EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** In operando study on the structural changes during charging-discharging cycles of Li-Si batteries	**Experiment number**: MA-3333
Beamline: ID01	**Date of experiment**: from: 03/05/2017 to: 05/05/2017	**Date of report**: 25/09/2017
Shifts: 9	**Local contact(s)**: Tao Zhou	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The objective of the experiment was to study the structural changes in Si based anodes during operando lithiation and delithiation cycles of Lithium-ion Batteries (LiBs) using the new Full Field Diffraction X-ray Microscope. Compared to the proof-of-principle experiment performed previously, (fig. 1) in this study we used for the first time the new version of the half cell which contains a third (reference) electrode. This allows us to have a better estimation of the actual potential of the other half cell. At the same time, more patient cycling was performed. Each Cyclic Voltammetry cycle lasts for 20 min, which contributes to the long measurement time. With the 9 shifts that were given, we were able to measure a total of 3 samples, all of which consist of planar Si anode. We did not measure the nanoparticle or the nanowire sample, as we realized during the experiment that there were still a lot important things to be learnt from the simplest model system. The 3 measurements (samples) constitutes hence a series of operando study on planar Si anodes, each designed to improve upon its predecessor, to answer a specific question, with a different cycling strategy. Below is shown a short summary on the last sample.

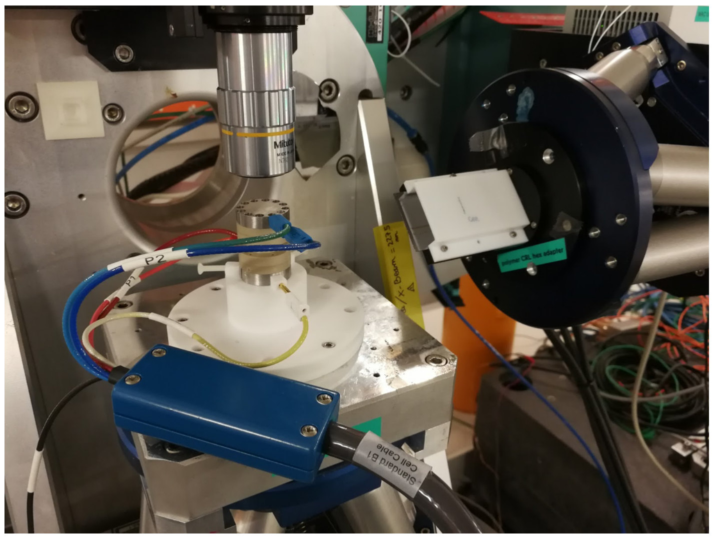

Figure 1: new three electrode half cell on ID01

During each CV cycle we used timescan at an off-Bragg (-0.033° in theta) position to monitor the nucleation of defects. Below is shown some FFDXM images of the second cycle (during the first cycle no changes were observed). Five different stages were observed.

(Point O to A, 100 mV< E < 700mV, I < 0) The lithiation occurs already for E < 700mV, althought no structural changes were observed (as we formed mostly amorphous LiSi alloy).

(Point A to B, E < 100mV, I < 0) As soon as E drops below 100 mV, two defects were observed (not present in cycle 1), probably due to the formation of a crystalline Li_xSi alloy with very high Li composition x (probably $Li_{22}Si_5$). With the CV cycle, we only stayed below 100mV for 38 sec, and the intensity at the defected area kept rising during this period.

(Point B to C, 100 mV< E < 700mV, I < 0) When E rose again above 100 mV, the defects, especially the one on the right, became less visible on the image, which may be understood as the previously formed Li_xSi alloy being transformed into one with lower Li composition (probably $Li_{13}Si_4$).

(Point C to D, 100 mV< E < 700mV, I > 0) The intensity at the defected area then rose again, this corresponds to the part where we were still below the voltage for lithiation but has a postive current. This phenomenon is still under investigation.

(Point D to E, E > 700mV, I > 0) As E became larger than 700 mV and with I > 0, the delithiation process began, the defects were still visible though less intense, hinting that the process was not completely reversible (or not completely irreversible).

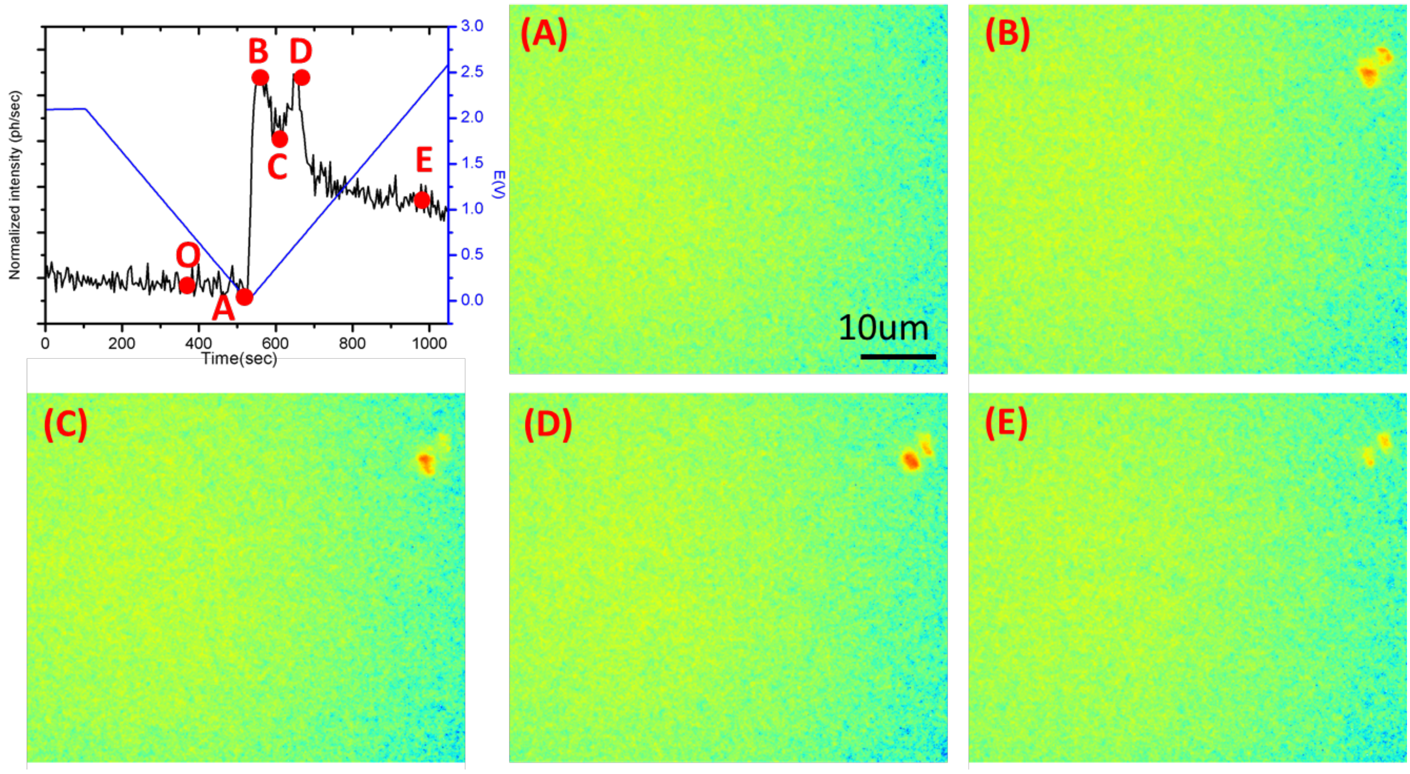

Figure 2 : FFDXM images during the 2nd CV cycle, taken during a timescan at an off-Bragg angle

We studied the nature of the defects we observed by 2D mapping of the reciprocal space between the CV cycles. It would appear that the contrast we observed come from tensily strained area (red contour in Fig. 3 left) of the crystalline Li_xSi surrounded by compressively strained area (blue contour in Fig. 3 left).

Cycle 3 (Fig. 3 mid) is very similar to cycle 2, though the variations in intensity during the process were less significant. Hardly any variation was observed in Cycle 4 (Fig 3. right)

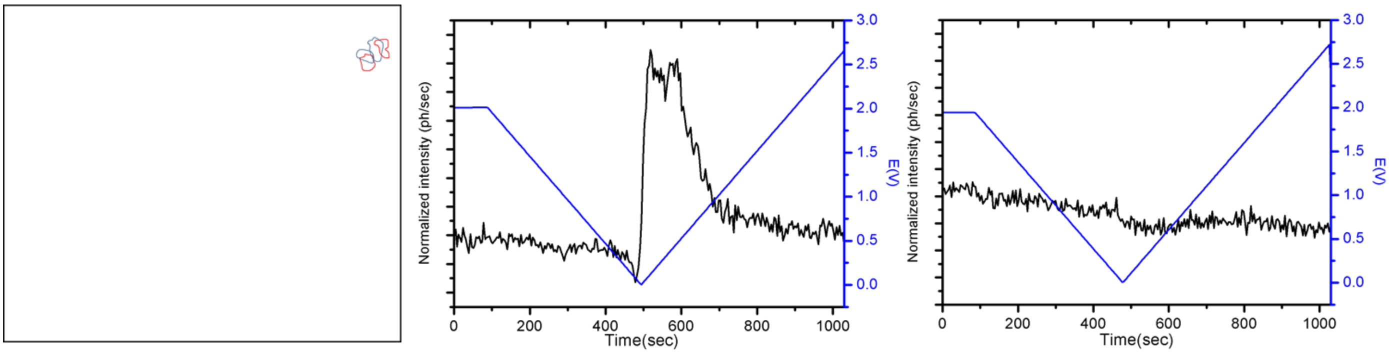

Figure 3 : left: contour showing the part of the FoV that is under tensile strain (red) and the part under compressive strain (blue). Mid: intensity variations in cycle 3. Right : intensity variations in cycle 4.

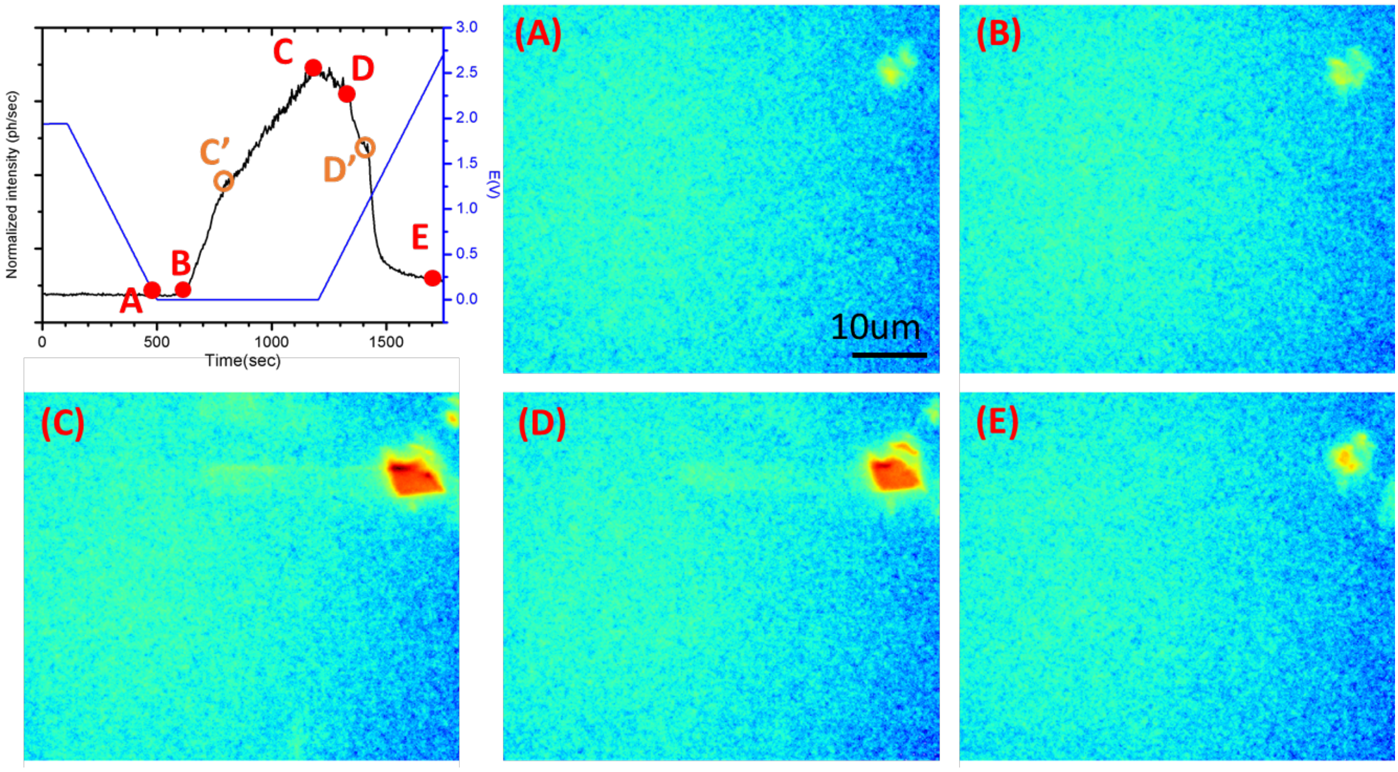

Figure 4: FFDXM images during cycle 6, taken during a timescan at an off-Bragg angle

Starting from cycle 5, we have increased the amount the time we stay below 100 mV.
On cycle 6 (Fig. 4), some new defect sites were observed. We were able to identify 4 (possibly 6) stages of the process.
(Point A to B, $E < 100$mV, $I < 0$) The morphology of the defects were changing but the intensity remained relatively constant. We do not yet understand the origin of this incubation period.
(Point B to C, $E < 100$mV, $I < 0$) Formation of probably $Li_{22}Si_5$, the intensity at the defected area increased abruptedly.
(Point C to D, 100 mV< $E < 700$mV) The transformation of $Li_{22}Si_5$ into probably $Li_{13}Si_4$. The intensity at the defected area decreased gradually.
(Point D to E, $E > 700$mV, $I > 0$) Delithiation: intensity dropped abruptedly.
There are hints of a secondary effect (change of slope around point C' and D'), we are still in the progress of understanding this. We then continuously increased the duration for which we stayed below 100 mV to have defect nucleation in the entire FoV. In Fig. 5 is shown the comparison between the state of the sample after cycle 2 and cycle 10.

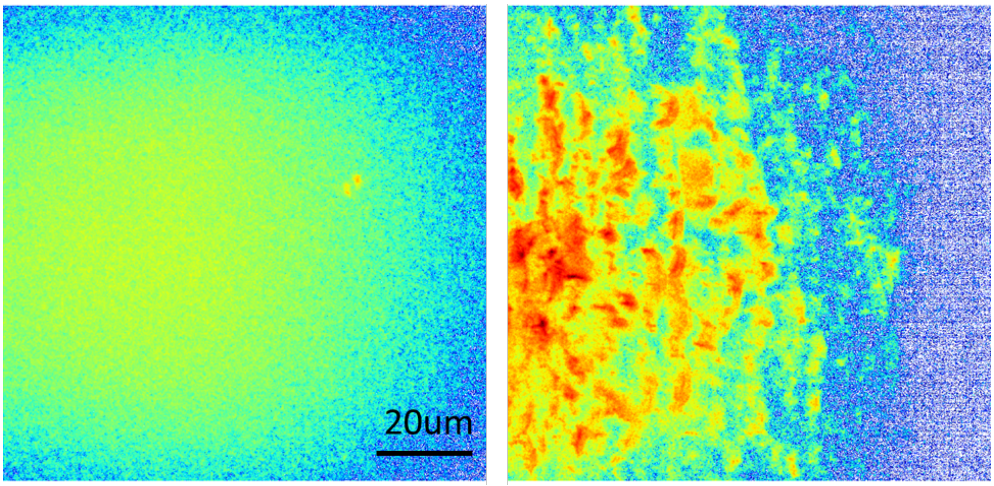

Figure 5 : FFDXM image taken after cycle 2 and cycle 10 over the entire FoV.

With FFDXM, we were able to study the dynamics of defect formation during the operando lithiation and delithiation cycles. By performing 2D mapping in between CV cycles, we were able to study quantitatively the nature of the defects.

The experiment was a great success, especially considering the relatively short beamtime, the irreverserble nature of operando experiments (had we missed one moment, we would have to repeat it on another sample) and the fact that we were among the first users for this brand new instrument (it takes sometimes missteps to find the optimal measurement strategy). We are also extremely excited about the observation of the very beginning of the structural failure of LiBs with planar Si anodes as well as the observation of the formation of different LiSi alloy during the process.