Chemical state analysis of Li and Si for Si negative electrode of solid-state lithium ion battery by using combination of windowless EDS and SXES on a SEM

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Introduction

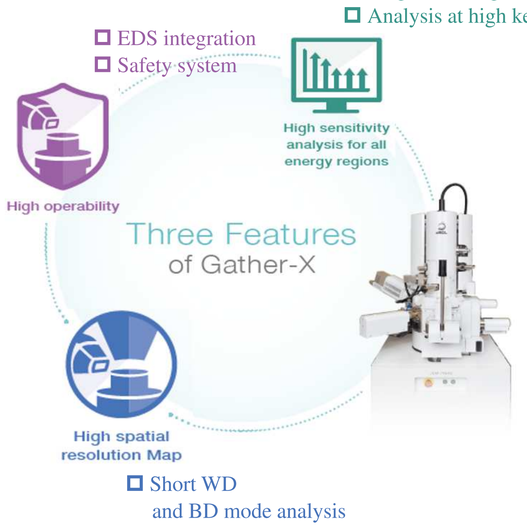
Silicon (Si) negative electrode material has problems such as volume expansion and decrease of charging efficiency during charging-discharging, but it has a large theoretical capacitance of 4200 mAh/g, and is attracting attention as a new material for Lithium (Li) ion secondary battery (LIB) to replace graphite which is widely used. Therefore, a chemical state analysis method using soft X-ray emission spectroscopy (SXES) has been reported for the purpose of structural analysis of the Si negative electrode active material in the charged state(1)(2). However, since elemental mapping by SXES takes at least a few hours of processing time, it is not easy to compare the chemical state of each Si particle across the entire negative electrode layer. In this study, we combined a newly designed windowless EDS and SXES, and tried to establish a simple method to analyze the chemical state of Si negative electrodes in charged states.

Instruments

The Schottky FE-SEM, JSM-IT800 (JEOL), combined with the SXES-LR, SS-94000SXES (JEOL), and the windowless EDS, Dry SD™ Gather-X (JEOL), was used for this study.

Features of Gather-X

- Windowless effect → Low-energy X-rays can be detected with high efficiency, since there is no absorption of X-rays by the window film. Specimen: Metallic Li 5 kV 100 pA 100sec.
- Large solid angle
- Analysis at high keV
- EDS integration
- Safety system

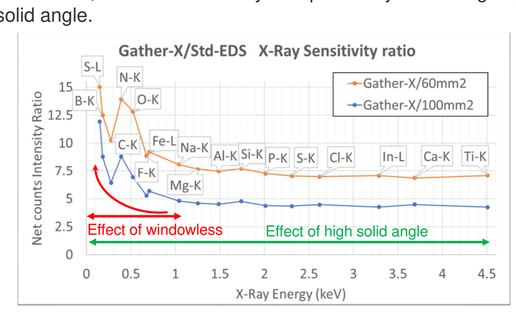


- Short WD and BD mode analysis

※Gather-X can be mounted on JSM-IT800

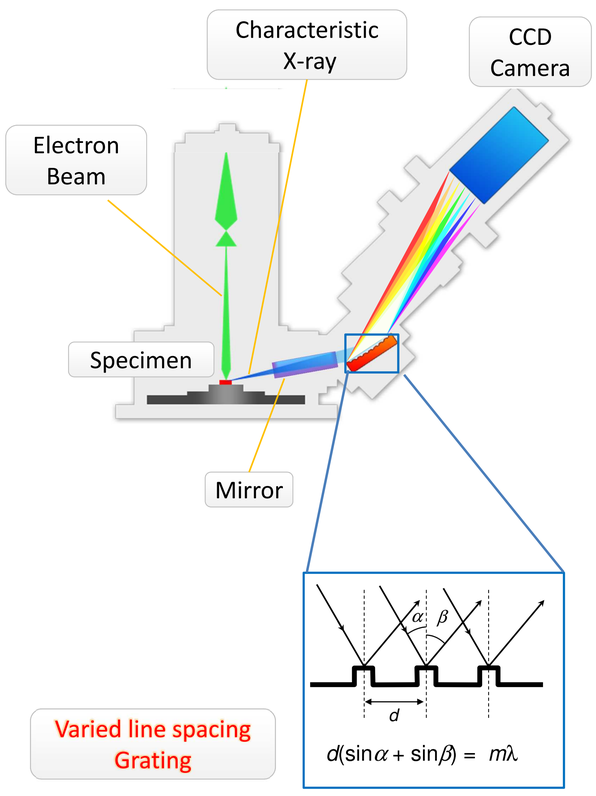
High detection efficiency

Below 1 keV, detection efficiency is improved by windowless. Over 1 keV, detection efficiency is improved by increasing the solid angle.

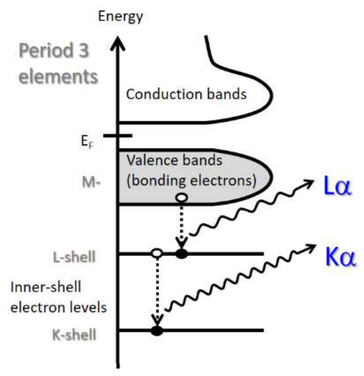


Principle of SXES

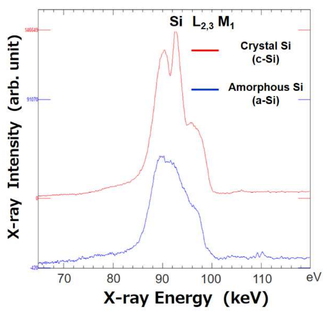
Schematic of SEM-SXES



Chemical state analysis



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 (difference between compound and crystal) is reflected in the spectral structure.

Strong and weak point of gather-X and SXES

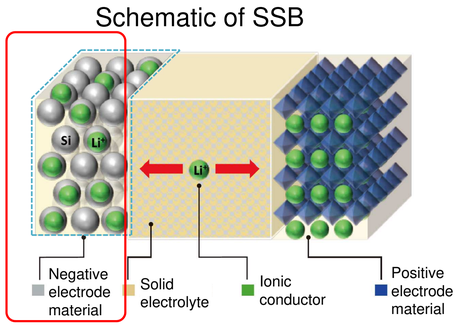
Gather-X：It features multi element detection and high resolution mapping in a short time.
SXES ：It features peak separation using high energy resolution and chemical state analysis.

	SXES	Gather-X
Peak separation(energy resolution)	High	Low
Detection energy range	50~2300 eV (Depends on grating)	50 eV～20 keV
Trace detection (in case of B)	100 ppm	5000 ppm
Simple Quantification	None	Possible
Chemical state analysis	Possible	Impossible
Acquisition time of spectrum	Long	Fast
Mapping (resolution)	~sub micron	~a few 10 nm
Mapping (acquisition time)	Long	Fast
Damage (probe current)	Large	Small

Specimen and analysis flow

As a specimen, a negative electrode prepared by mixing Li_2S-P_2S_5-LiI solid electrolyte by liquid-phase syntheses(3) and Si particles were used. A half-cell was prepared using this negative electrode and charged at 80% of the theoretical capacitance value of Si. After charging, it was cross-sectioned by an Ar ion beam using IB-19520CCP (JEOL) under cooling conditions. All processes were performed under an air isolation environment.

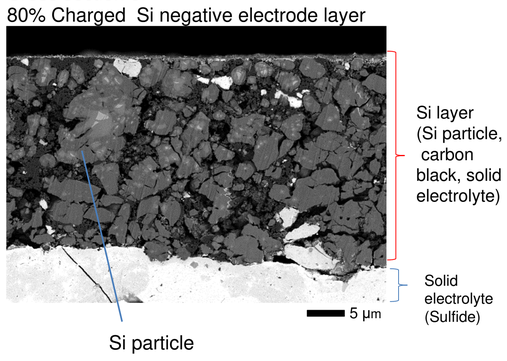
Schematic of SSB



Theoretical capacity of Si: 4,200mAh/g → Ten times larger than carbon (graphite)

Problem：
Si structural changes due to charging-discharging are large, and the capacity tends to decrease.

Cross section of 80% Charged Si negative electrode layer



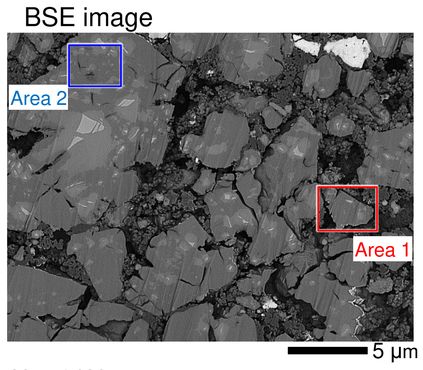
Analysis flow

preparation (IB-19520CCP)
↓
SEM （IT800）
↓
EDS （Gather-X）
↓
SXES (SXES-LR)

Result 1: Screening of Li distribution and SXES analysis of charging state

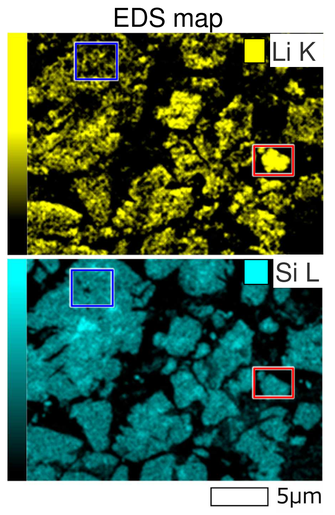
As a result of the elemental mapping, the difference in Li intensity was confirmed among the Si particles that did not show clear contrast differences in the BSE image. The windowless EDS facilitates elemental mapping and enables a rough understanding of the Li distribution in the negative electrode layer in a short time. From the results of SXES analysis of particles with different Li intensities in areas 1 and 2, it can be seen that the Li K emission peak position (≈53.4 eV) is different from that of metallic Li (≈54.2 eV). Moreover, from the difference in the structure of the Si L emission spectra, it was found that there are particles with different rates of Li-Si alloying by charging.

BSE image

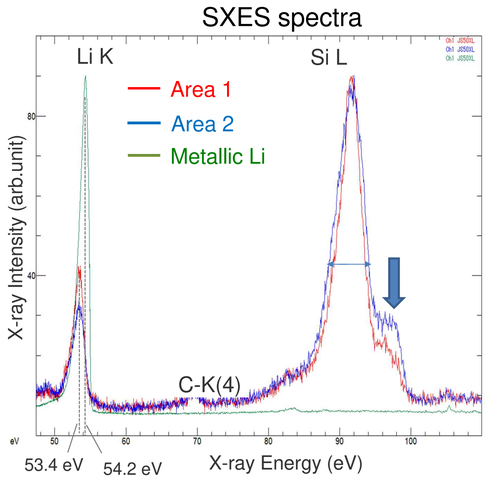


Vac.:3 kV
Probe current: EDS 2 nA
SXES 20 nA
Process time: EDS map 20 min.
SXES spectra 5 min.

EDS map



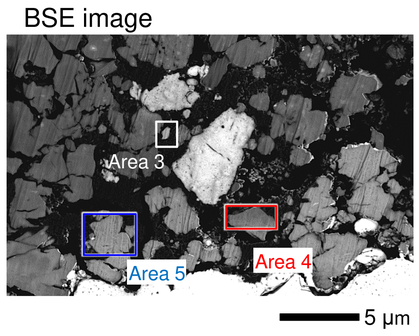
SXES spectra



Result 2: Detection of Si in the early stage of lithiation and chemical state analysis

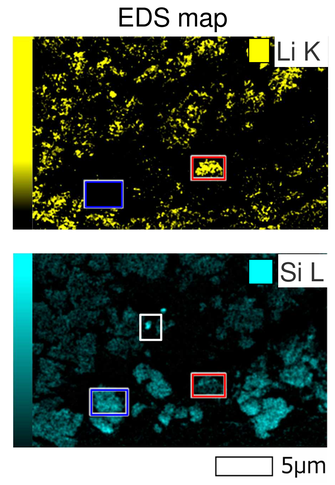
In case of result 2, the EDS map shows no Li distribution in area 5. On the other hand, in the Si EDS map, the Si intensity is lower in area 4 than in area 3, which suggests that lithiation is occurring due to charging process. The results of the SXES analysis show a small peak of Li K in area 5, indicating that lithiation is occurring. And it can be seen that the Li K emission peak position (≈53.9 eV) of area 5 is different from that of area 4 (≈53.4 eV). Moreover, the significantly different structure of the Si L emission spectrum suggests that the particles in Area 5 are in the initial state of Li-Si alloying in the charging process. These results indicate that the Li distribution in Si particles that have reached a certain stage of lithiation can be detected by windowless EDS. And the Li in Si particles at a relatively early stage of lithiation can be detected and analyzed differences in chemical states at different charging state by SXES. Thus, windowless EDS and SXES can be used in a complementary correlation.

BSE image

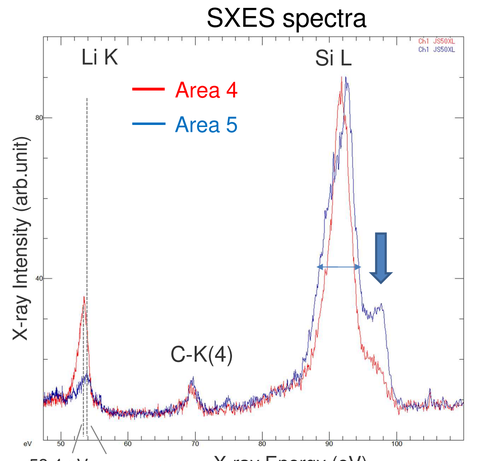


Vac.:3 kV
Probe current: EDS 2 nA
SXES 20 nA
Process time: EDS map 12 min.
SXES spectra 5 min.

EDS map



SXES spectra



Summary

Li analysis by using Gather-X

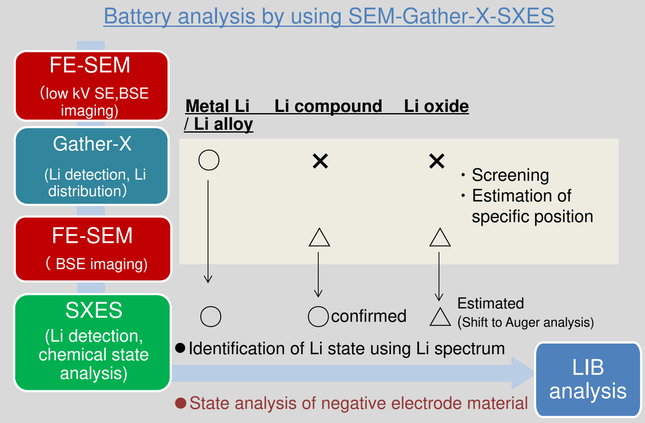
①Possible screening of metal Li distribution in a wide area.
②Possible to confirm the compositional information from BSE image contrast.

Li analysis by using SXES

- Confirmation of information by EDS（State of Li）.
- Confirmation of negative electrode material state.

Gather-X which enables to measuring in a short time is used for screening, and SXES which enables detailed analysis is used for final judgement. Each features of both detectors has a complementary correlation, and new analysis methods have been created using both detectors by linking them well.

Battery analysis by using SEM-Gather-X-SXES



References
(1) Yamamoto. Y et al., Microscopy and Microanalysis 26 (S2):68-70(2020), (2) Yamamoto. Y et al., Microscopy Conference 2021, MS1.P021, (3) Hikima. K et al., Solid State Ionics, Volume 354, (2020), 115403