffraction and electron energy loss spectrum (EELS) measurements of the nano-scaled Si edge, which was fabricated by Ar ion milling pre-processing, Li_2O was determined to be the main component of the SEI produced in the charging reaction.

1. Introduction

One important area of work in development of high performance lithium ion secondary cells1) is research and development of alloy anode materials, which can be expected to realize dramatically higher capacity in comparison with the conventional graphite materials. In particular, Si is one of the most promising anode materials, because of the theoretical capacity of Si is one order higher than that of graphite, and practical application is progressing in some cases.

One of the most critical disadvantage in Si anode is prone to capacity degradation in comparison with graphite anode materials. As the mechanism of the capacity degradation, it is considered that the electrical contacts are dissociated in the anode composite layer, which caused by pulverization of Si during repeated lithiation and delithiation. Therefore, various attempts have been made to improve cycling characteristics by using thin-film Si, Si nanotubes, SiO materials2), etc. However, the detailed mechanism of charging and discharging of Li in Si active materials had not been clarified due to limitation of physical analysis of this system in opposition to widely researched that of the electrochemical properties.

In Si anodes, as in graphite materials, it is know that a solid electrolyte interphase (SEI) forms on the surface of the Si by decomposition of the electrolyte accompanying initial capacity degradation3). In graphite materials, it is thought that SEI functions as a protective film that prevents further decomposition of the electrolyte after formation, but, in the case of Si anodes, the morphology of the SEI and its effect on anode charging and discharging still had not been clarified yet.

Therefore, we carried out a study to elucidate the mechanism of lithiation and delithiation by Si anodes by a physical analysis of the microstructural changes in Si anodes with different charging and discharging state. In this report, the absorption structure of Li ions in Si anodes in the charging state was observed by scanning electron microscopy (SEM), and the relationship with the crystallographic orientation of the Si crystals was investigated by electron backscatter diffraction (EBSD).

In addition, we also developed a novel *ex-situ* analysis method in order to observe the SEI that forms on the Si surface by spherical aberration corrected scanning transmission electron microscope (Cs-corrected STEM). In common technique, specimens which were thinned to obtain thin-films suitable for observation by transmis-

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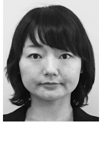

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sion electron microscopy (TEM) observation had been analyzed in observation of the SEI that formed on the surface of anodic active materials, but changes in the SEI composition due to damage during thinning, and damage and loss could have been occurred when this technique was used. Therefore, in this research, the thin film electrode including nano-scaled Si edges was prepared by focused ion beam (FIB) processing, and TEM observation of those specimens was performed before and after charging. As a result, the condition of the SEI before and after charging and discharging was successfully observed and analyzed under a condition in which the influence of processing was eliminated. The results of observation and analysis of the SEI that formed on the Si active material by using the new technique are reported in the following.

2. Experimental Method

Specimens were prepared as described below in order to analyze the microstructure of Si anodes after absorption of lithium (Li). First, N-methylpyrrolidone (NMP) was added to a mixture of single crystal Si powder (average particle size: several μm): acethylene black (AB): polyvinylidene difluoride (PVdF)=80: 10: 10 mass%, which was then mixed, coated on a Cu foil collector (20 μm in thickness), dried, and pressed to form negative electrodes. The electrode film thickness was arranged to be 10 μm or less to form a monolayer of Si particles. Coin batteries were assembled using this anode, 1 mol/l $LiPF_6$ (EC: DEC=1: 1 v/v%) as the electrolyte and Li as the counter electrode. A constant current charge-discharge test of the batteries was performed to prepare Si anodes with states of charge (SOC) of 0, 20, 40, 60, 80 and 100%. After the charge-discharge test, the batteries were disassembled in an Ar glove box, and the negative electrodes were recovered in the charged state. Anode cross sections were finished by ion milling, and observed by SEM. An EBSD analysis of the cross section of the SOC 40% anode was also performed. Thin-film specimens of the SOC 40% specimen and an anode specimen that had been discharged from SOC 40% to 1.5 V (vs. Li) were prepared by FIB milling, and Cs-corrected STEM observation and electron energy loss spectrum (EELS) analysis were performed.

To analyze the microstructure of the SEI, the anode composition was set to Si powder: AB: PVdF=76: 12: 12 wt%, and electrodes with a weight of approximately 2.06 mg/cm^2 per unit of electrode area were prepared. An electrode with a thin-film region was produced by angled Ar ion irradiation of a punched electrode having a diameter of 3 mmφ, and the analysis position was decided by TEM observation. A battery was fabricated using this thin-film electrode, and was charged to SOC 25%. After charging, the thin-film electrode was taken out from the battery and its morphology was observed by Cs-corrected STEM, and electron diffraction measurements and EELS analysis were performed.

It should be noted that all battery fabrication and disassembly, specimen preparation and observation were performed under an atmospheric non-exposure (atmospheric isolation) condition.

3. Experimental Results

3.1 Microstructural Analysis of Si Anode with Absorbed Li

Photo 1 shows the results of SEM observation of the cross sections of Si anodes with SOC 0, 40 and 100%. The film thickness of the Si anode increases by approximately 5 times from SOC 0% to 100%. At SOC higher than 40%, the shape of the Si crystals had collapsed, and a large number of voids having sizes from several μm to several 10 μm had appeared between the Si particles. Furthermore, there were also some places where the anode film had detached from the foil collector. At SOC 40%, the Si crystals had retained their shape, but degraded regions with different contrasts appeared at the surface and in the inside of the active material. These degraded parts did not spread homogeneously from the Si surface to the interior of the active material, but rather, formed in a reticulate shape having a width of several 100 nm or less.

Photo 2 shows the results of EBSD analysis of the Si crystal with SOC 40%. The cross section of the Si crys-

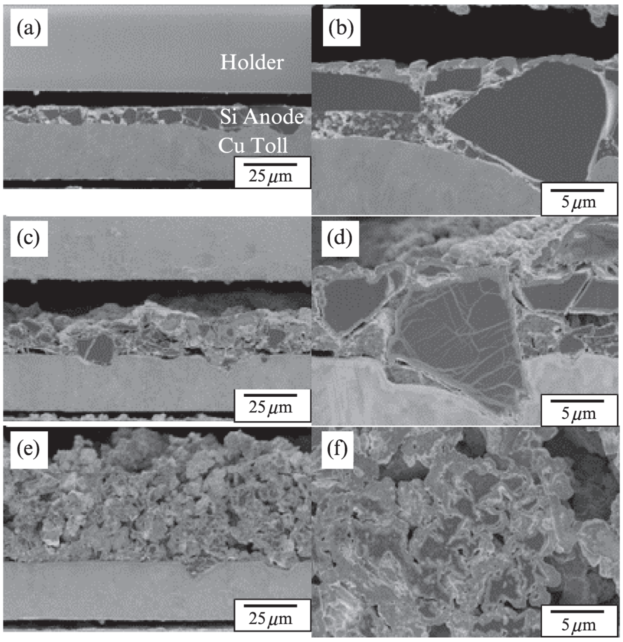

Photo 1 Si Anode images at state of charge (SOC) 0%((a), (b)), 40%((c),(d)), 100%((e),(f))

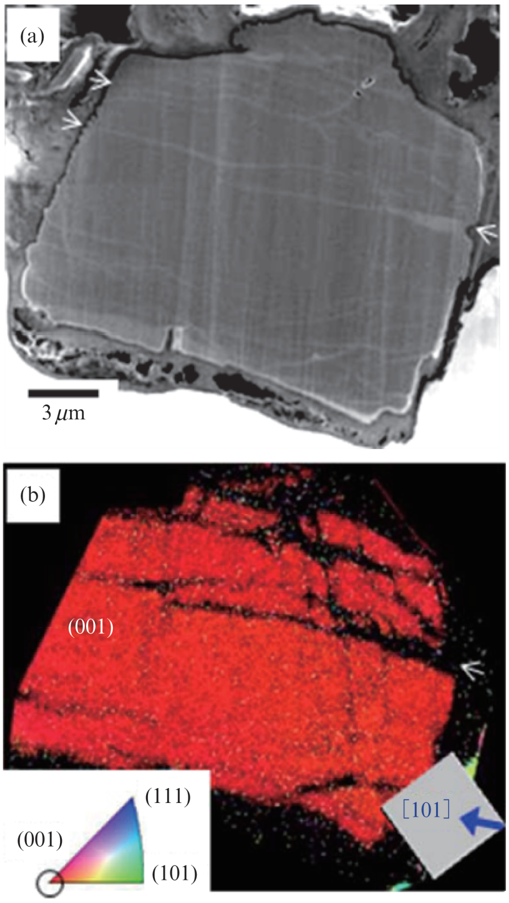

Photo 2 Scanning electron microscopy (SEM) image (a) and electron backscatter diffraction (EBSD) map (b) with inversed pole figure and [101] of Si crystal after charged at state of charge (SOC) 40%

tal that was analyzed here was the (001) plane. Analysis of the crystallographic orientation revealed that the linear-shaped degraded part observed in the Si crystal was developed to the [101] direction.

On the other hand, as in the SEM observation results, the reticulate structure with a different contrast was also observed in the results of annular dark field (ADF) -STEM observation (**Photo 3**) of the Si anode with SOC 40%. The width of this reticulate shape was from several 10 nm to several 100 nm. An internal crack had founded in the microstructure, and from the results of mapping of Li-K EELS (Photo 3 (b)), a region with a particularly high concentration of Li was detected in the vicinity of this crack. Based on the EELS analysis (Photo 3 (e)), the constituent elements of the reticulate structure were found out to be Li-Si, and from the electron diffraction measurements (Photo 3 (c, d)), the reticulate structure was found out to be amorphous (non-crystalline). Li was not detected outside of the reticulate structure, and it was found that the crystal structure conformed to the Si crystal.

Summarizing the results of SEM and STEM observations, this study clarified the fact that Li ions are inserted preferentially from the Si [101] orientation in the initial stage of the charging reaction, and form a reticulate Li-Si alloy layer.

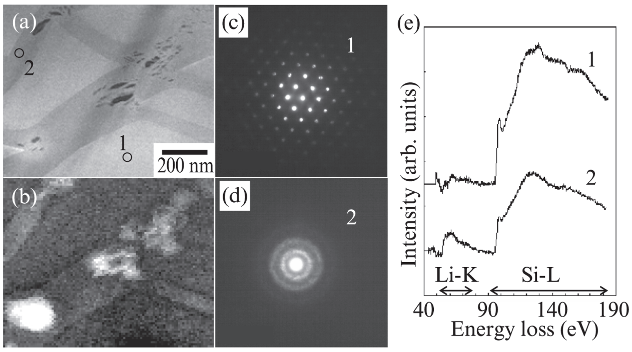

Photo 3 (a) Scanning transmission electron microscopy (STEM) image,(b) mapping of Li-K (Electron energy loss spectrum: EELS), and (c),(d) diffractions with (e) EELS spectra at points 1, 2 for Si anode (State of charge (SOC) 40%)

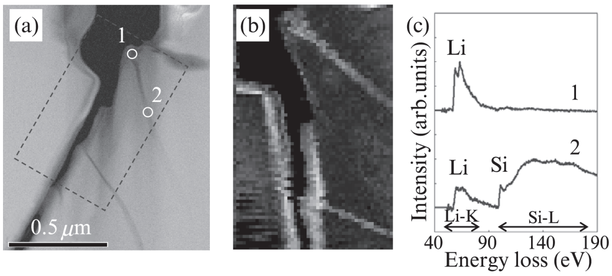

Photo 4 (a) Scanning transmission electron microscope (STEM) image,(b) mapping of Li-K (Electron energy loss spectrum: EELS), and (c) EELS spectra at points 1, 2 for Si anode after discharged from state of charge (SOC) 40% to 0%

Photo 4 shows the results of STEM observation of the Si anode after discharging from SOC 40% to 0%. A striated degraded part with a width of approximately several nm was observed in the ADF-STEM image. From the spectral shape (2 in Photo 4 (c)), this was found out to be the Li-Si phase. Based on this, it was thought that the Li in the Li-Si phase that formed as a result of charging to SOC 40% was not completely discharged during the discharge reaction, and it remained as a Li-Si phase with a width of several nm. In region 1 near the surface of the active material in the reticulate structure, the width has expanded more than in the interior, and based on the facts that Si-L edge was not observed in the EELS spectrum and O was detected in the EDX analysis, etc., a component which is estimated to be SEI had formed.

3.2 Microstructural Analysis of Si Anode SEI

Photo 5 shows the results of TEM observation of the thin-film anode which was prepared for observation of SEI before charging. The central part (a) of the thin-film electrode was partly vanished. When the edge of the Si

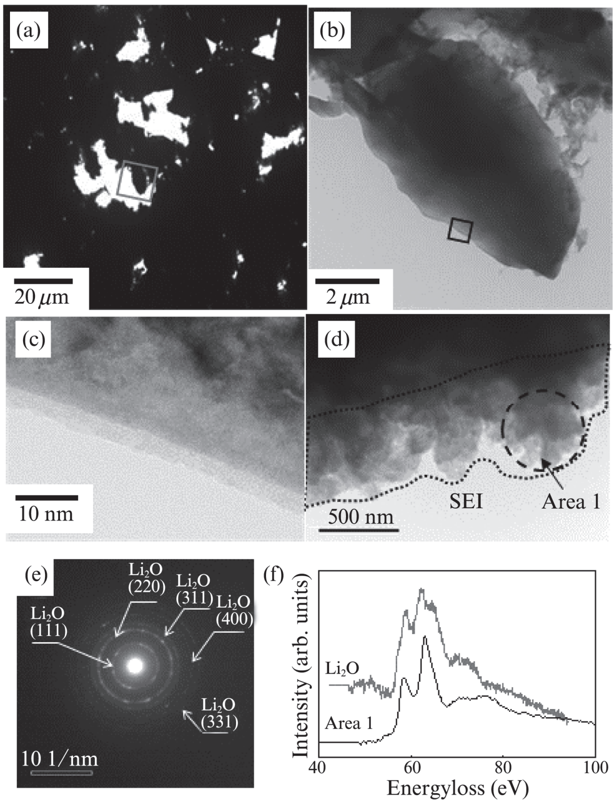

Photo 5 Transmission electron microscope (TEM) images of Sinano-edge before (a)～(c) and after (d) charging reaction with (e) diffraction and (f) EELS spectrum of (1) solid electrolyte inter-phase (SEI) region with (2) reference Li_2O

crystal particles which were found at the boundary part on the thin-film electrode (b) were magnified, a Si lattice image (c) was also observed, confirming that a Si nano-edge suitable for observation of SEI by TEM has formed.

Subsequently, Photo 5 (d) shows the result when the thin-film electrode including this Si nano-edge was charged to SOC 25% and observed by Cs-corrected STEM. A condition in which SEI has formed on the surface of the Si active material could be confirmed. The fromed SEI was not a homogeneous layer, but had grown randomly on the Si active material, and its thickness was approximately 500 nm. When electron diffraction measurement of Area 1 in the SEI was performed, diffraction rings showing a microcrystal were obtained (e). The diffraction rings were consistent with the spacing of Li_2O within an error of 2%. Furthermore, as a result of an EELS analysis of Area 1, an absorption edge of Li-K was detected in the vicinity of 60 eV (spectrum 1 in (f)). This Li-K profile shows extremely good agreement with the spectrum of the reference Li_2O and with a previously-reported Li_2O spectrum[4], clarifying the fact that Li_2O has formed as an SEI on the surface of the Si electrode. From the results of EDX analysis of the SEI, O together with very small amounts of Si, C and F were detected. This suggested that the SEI did not composed only Li_2O, but was a composite structure of compounds which included the above-mentioned elements.

4. Discussion

The charging and discharging process of Li ions in a Si anode will be discussed based on the experimental results. The results revealed the fact that Li ions are not absorbed in Si crystals homogeneously in the initial charging period, but rather, penetrate the interior to the [101] direction of the Si crystal while forming a Li-Si alloy with a reticulate shape. At SOC 40%, it was found that the Si crystals were divided into several domains by a reticulate Li-Si structure with a width of several 10 nm to several 100 nm, and further concentration of Li and cracking occurred in the Li-Si layer; these are considered to be prior phenomena of Si fragmentation. With further progress of the charging reaction, a condition in which the Si crystal structure was dessosiated and fragmentation progressed could also be observed. As a result, it is thought that electrical contact from the foil collector is lost, and this causes irreversible capacity.

Even if discharging treatment is performed from SOC 40%, at which the Si maintains its crystal structure, to SOC 0% (1.5 V vs. Li), it was found that the reticulate Li-Si microstructure still remains with a width on the order of several nm. Not only Li and Si, O was also detected near the surface of the reticulate structure. It is thought that the SEI is not limited to the surface, but penetrates into the interior of the crystals by way of the reticulate structure. The formation of SEI in this region is estimated to be a trigger that encourages the formation of a residual Li-Si phase in the interior of Si crystals and fragmentation of the crystals.

On the other hand, for precise morphological observation of the SEI, a thin-film electrode for use in TEM observation was produced by Ar ion milling, and an *ex-situ* analysis was performed during the charging reaction. As a result, it was clarified that SEI formed on the Si surface was mainly composed of an aggregate of Li_2O microcrystals after charging to SOC 40%. On the other hand, because the composition of the SEI included small amounts of Si, C and F in addition to Li and O, the SEI was found out to be a composite of these elements.

5. Conclusion

JFE Techno-Research carried out a physical analysis of the changes in the microstructure of Si anodes in the charging and discharging reactions. The fact that the Li absorption reaction in the initial charging period occurs selectively in the Si crystal orientation was revealed by EBSD analysis, etc. A new *ex-situ* analysis method for the SEI by TEM was developed as part of this research. Analysis by this method revealed that the main component of the SEI that forms on the Si surface is microcrystalline Li_2O.

In the future, JFE Techno-Research will continue to apply structural analysis techniques to elucidate the possibility and problems of Si anodes, which are a promising next-generation negative electrode material.

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