EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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.

	Experiment title: Operando PDF and XAS studies on amorphous phases in Na battery anodes	**Experiment number**: A31-1 207
Beamline: BM31	**Date of experiment**: from: 17 June 2023 to: 21 June 2023	**Date of report**: 12/09/2023
Shifts: 12	**Local contact(s)**: Kenneth Marshall, Wouter van Beek	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Amalie Skurtveit*, Anders Brennhagen*, Erlend T. North*, Alexey Koposov*, David Wragg* - University of Oslo

Report:

Preliminary report: The experiment was successful. We measured on two types of compounds: Bi- and Sb-based materials as anode materials in Na-ion batteries. There were some minor issues at the start of our experiment (luggage with all samples was lost by the airline), but we managed to make up for lost time.

Bi-based materials (Bi_2MoO_6 and $BiFeO_3$): We extensively measured ex situ samples of $BiFeO_3$ and Bi_2MoO_6 at different stages of (dis)charge in capillaries using XRD, PDF, and XAS (with full EXAFS region, Bi- and Mo-edge). We were also able to successfully measure the combined quasi-simultaneous operando PDF/EXAFS on Bi_2MoO_6 as anode in NIB using the electrochemical cell equipped with glassy carbon windows (see Drozhzhin et al (doi: 10.1107/S1600577517017489) for cell design). The data is still currently being analysed, but our preliminary results show that we are able to gain a deeper understanding of Bi_2MoO_6 and a manuscript is in progress Figure 11). Operando XRD of $BiFeO_3$ at high cycling rate (1000 mA g^{-1}, approx. 2C) was also collected at this beamtime, and we are including this dataset in a publication Figure 22

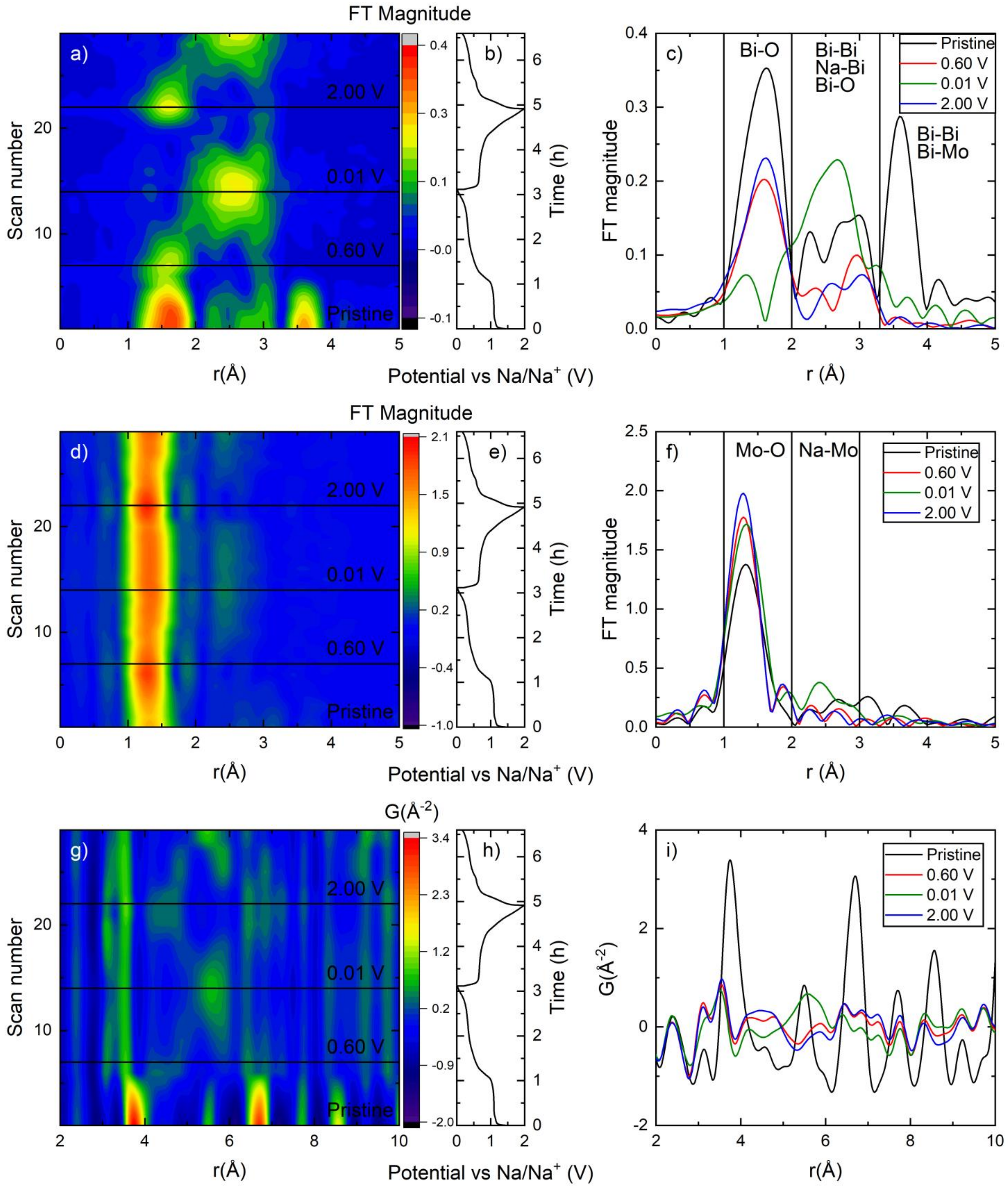


Figure 1: Combined operando PDF/EXAFS measurement on Bi_2MoO_6. FT EXAFS contour plots of a) Bi L3 edge and d) Mo k edge, b), e) and h) (de)sodiation curves. g) PDF contour plot. c), f) and i) selected scans extracted from the plots in a), d) and g) marked with black lines.

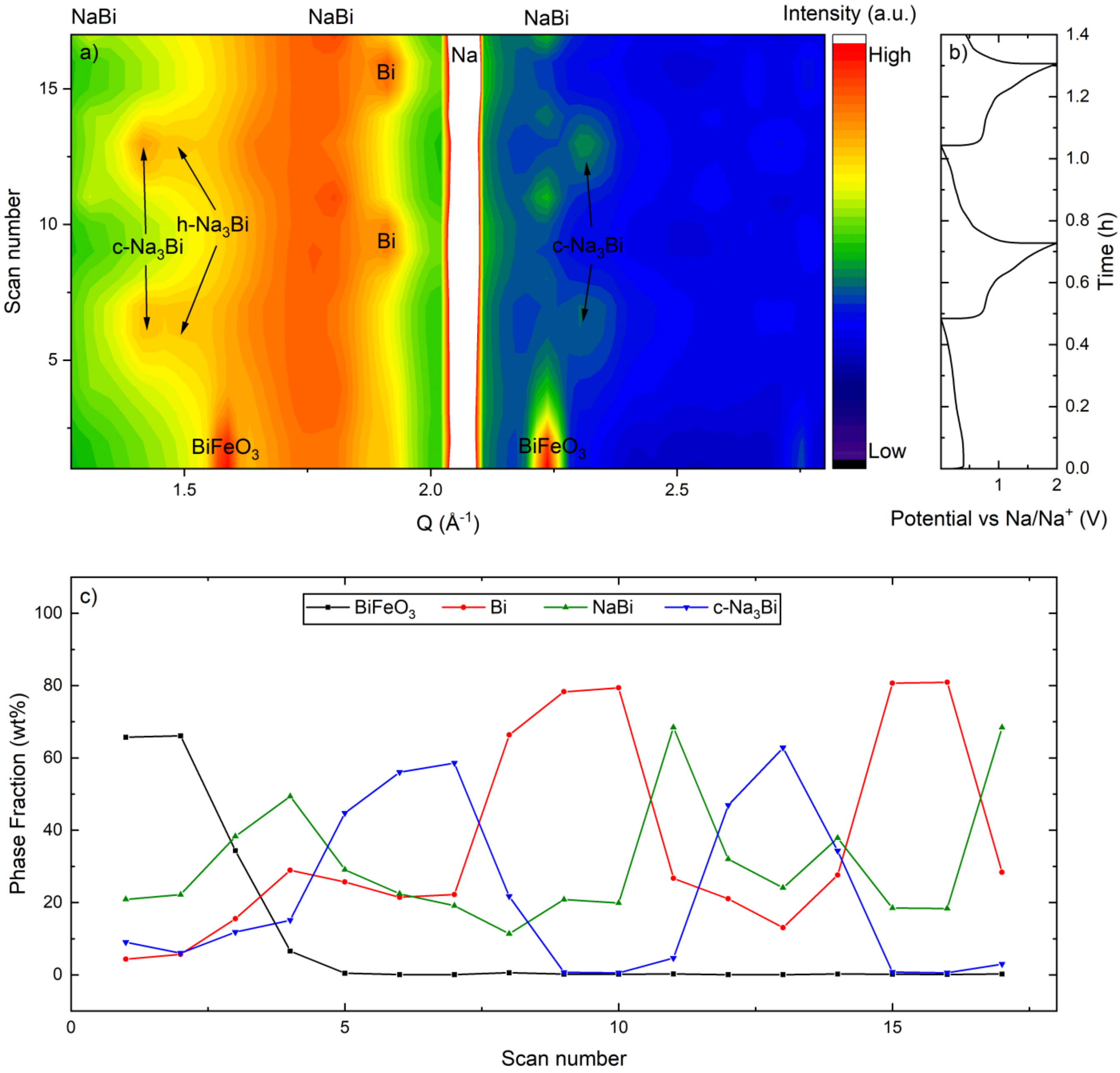
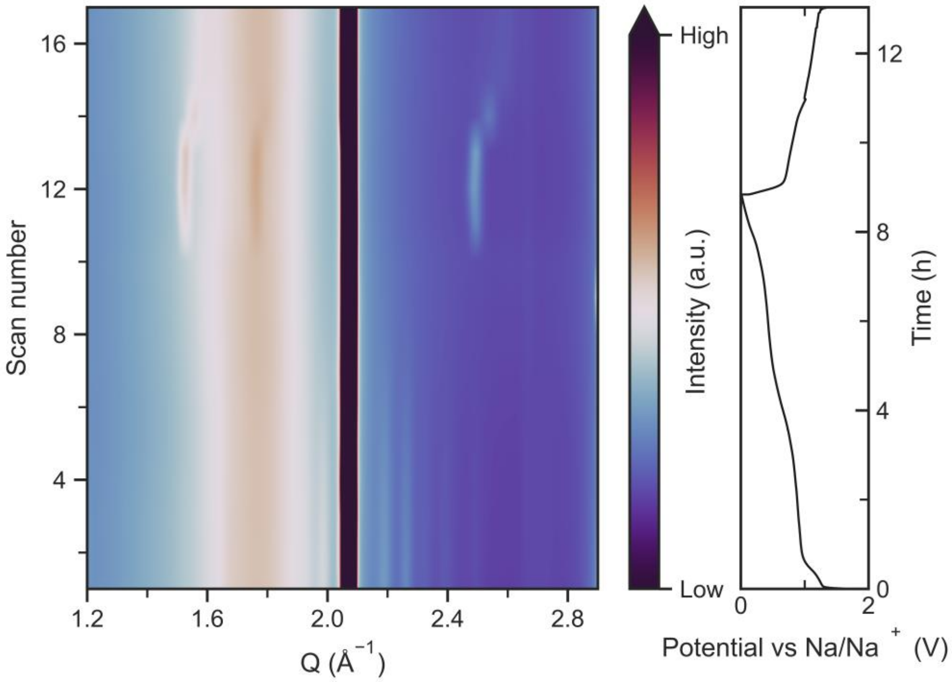


Figure 2: Operando XRD of $BiFeO_3$ at the high rate of 1 A g^{-1}. a) contour plot showing the development of the diffraction peaks, b) (de)sodiation curves and c) development of phase fractions during cycling obtained from surface Rietveld refinement.

Sb-based materials (Sb_2Se_3, Sb_2Se_3/Sb, and Sb_2S_3): We spent the better part of a day to get our cells working properly (see description above). However, when we managed to sort out our electrochemistry problems, we measured 3 x operando PDF/XAS (Sb-edge) simultaneously with current densities of either 100 mA g^{-1} or 1000 mA g^{-1}. In all, we have 6 number of operando PDF/XAS datasets successfully collected of Sb_2X_3. An example of the operando XRD of Sb_2Se_3 is given in the figure below. Converting analysis of the PDF are still ongoing for all collected data.



In all operando PDF experiments, there are significant amounts of copper current collector and Na sampled along with the active material. This causes problems with the PDF analysis as the crystalline copper dominates the PDF, but we have implemented methods for removing crystalline Cu and Na peaks from the diffractograms. Furthermore, the use of thin electrodes for Sb_2X_3 means that difference PDF is the method of choice for analysis of the data as the changes between the individual PDF scans are extremely small.
However, SNBL has developed a new, user-friendly electrochemical cell (BASSET cell) where we can shoot the beam only at the top of the electrode (thus, only including PDF of interested active material part), instead of shooting the beam through the whole battery stack. This has the potential of limiting Cu and Na domination in the PDF. Sb_2Se_3/Sb was tested in this cell. The electrodes of Sb_2Se_3/Sb might have been too thin, so that we are hitting some crystalline copper current collector in addition to the active material (see figure below). We conclude that more investigations are highly necessary for the BaSSET cell, where optimization of the cell design (currently working on) to improve the electrochemical performance and optimization of the electrode preparation are main objectives for further developing this cell.