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

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** Operando PDF studies of silicon-based anodes for lithium-ion batteries	**Experiment number**: A31-1-183
Beamline: BM31	**Date of experiment**: from: 11 Nov 2022 to: 14 Nov 2022	**Date of report**: 28/02/2023
Shifts: 9	**Local contact(s)**: Kenneth Marshall, Dragos Constantin Stoian	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

David Wragg*, Alexey Koposov* - University of Oslo
Casper Skautvedt*, Agnieszka Magdziarz*, Erlend T. North* - University of Oslo (not original proposers)

Report:

The experiments from this proposal was devided into two parts. One part analysed ex-situ samples of Si and SiX (where A = O, N, C, P, x< 1) samples from different steps of charge. The second part was operando studies.

Figure 1 shows pristine Si in capillary with the calculated PDF pattern compared. There were some issues with the samples where some capillaries was difficult to get a scattering pattern. But we were able to validate the pristine electrode powders and their nearest neighbour distances from PDF analysis.

In figure 2 we plotted the PDFs for a half cell with crystalline Si anode in a heatmap format alongside electrochemical data. The data we got was unfortonatly overshadowed by Cu and Li diffraction and we had to remove peaks manually to obtain the PDF for Si. however by subtracting the first PDF from the subsequent ones in the opeprando series (difference PDF[1], figure 3) it is possible to see the movement of peaks in low (2 – 3.25 Å) and high (6.5 – 8 Å) r regions which match with distances that Key et al.[2] reported to change during lithaition of silicon. The changes in peak position appear to be strongly correlated with the electrochemistry.

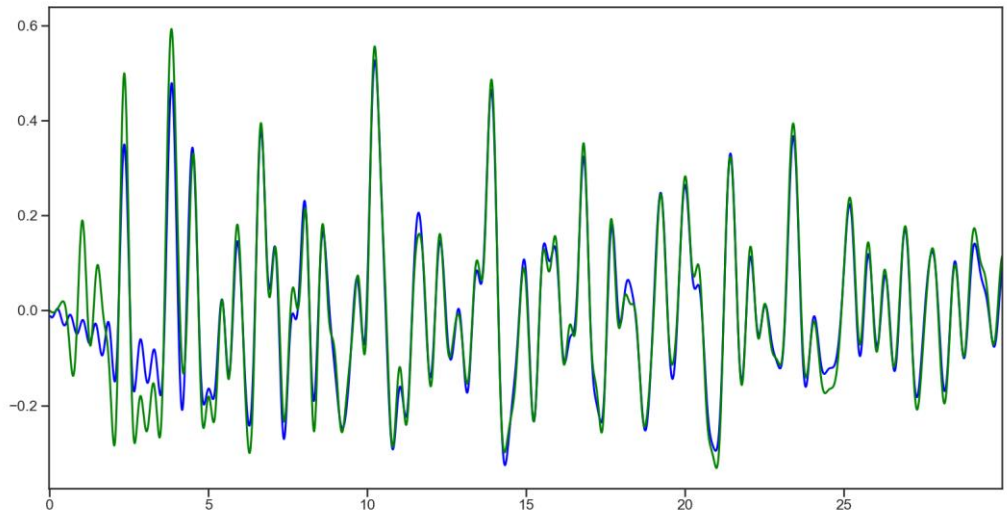

Figure 1: PDF pattern of Si from capillaries (green) and the calculated PDF pattern (blue).

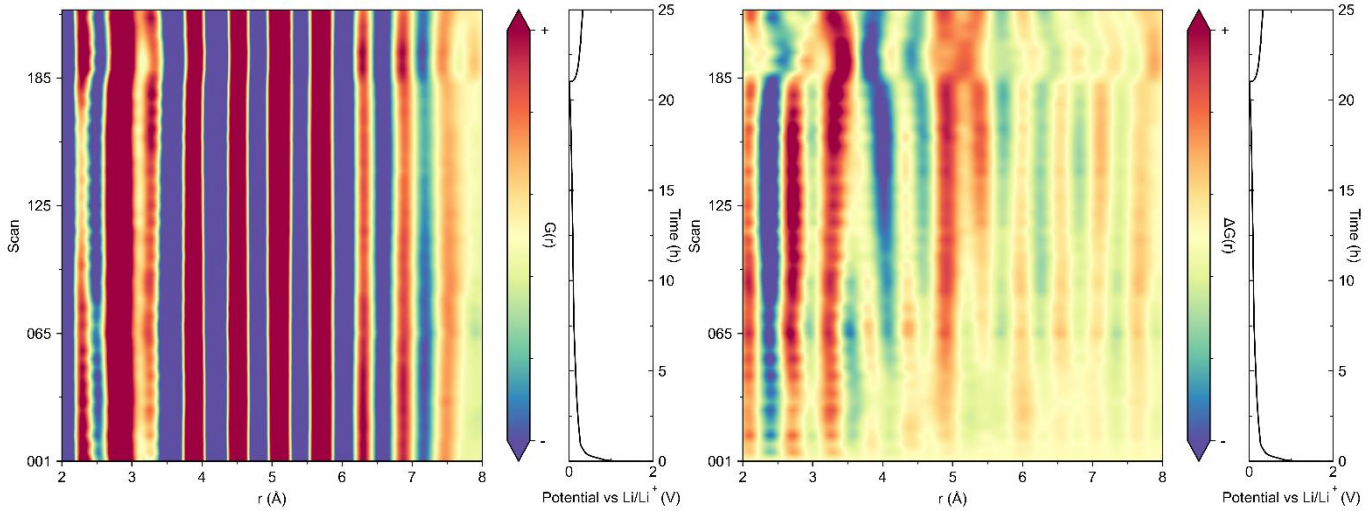

Figure 2 (left) and 3 (right): PDF patterns of Si put in a heatmap to see the changes during discharge of the battery (left). To highlight the changes one can see a differiential PDF (right) where the first PDF pattern was substracted from the following PDF patterns.

References

(1) Stratford, J. M.; Kleppe, A. K.; Keeble, D. S.; Chater, P. A.; Meysami, S. S.; Wright, C. J.; Barker, J.; Titirici, M.-M.; Allan, P. K.; Grey, C. P. Correlating Local Structure and Sodium Storage in Hard Carbon Anodes: Insights from Pair Distribution Function Analysis and Solid-State NMR. *Journal of the American Chemical Society* **2021**, *143* (35), 14274-14286. DOI: 10.1021/jacs.1c06058.

(2) Key, B.; Morcrette, M.; Tarascon, J.-M.; Grey, C. P. Pair Distribution Function Analysis and Solid State NMR Studies of Silicon Electrodes for Lithium Ion Batteries: Understanding the (De)lithiation Mechanisms. *Journal of the American Chemical Society* **2011**, *133* (3), 503-512. DOI: 10.1021/ja108085d.