Chemical state analysis of Silicon negative electrode material using SEM-SXES

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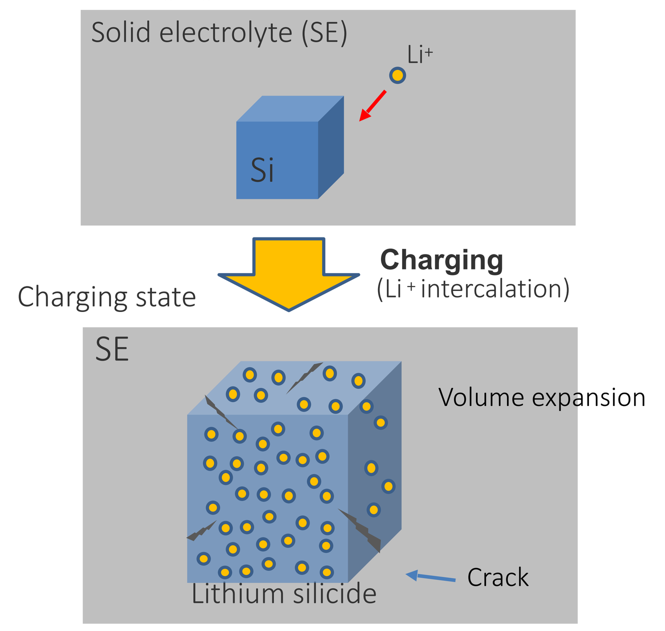
Introduction

Silicon (Si) has a large theoretical capacitance of 4200 mAh/g, and is attracting attention as a negative electrode material for Lithium (Li) ion secondary battery (LIB) to replace graphite. However, Si has problems such as volume expansion and decrease in charging efficiency during charging and discharging. Therefore, analysis for Si structure is being proceeded (1). However, the analysis of Li intercalation and desorption into Si is often evaluated based on electrochemical properties, and the detailed process of Li intercalation and desorption on the micron scale has not been clarified. Therefore, there is a need for micron-scale structural analysis of Si in the charge-discharge process based on chemical state analysis.

The purpose of this study is to perform elemental analysis using Energy dispersive spectrometry (EDS), chemical state analysis using Soft X-ray emission spectrometry (SXES), and crystal structure analysis using Electron backscattered diffraction (EBSD), with a Field Emission-Scanning electron microscope (FE-SEM) for the Si negative electrode of LIB, and attempting structural analysis of Si particles in charging state.

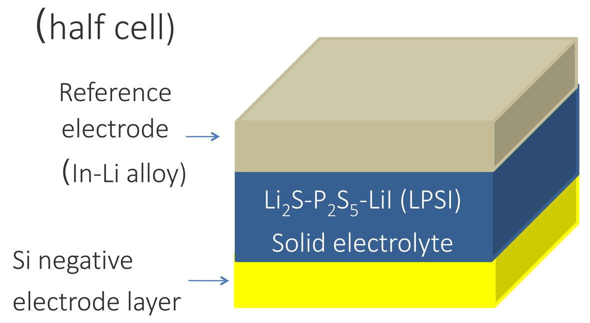
Charging process of Si in Solid LIB



Materials and Preparation

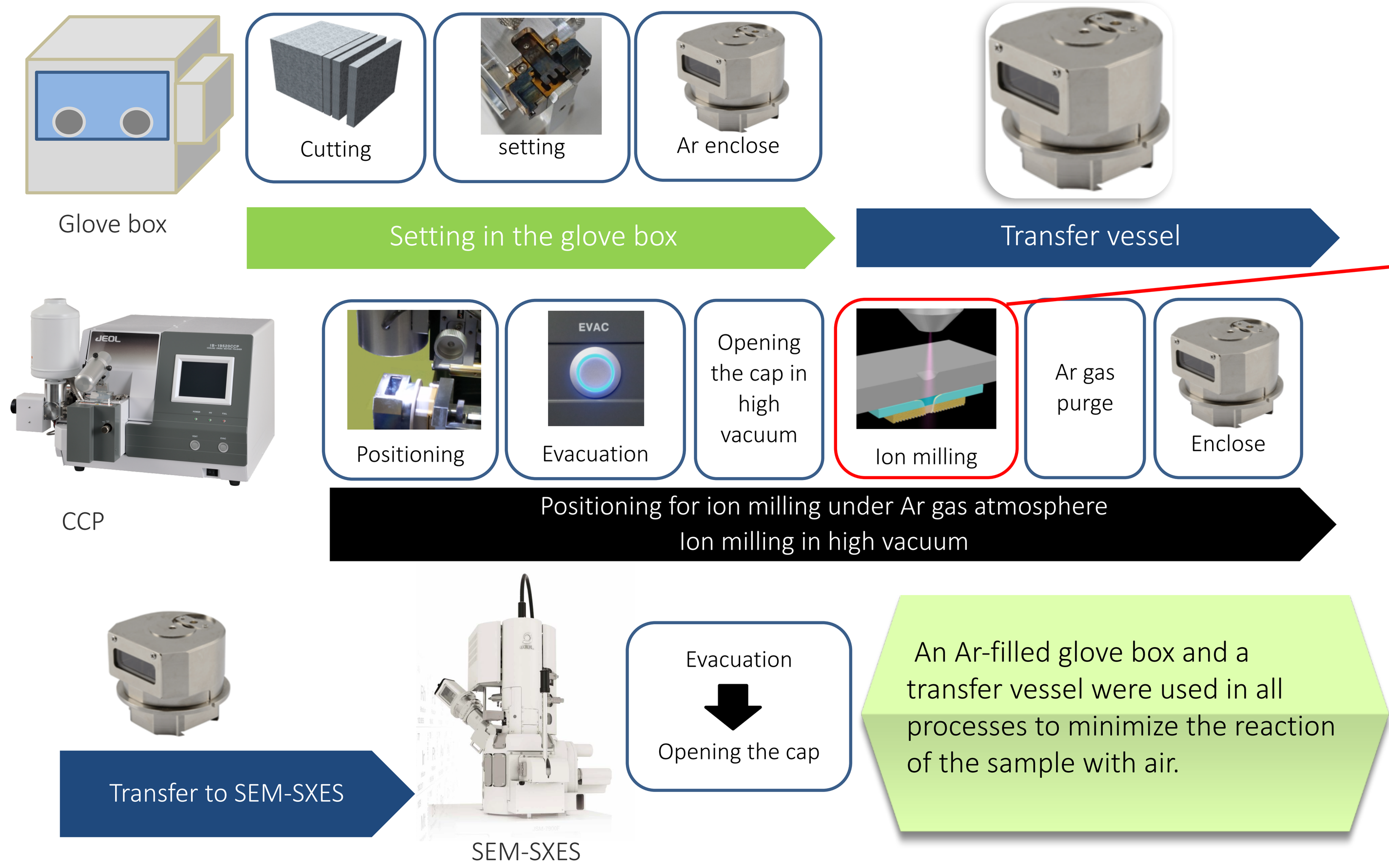
Sample

90% Charged Si negative electrode (half cell)

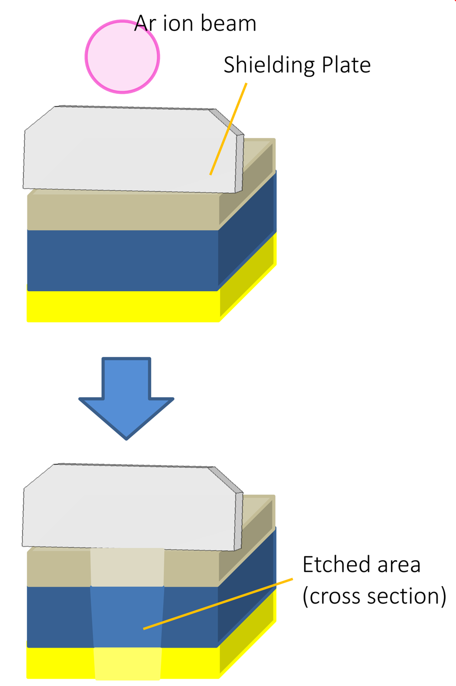


LPSI solid electrolyte prepared by liquid-phase syntheses (2) and Si particles were used for negative electrode. A half-cell was prepared using this negative electrode and charged at 90% of the theoretical capacitance value of Si.

Transfer system under air isolation condition



An Ar-filled glove box and a transfer vessel were used in all processes to minimize the reaction of the sample with air.



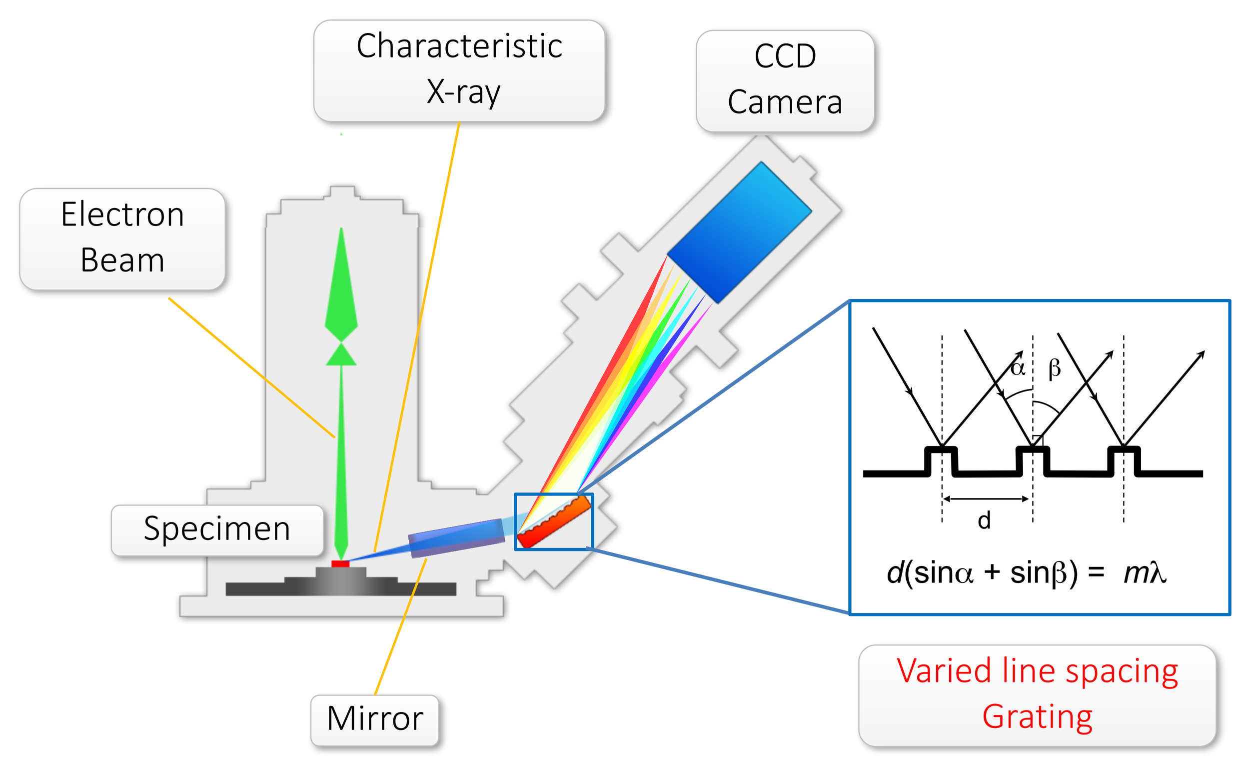
Cross-sectioned by an Ar ion beam using a COOLING CROSS SECTION POLISHER™ (CP) (JEOL, IB-19520CCP) under high vacuum and cooling conditions.

【Acc. Volt: 4 kV, Cooling temperature: <-120℃, Process time: 4 hr】

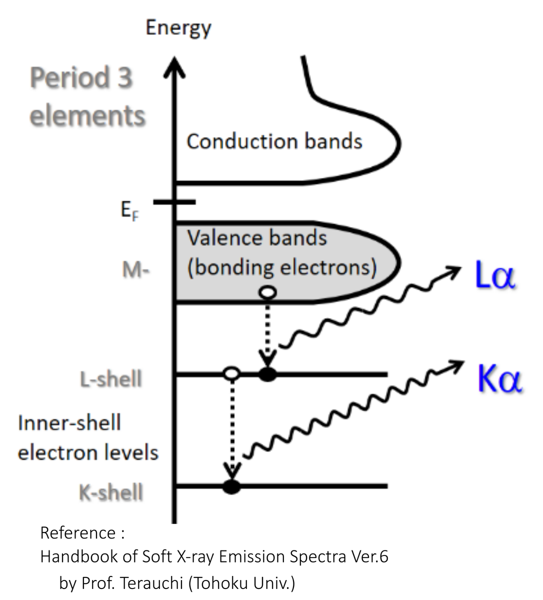
Instruments **for chemical state analysis**

The system for this study is Schottky FE-SEM (JEOL JSM-IT800) combined with SXES (JEOL SS-94000SXES), EDS (JEOL DrySD™ and OXFORD Instruments Ultim® Extreme) and EBSD (OXFORD Instruments Symmetry). In recent years, SXES that can be combined with an electron microscope has been developed (3). Chemical state analysis of sub-micron region on bulk materials can be successfully performed using a low voltage electron beam in the case of mounting SXES on a FE-SEM (4).

Schematic of SEM-SXES

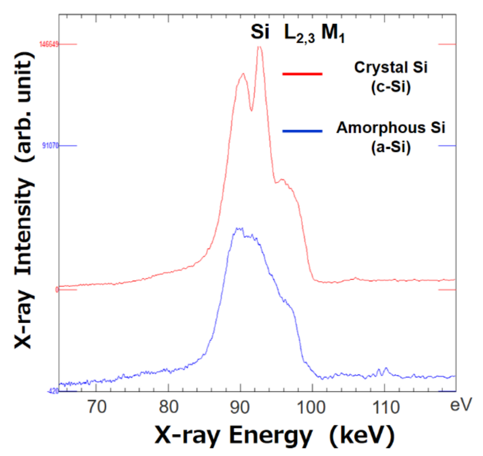


Chemical state analysis



Reference : Handbook of Soft X-ray Emission Spectra Ver.6 by Prof. Terauchi (Tohoku Univ.)

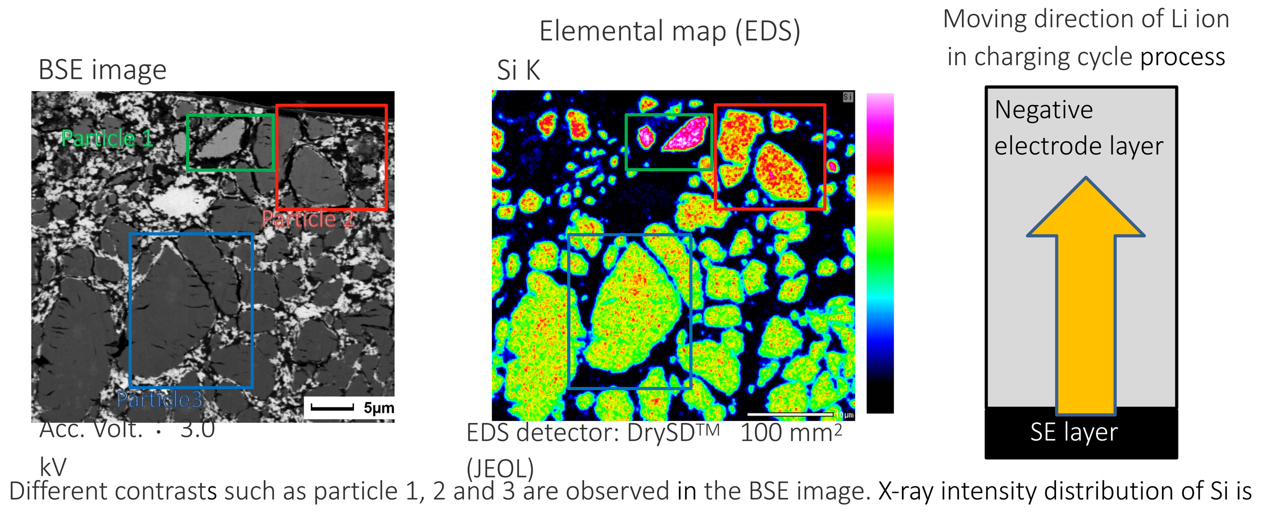
Low energy X-rays can be measured by SXES . This is important as these X-rays give information about the valence band.



It is possible to obtain valence band information with high energy resolution. The chemical state (differences of compound and crystal) is reflected in the spectral shape.

Results

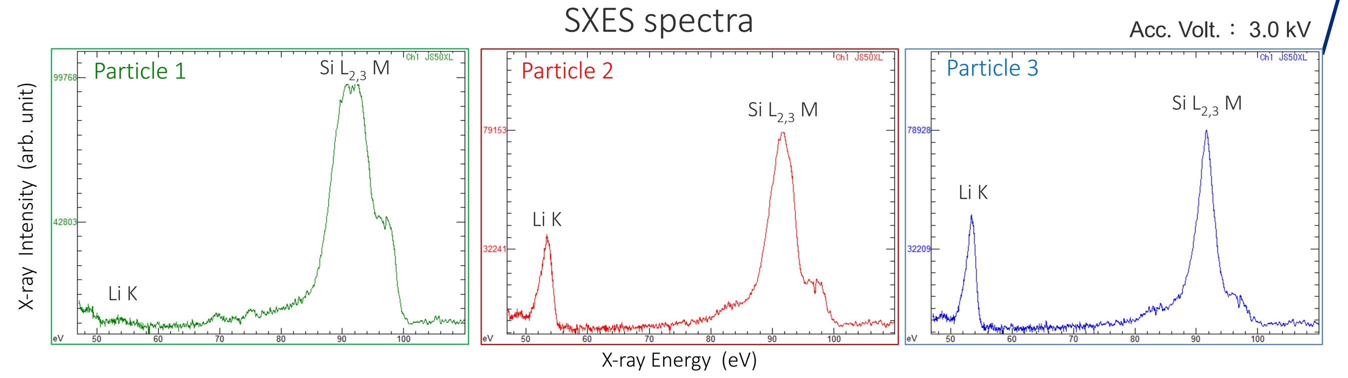
Analysis of Si negative electrode layer



Different contrasts such as particle 1, 2 and 3 are observed in the BSE image. X-ray intensity distribution of Si is correlated with BSE contrast and moving direction of Li ion in charging process.

⇒Analyzing chemical state of Si and Li for each particles using SEM-SXES.

SXES spectra



Si $L_{2,3}$ M spectrum state analysis result

	Spectral shape	Crystal State
Particle 1	Similar as a-Si	Amorphous
Particle 2	Sharpe main peak	Alloy
Particle 3	Sharpe main peak	Alloy

Li K spectrum analysis result

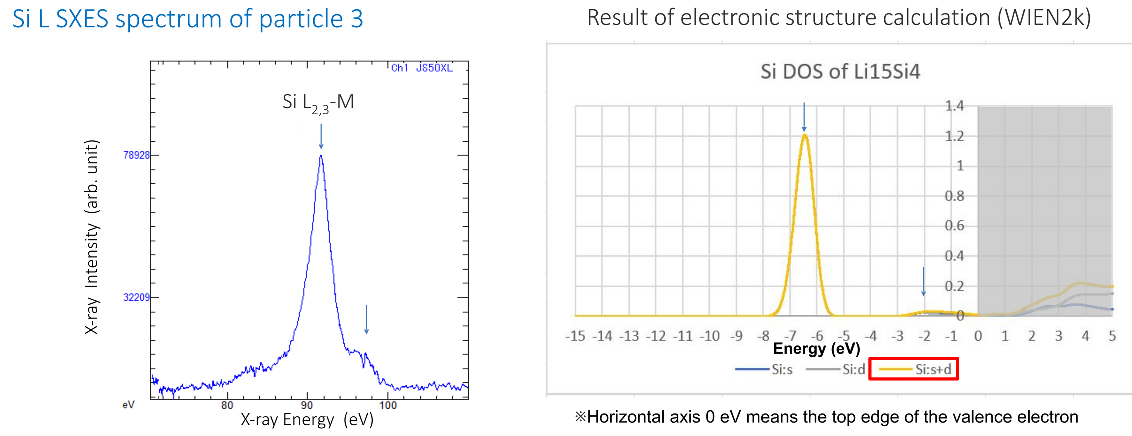
	Peak Position [eV]	Area [ct*eV]
Particle 1	-	-
Particle 2	53.38	73918.30
Particle 3	53.38	78672.86

Si L SXES spectral shape of particles 1 is similar to that of amorphous Si, and almost no Li has been detected. It is presumed Particle 1 is hardly charged. However, Li is detected in particle 2 and 3, and Si L spectrum suggests alloying.

⇒ Considering the obtained SXES spectrum of particle 3 using electronic structure calculation.

Discussion about SXES spectrum of particle 3

Si L SXES spectrum of particle 3 Result of electronic structure calculation (WIEN2k)

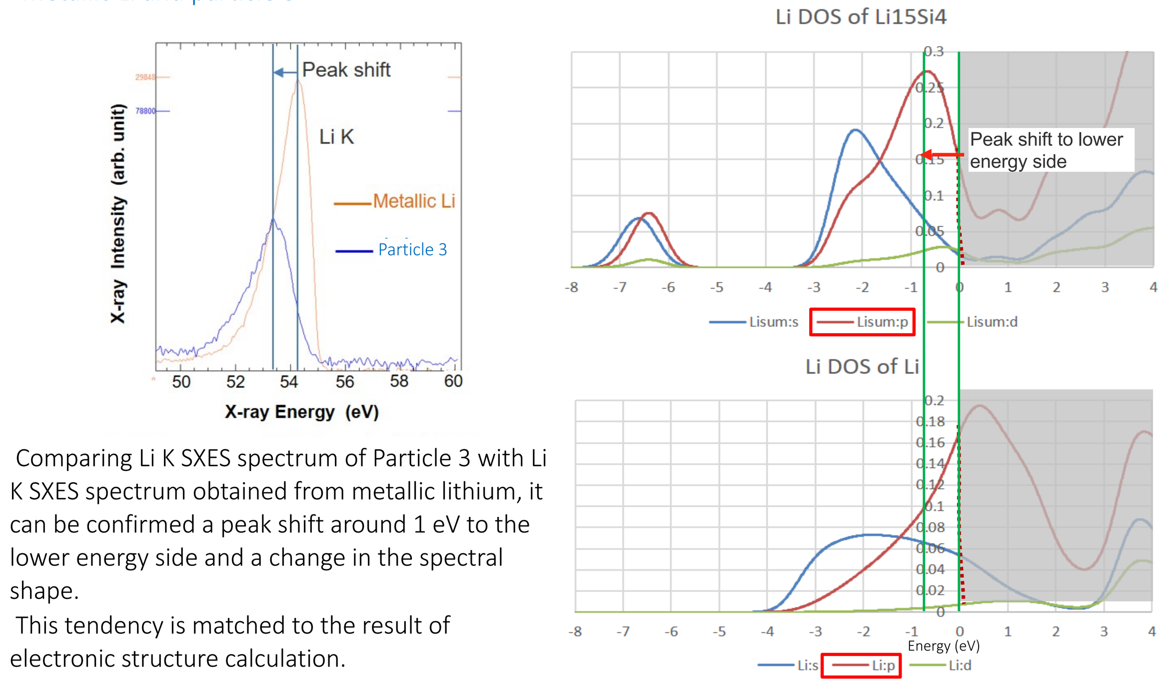


※Horizontal axis 0 eV means the top edge of the valence electron

SXES spectral shape of Si L consists of a sharp main peak and a higher energy side subpeak. This SXES spectral shape of Si L is matched to Si DOS expected for crystalline structure of $Li_{15}Si_4$ which is formed by charging (1).

Comparison with Li K SXES spectrum: Metallic Li and particle 3

Result of electronic structure calculation (WIEN2k)

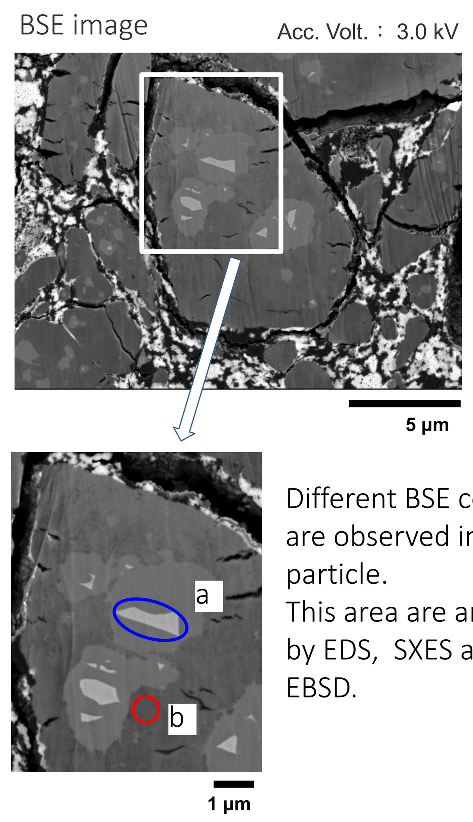


Comparing Li K SXES spectrum of Particle 3 with Li K SXES spectrum obtained from metallic lithium, it can be confirmed a peak shift around 1 eV to the lower energy side and a change in the spectral shape.

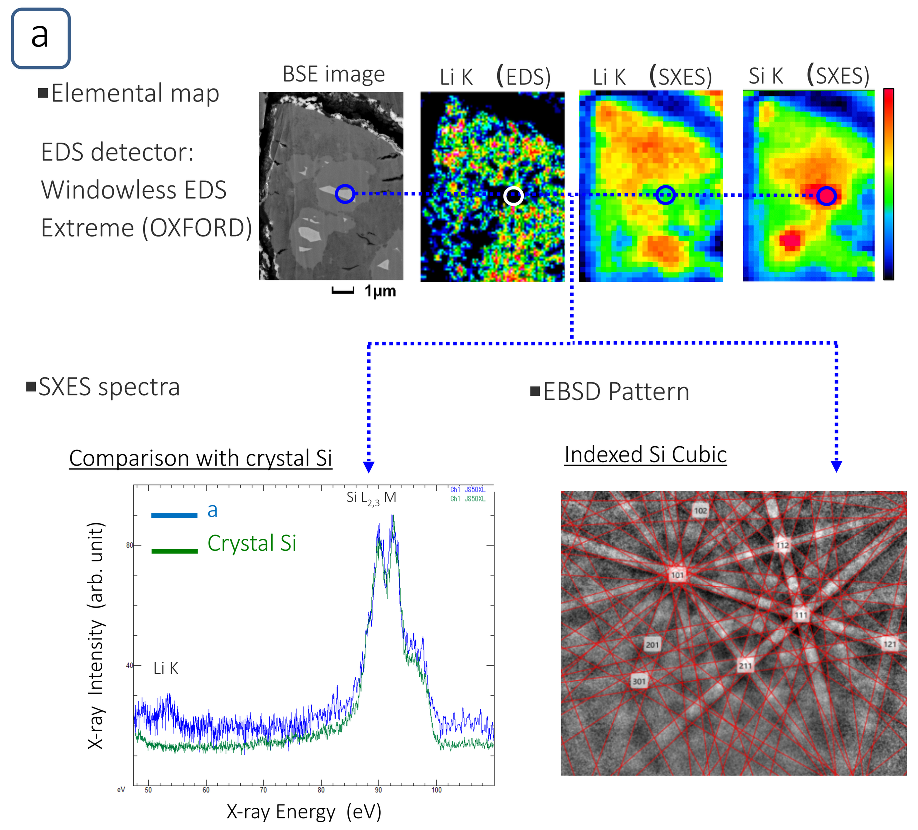
This tendency is matched to the result of electronic structure calculation.

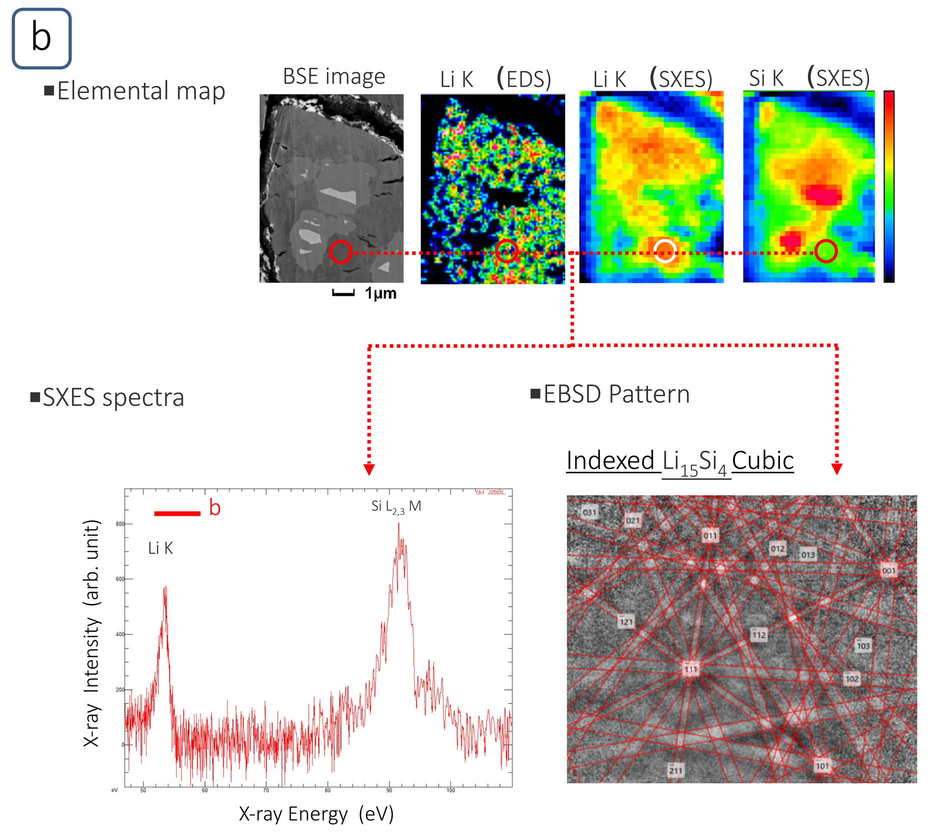
⇒SXES spectra suggesting the alloying of $Li_{15}Si_4$ were obtained from the Li K spectrum and the Si L spectrum of the particle 3.

Analysis inside Si particle of negative electrode



Different BSE contrasts are observed inside Si particle. This area are analyzed by EDS, SXES and EBSD.





Analysis condition EDS: Acc. Volt. 3.0 kV SXES: Acc. Volt. 3.0 kV EBSD: Acc. Volt. 15 kV

The shape of Si L emission spectrum of (a) coincides with that of the spectrum of crystalline Si as a reference. The EBSD pattern of (a) is also indexed with the EBSD pattern expected for crystalline Si. Therefore, uncharged crystalline Si remains in this part. On the other hand, the shapes of Si L and Li K emission spectra obtained at (b) suggest that Si and Li are alloyed. The EBSD pattern of (b) is indexed with the EBSD pattern expected for crystalline structure of $Li_{15}Si_4$ which is formed by charging. From these results, it can be confirmed that the alloys of Si and Li are mixed in several states inside the Si particle during the charging process.

Summary

In the analysis of the negative electrode Si, the Li content and the chemical state such as crystallinity can be detected at once using SEM-SXES. The distribution of Si and Li in the negative electrode layer correlates with the BSE image and EDS elemental maps. In the BSE image, the bright part had a low Li concentration and the dark part had a high Li concentration. This suggests that the Li concentration is high near the solid electrolyte layer and the Li concentration decreases toward the surface of the negative electrode layer. In the analysis inside the Si particle, the Li content, crystallinity, and alloying state were determined by SEM-SXES, the alloy type was determined by EBSD, and these two phases could be identified as $Li_{15}Si_4$ and crystalline Si. The combination of the SEM-SXES method, EDS analysis, and EBSD analysis provided information on the crystal structure and chemical state, and the structural analysis inside a single particle of Si could be performed on a micron-scale. These results demonstrate the effectiveness of this method for Si negative electrode analysis in LIB.

References:
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(3) Terauchi. M et al., Journal of Electron Microscopy, Vol. 61, (2012), P. 1–8
(4) Yamamoto. Y et al., Microscopy and Microanalysis 24(S1), (2018), 1062-1063