

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 electrochemical studies of carbon loaded greigite reactivity with carbon dioxide	Experiment number: 26-01-975
Beamline: BM26A	Date of experiment: from: 12-Apr-2013 to: 16-Apr-2013	Date of report: 02-Mai-13 <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Sergey Nikitenko Dipanjan Banerjee	
Names and affiliations of applicants (* indicates experimentalists): Dr Mariette Wolthers, Utrecht University, Netherlands Miss Husn-Ubayda Islam*, University College London, UK Prof. Gopinathan Sankar*, University College London, UK Dr Katherine Holt*, University College London, UK Dr Nathan Hollingsworth*, University College London, UK Miss Anna Roffey*, University College London, UK		

Report:

Outline

The aim of this beamtime was to complete investigations into the structural changes that occur to a catalytically active iron sulfide system in an electrochemical environment. The focus of investigations was a sample consisting of carbon loaded greigite particles obtained through solvothermal decomposition of dithiocarbamate complexes and demonstrating high surface area. The reaction that supposedly occurs on the greigite surface is the assisted conversion of $\text{CO}_2 + \text{H}_2$ to HCOOH .

A study was performed to discover interaction of carbon dioxide species with the carbon loaded greigite in a range of pH's and with different gases.

Time Effects

The first experiment was performed to confirm that gradual changes do not occur over time. The experiment reveals that changes occur at a significantly reduced rate. Once the potential is switched back on, changes in the XANES region occur rapidly, and then when the circuit is broken, the initial structure is completely restored thus indicating reversibility.

Gas Effects

The buffer solution is prepared by degassing with either argon or nitrogen, or saturating with carbon dioxide. When the greigite is in contact with buffer solution before a potential is applied, a range of changes can occur at the solid solution interface depending on the buffer gas used and pH of the buffer solution. The greigite structure is unchanged when the buffer solution is degassed with Ar, N_2 or saturated with CO_2 at pH4.5 and pH10 suggesting a lack of strong interaction of buffer solution components with the greigite surfaces. At

pH6.5 however, the greigite is unchanged when solution is degassed with N₂ or saturated with CO₂ but significant increase in white line intensity is observed when the buffer solution is degassed with Ar.

pH Effects with CO₂ Buffer

in situ experiments show that a gradual change occurs with both pH4.5 where CO₂ remains in solution and pH6.5 where CO₂ is expected to primarily form carbonate. Crucially, the differences in the spectra (at the peak labelled C) reveals the difference in binding of absorbant species as a result of pH.

The same experiment was performed at pH10, which in the interest of time was only held at -0.8V potential. The changes here, where CO₂ is known to form dicarbonate, are much less prominent suggesting less adsorbate-surface chemical interaction.

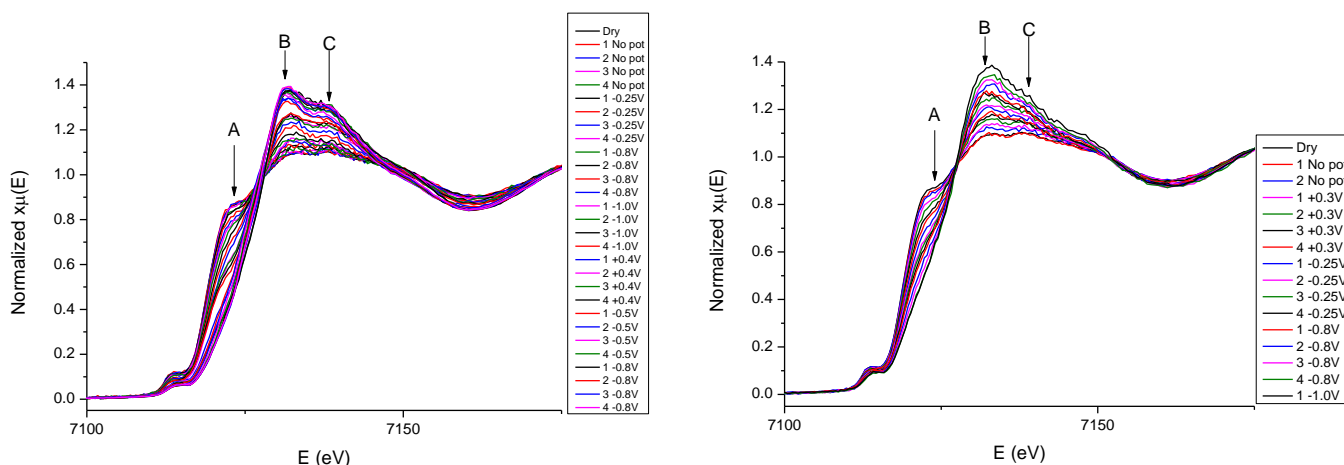


Figure 1: in situ electrochemical XANES data of greigite at held potentials in pH6.5 (left) and pH4.5 (right) buffer solutions.

Conclusion

In all cases, XANES shows that the edge position remains constant throughout in situ and ex situ experiment: the apparent shifts are due to appearance and disappearance of the 1s to 4s shoulder indicating that all electrochemical changes are indeed from the coordinated species. This change is either from the introduction of surface adsorbates, or from the changes in sulfur species, most likely from a combination of both. Modelling of first shell EXAFS data will reveal more in the near future.

Solvothermal Decomposition

In a separate ongoing experiment, a sample of iron tris dithiocarbamate was dissolved in dodecane and heated to 200° C. This decomposition process is normally performed in oleylamine and is the primary route to the synthesis of high surface area iron sulfide material used for the electrochemical CO₂ capture investigated above. This experiment set out to prove that the coordinating nature of oleylamine plays a heavy role in the decomposition process that forms the sulfide, by proving that decomposition does not occur in non-coordinating dodecane. The data reveals that the structure remains intact. In addition, subtle changes in the XANES indicate shifting bond distances and possible high-spin low-spin conversion. Further analysis of EXAFS will reveal more.

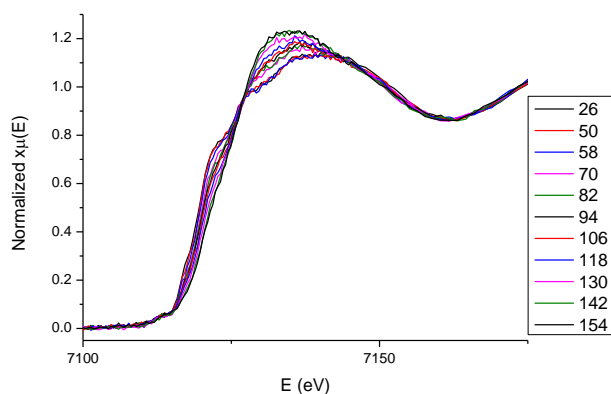


Figure 2: in situ solvothermal decomposition data of iron tris isobutyl dithiocarbamate in dodecane up to 154° C.