

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://www.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

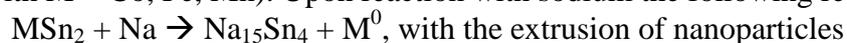
- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you 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.



	Experiment title: In situ investigation of the role of the transition metal in intermetallics of the form $M\text{Sn}_2$ ($M = \text{Co}, \text{Fe}, \text{Mn}$) during sodiation and de-sodiation in Na-ion batteries	Experiment number: MA-2535
Beamline: BM01B	Date of experiment: from: 22.04.2015 to: 27.04.2015	Date of report: 20.08.2015
Shifts: 15	Local contact(s): Hermann Emerich	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Leonie Vogt*, Petr Novak, Peter Bleith, Claire Villevieille Paul Scherrer Institut, 5232 Villigen PSI, Switzerland		

Report:

In this experiment we aimed to use our in situ XAS and XRD battery cell, previously tested in an experiment at the same beamline (01-01 914), to explore an interesting class of conversion based anode materials. The materials crystallise in the tetragonal $I4/mcm$ space group and have the following chemical composition $M\text{Sn}_2$ (with $M = \text{Co}, \text{Fe}, \text{Mn}$). Upon reaction with sodium the following reaction is expected



With a combination of XAS and XRD in situ measurements we aimed to certify this reaction mechanism by identifying $\text{Na}_{15}\text{Sn}_4$ in the XRD and tracking the oxidation state of the transition metal as the structural changes occur.

The experiment was performed successfully, allowing us to gather data sets on four in situ cells as well as on some ex situ samples. The battery sample holder available at the beamline was converted to hold ex situ samples on Kapton foils tremendously reducing the time needed for the exchange between different ex situ samples. With no technical difficulties on the electrochemical equipment nor on the beamline (except on the final evening), the allocated beamtime was thus put to optimal use. XANES on the transition metal K-edges were collected in fluorescence (due to the highly absorbing Sn in the structure) and XRD was recorded throughout the cycling of the in situ cells. The proposed reaction mechanism is, however, difficult to verify with the in situ data.

The XANES data show no significant shifts in the absorption edge throughout cycling (Figure 1a). The XRD data show a similar stationary trend (Figure 1b). The FeSn_2 peaks surprisingly didn't change in intensity and no peaks ascribable to $\text{Na}_{15}\text{Sn}_4$ could be identified. We attribute this to the fact that the material was not crystalline enough to allow subtle changes to be observed. A few peaks, probably related to side reactions, are observed to grow with scan number but could not be identified. However, both in situ XAS and XRD results are in accordance. There could be two possible reasons for this stationary trend, either (i) the oxidation state of the transition metal is the same in the alloy as in the transition metal nanoparticle, roughly 0, such that no shift in the XANES absorption edge occurs even though the extrusion takes place, or (ii) the timescale of the first cycle studied in situ is not enough for the extrusion to occur to completion to be visible by the technique but rather this process happens over multiple cycles. For option (i) the nearest neighbour environment would still be expected to change upon extrusion, causing shifts in the oscillations after the edge jump, yet no such shifts were seen making this option unlikely. Option (ii) would mean that more specific

charge would have to be achieved in later cycles when the transition metal is fully extruded. Indeed, electrochemical results show that the material undergoes an activation over multiple cycles slowly increasing the specific charge that it achieves, making the latter reason the most likely explanation for the trend seen.

The electrochemistry of the in situ cell was similar to the one performed in our laboratory and the galvanostatic curves are compared to our standard electrochemical cell in Figure 1c for FeSn₂. At 0.8 V on the first sodiation an extra potential plateau is observed for the standard cell, which can be attributed to the fact that the cells are made from different materials, leading to different surface reactions occurring at this potential. The onset of the low potential plateau is at the same potential for both systems and the specific charge achieved in the cells after the 20 hour potentiostatic step at 5 mV is comparable achieving just above 400 mAh/g. On desodiation the overpotential is slightly higher in the in situ cell and the reversibility is not quite as good as for the standard cell. Potentially a longer potentiostatic step at the end of sodiation in the in situ cell could combat such a trend.

EXAFS data was recorded on ex-situ samples at different states of sodiation and the analysis for the FeSn₂ electrodes is presented in Figure 1d. The spectra were treated for a k value between 1 and 9.5. A small trend is visible here showing that the peak at 2.8 Å, corresponding to the Fe-Sn bond length, diminishes on sodiation and grows again on desodiation. This is in line with our hypothesis as the sodiation occurs by Na alloying with Sn, which consequently destroys some Fe-Sn bonds. This process is probably the reason of the specific charge obtained for this material.

Further investigations of the data are ongoing. Additionally first trial experiments whether it could be possible to investigate this material after a few cycles and with a longer potentiostatic step at the end of sodiation are in progress.

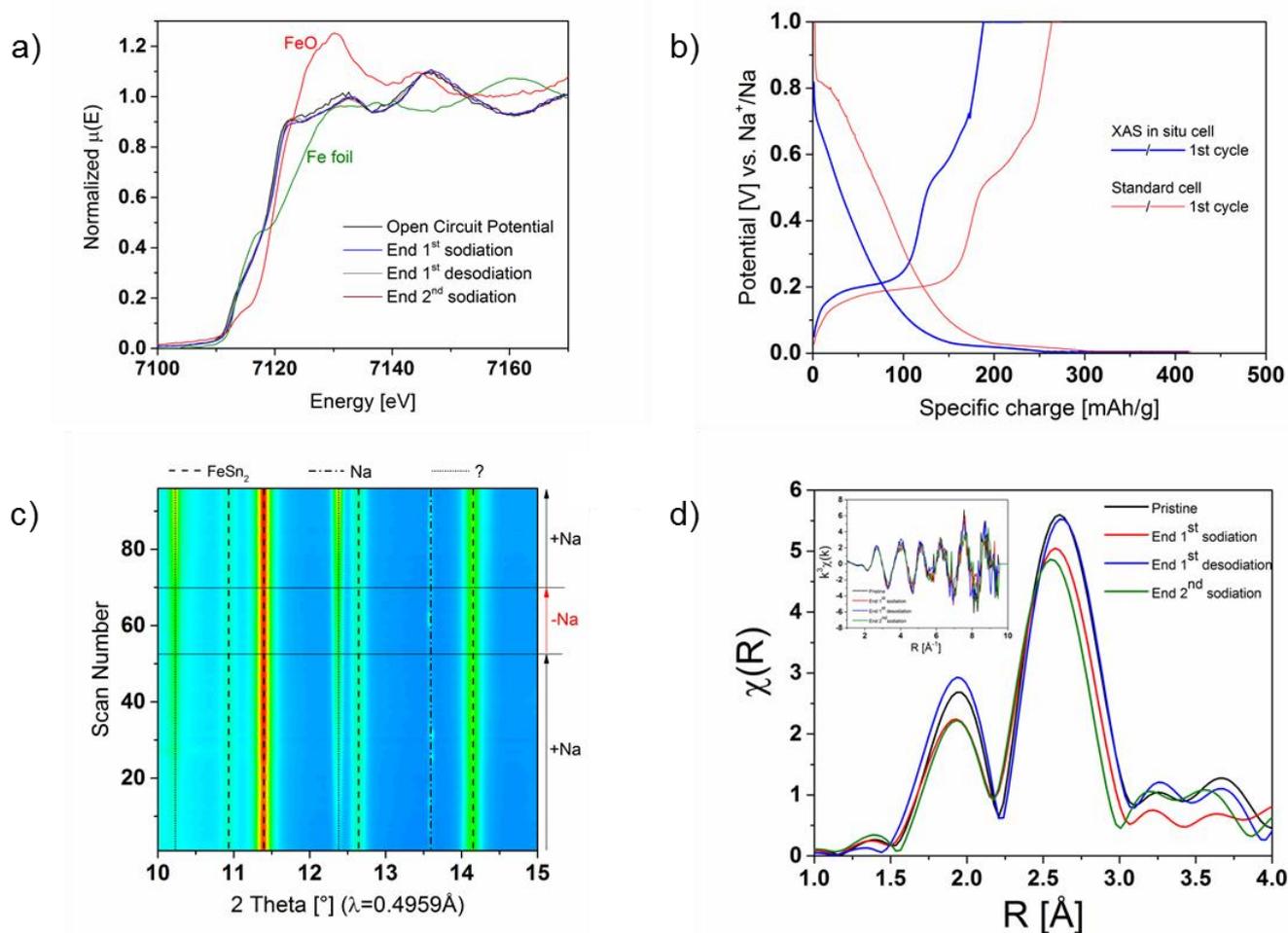


Figure 1 a) Fe K-edge XANES spectra at different states of sodiation of the in situ cell and with references, b) Contour plot of the XRD spectra taken during the cycling of FeSn₂ in the in situ cell with red indicating highest intensity and blue the lowest intensity, c) Electrochemistry of the in situ cell compared to our standard cell for FeSn₂ and d) EXAFS of FeSn₂ ex situ samples.