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:** Operando XRD/PDF-CT to study novel alloying anodes for Na-ion batteries	**Experiment number**:
Beamline:	**Date of experiment**: from: 5/7/17 to: 11/7/17	**Date of report**: 8/9/17
Shifts: 18	**Local contact(s)**: Gavin Vaughan	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Jonas Sottmann*, David Wragg*, Amund Ruud*, Øystein Fjellvåg*. University of Oslo, Department of Chemistry.

Report: The experiment aimed to study battery cycling of bismuth molybdate and vanadate against sodium. The experiment was successful in terms of data collection, with four cells measured under working conditions in the new version of the Oslo/ID15 battery XRD-CT sample container (figure 1 left panel). Making the sample container from quartz significantly eased the process of tomographic reconstruction compared to the original Teflon walls. The glassy carbon contact rods were also a major improvement (compared with the previous aluminium rods), ensuring a flat platform for the electrode and good electrical contact as well as a clear starting point for measurements. The second cell measured (Bi molybdate vs Li) cycled much faster than expected as it was difficult to determine the small mass of electrode material (0.1-0.3 mg) with the balance available in the electrochemistry. This may mean that the data are not useful due to insufficient time resolution. A 7-place balance would be useful in future. Around 40 *post mortem* capillary samples were also measured as references, giving high quality PDF data.

The new (Python based) data processing programs being developed at ID15 worked well and all tomographic reconstructions were completed shortly after the experiment. PDF conversion scripts have just been completed (the data shown in fig. 1 used an early version of the script which could only average voxels over a square within the circular tomogram).

Preliminary data analysis on the first operando dataset indicates that we will be able to extract information from the data using both Rietveld and PDF methods. The right panel of figure 1 shows PDFs from the start and end of the first sodiation of bismuth molybdate along with a sample PDF of "Super-P" carbon, the other main component of the anode material. The main

features due to “Super-P” at ca 1.5 and 2.4 Å are easily picked out in the operando data, giving a reference indicating the reliability of the PDF conversion. In the sodiated PDF peaks at ca. 3.1 and 3.4 Å correspond to Na-Bi distances in Na_3Bi, while 5.1 and 5.5 Å peaks fit with the Bi-Bi contacts. The PDF of the initial bismuth molybdate has strong peaks at around 4 Å related to the Mo-Bi distances and other peaks at shorter radial distances which clearly fit with the Mo-O and Bi-O bond lengths. We can also see from PDFs over a longer radial range (not shown) the transition from crystalline bismuth molybdate to amorphous Na_3Bi/sodium molybdate with no PDF peaks beyond 10 Å.

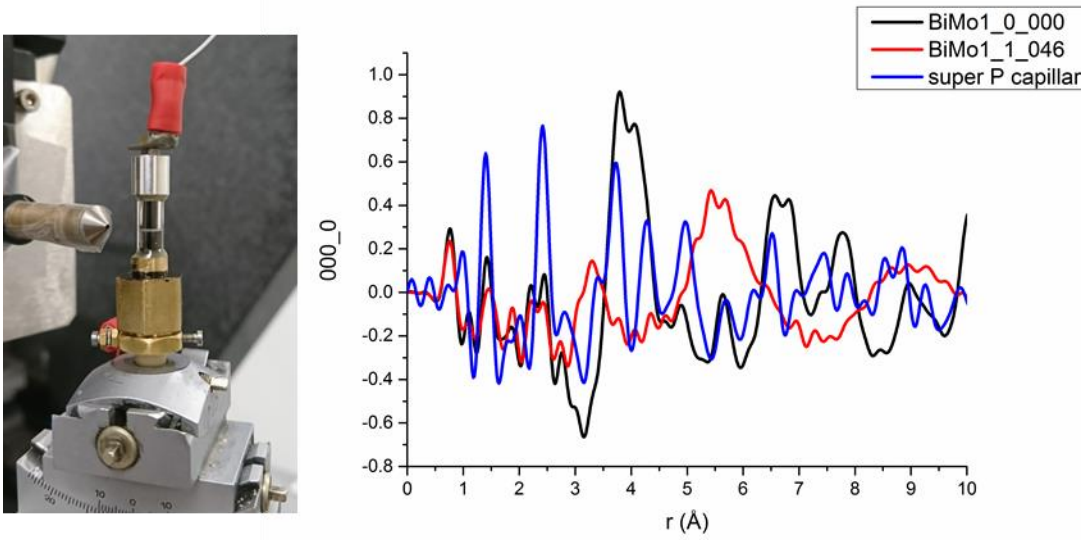

Figure 1. The new XRD/PDF-CT battery sample holder (left); Example PDF data for bismuth molybdate vs sodium, first sodiation, first pass PDF conversion (right).

Rietveld analysis of the same dataset has allowed us to determine phase fractions of the crystalline and, unexpectedly, some amorphous phases using the methods described in our earlier paper for Bismuth sulfide[1].

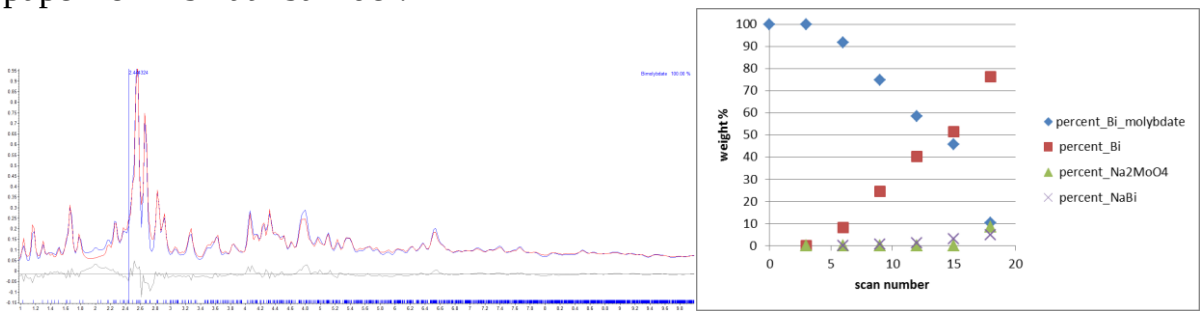

Figure 2 Rietveld fit for bismuth molybdate (left) and phase fractions from Rietveld QPA for the intial part of the first sodiation of bismuth molybdate (right)

We expect to have the final version of the PDF data soon and will be able to complete the data processing.

1. Sottmann, J.; Homs-Regojo, R.; Wragg, D. S.; Fjellvag, H.; Margadonna, S.; Emerich, H., Versatile electrochemical cell for Li/Na-ion batteries and high-throughput setup for combined operando X-ray diffraction and absorption spectroscopy. *J. Appl. Cryst.* **2016,** *49* (6).