

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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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: Chemical and Structural Characterisation of Tin Oxide thin films: An in situ XAS study	Experiment number: SI - 1010
Beamline: BM29	Date of experiment: from: 21/4/04 to: 26/4/04	Date of report: 5/1/05
Shifts: 18	Local contact(s): Olivier Mathon	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): R. Lindsay* Institut de Ciència de Materials de Barcelona (CSIC), Spain F. Sanz, I. Díez-Pérez*, A. Garcia Güell* Dept. de Química Física, Universitat de Barcelona, Spain J.F.W. Mosselmans* CCLRC, Daresbury Laboratory, UK J. Zegenhagen ESRF, France		

Report:

Tin, a reasonably corrosion resistant metal due to the presence of a passive oxide/hydroxide surface film, is rather widely employed in a variety of applications, including a significant number involving humid and/or aqueous environments. Given this usage, there is a need to understand the electrochemical behaviour of this metal. Recently, such interest has led to studies of *tin/liquid* interfaces to gain an insight into the growth and structure of the passive films formed [1,2]. From this work it has been deduced that in a borate buffer electrolyte (pH = 7.5) the nature of the passive film changes from tin (II) hydroxide (~ -0.5 V vs Ag/AgCl), through SnO_x ($\sim +0.5$ V), to $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ ($\sim +1.5$ V) as the potential of the sample is increased. The goal of this study was to further characterise these oxidic tin films, employing *in situ* Sn K-edge X-ray absorption near edge structure (*XANES*).

Measurements were performed on *BM29*. Initially, reference *XAS* spectra were recorded in transmission mode from metallic Sn, SnO, and SnO₂. Very highly polished polycrystalline Sn disks were employed for the *in situ XANES* from the tin/borate electrolyte interface. The sample was inserted into an appropriately designed electrochemical cell from the *ESRF's* electrochemistry laboratory, which was attached to a high precision three circle diffractometer. Such a mounting was necessary in order to be able to easily impinge the x-ray beam onto the Sn surface at below the critical angle for total external reflection, to achieve a high sensitivity to the Sn/electrolyte interfacial region. The angle for total external reflection was determined empirically during the measurements. A solid state fluorescence detector was used to record the *in situ XANES* data in this grazing incidence geometry.

Reference *XANES* spectra from metallic Sn, SnO, and SnO₂ are displayed in Figure 1. Clear differences in spectral profiles are apparent, thus allowing these data to be used as fingerprints for interpreting the *in situ XANES* from the Sn/electrolyte interface. Acquisition of these latter *XANES* data was not so straightforward. Initially, we found that the critical angle for total external reflection was not very well defined, and so we had some difficulty in orienting the sample correctly. We believe that the origin of

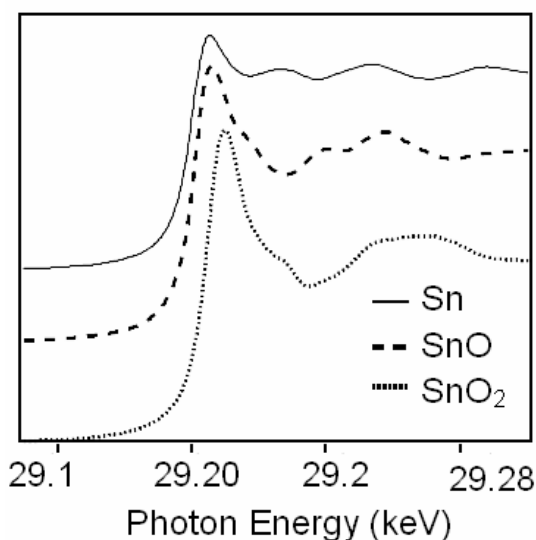


Figure 1. Sn K-edge XANES of Sn, SnO, and SnO₂.

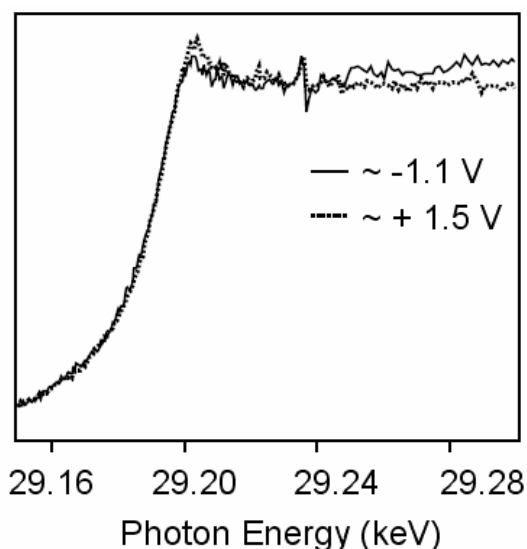


Figure 2. Sn K-edge XANES of Sn/borate buffer electrolyte interface acquired at potentials of approximately -1.1 V and $+1.5$ V.

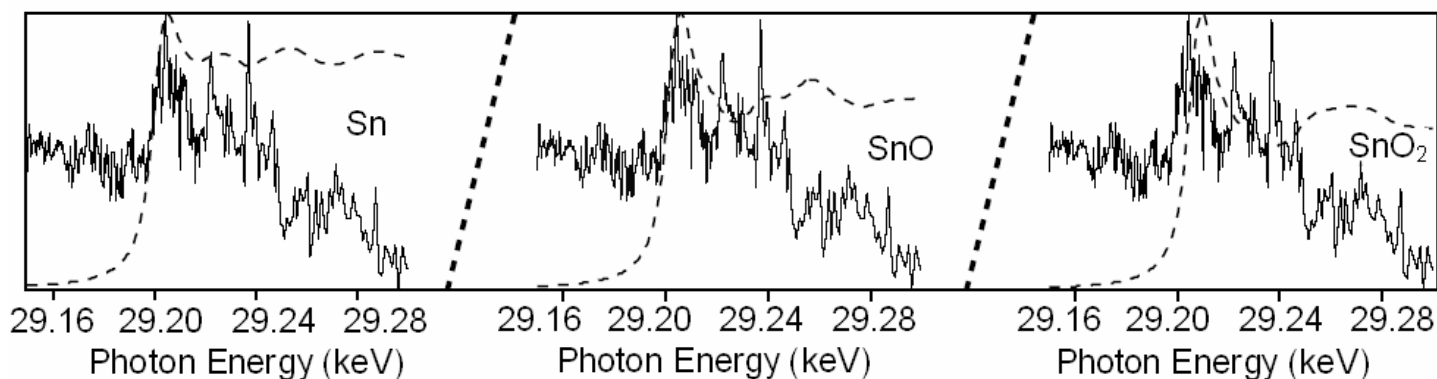


Figure 3. Plots comparing the XANES difference spectrum (solid line), generated by subtracting the two spectra in Figure 2 (i.e. $+1.5$ V) $-$ (-1.1 V), and the reference XANES in Figure 1.

this problem may be the roughness of the tin samples, which proved to be rather challenging to polish to the required flatness, due to the fact that tin is a relatively soft material. Once oriented, we also found that the XAS data were not always consistent *i.e.* spectra recorded consecutively, without changing any experimental parameters, sometimes varied significantly. A possible source of this trouble is small instabilities in the beam position combined with the very grazing angle of beam incidence (30 – 40 mdeg).

Despite the hurdles described above, we were able to make some progress towards our experimental target. Figure 2 shows XANES spectra recorded from the Sn/electrolyte interface, obtained with the sample at potentials of approximately -1.1 V and $+1.5$ V. For the lower potential it is known [1,2] that the Sn surface is metallic, whereas at the more anodic potential an oxidic film should be present. Although the spectra are not of very high quality, and their normalisation is rather imperfect, it may be argued that an increase in the intensity of the resonance is discernable. Such a trend is consistent with that observed in the reference spectra (Figure 1) on going from Sn to SnO_x. To examine this change further we have subtracted the XANES spectrum recorded at -1.1 V from the one acquired at $+1.5$ V. In figure 3 the resulting difference spectrum is compared to each of the three reference spectra. From this comparison one may conclude that at $+1.5$ V the oxide film has SnO-like character, which contradicts Refs. 1,2. One possible explanation for this discrepancy is the higher surface sensitivity of the techniques used previously. Clearly, given the problems associated with our study, further measurements are required to confirm, or otherwise, our result.

References

- [1] R. Diaz *et al*, J. Braz. Chem.Soc. 14, 523 (2003).
- [2] R. Diaz *et al*, J. Phys. Chem. B 108, 8173 (2004).