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 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.

ESRF	**Experiment title: Resonant Surface X-ray Scattering Study of the Effect of Charge Transfer on the Structure at the Electrochemical Interface**	**Experiment number**: SI-1988
Beamline:	**Date of experiment**: from: 24/2/2010 to: 01/3/2010	**Date of report**: 29/3/2010
Shifts: 15	**Local contact(s)**: Paul Thompson	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Christopher Lucas* – University of Liverpool

Naomi Wong* – University of Liverpool

Michael Darlington* – University of Liverpool

Yvonne Gruender* - University of Kiel

Report:

The general aim of the experiment was to probe charge transfer at the electrochemical interface using resonant surface x-ray diffraction. A fundamental understanding of the nature of the charge transfer, especially the influence of the applied potential and the screening by the electrolyte, is a major goal in electrochemistry (which is itself a key enabler in many energy technologies) and we expect the results to have a significant scientific impact. After previous measurements on the I/Au(111) system we had identified halide adsorption onto Cu(001) electrodes as the ideal system in which to attempt this measurement, as the halides, Br and Cl, both form simple ordered c(2x2) adlayers on the Cu(001) surface. These measurements demonstrate the feasibility of the experiment and are very exciting in that clear shifts in the resonance behaviour can be observed for Cl adsorption but not Br adsorption. This indicates a difference in the bonding mechanism despite the identical nature of the atomic structure.

Illustrative figures are shown below. For both Cl and Br adsorption onto Cu(001) the adsorbates form c(2x2) adlayers, which are simple square structures with a coverage of 0.5 halide atoms per surface Cu atom and adsorption uniquely into the 4-fold Cu hollow site. The c(2x2) cell gives rise to additional surface scattering that is independent from the Cu crystal truncations rods (CTR's). Due to the symmetry of the surface the contribution to the superstructure scattering is due to the halide anion and the second (sub-surface) atomic layer of Cu atoms which are buckled. In the experiment it is therefore possible to probe the surface Cu atoms, by performing resonant measurements at the 'anti-Bragg' positions of the Cu CTR's (in this case the (1, 1, L) CTR which has Bragg reflections at L=1,3,…..) and the sub-surface Cu atoms (second atomic layer) by performing resonant measurements at the c(2x2) superstructure positions. The c(2x2) structure forms at the open circuit potential, i.e. when no potential is applied across the interface so it was at this potential that we initially performed the resonant x-ray measurements.

Figure 1 shows the resonant diffraction data through the Cu K edge (8979 eV) measured at different positions along the (1, 1, L) CTR, i.e. at L=0.8 close the the Bragg peak where the contribution is dominated by the bulk Cu atoms, down to L=0.2 which is very close to the anti-Bragg position at (1, 1, 0) where the scattering from the bulk of the Cu crystal is essentially cancelled and the surface signal dominates. Clearly at this surface-sensitive position a shift in the adsorption edge can be seen indicative of a change in the charge state of the surface Cu atoms. These results are currently being analyzed using calculation of the structure factors (including the anomalous dispersion corrections obtained from simultaneous measurements of the fluorescence from the bulk Cu crystal and measurements of Cu standards, e.g. CuBr). Figures 2 and 3 compare the resonant measurements made at two positions on the (1, 1, L) CTR for Cl and Br adsorbates (in both cases the c(2x2) structure was formed). At (1, 1, 0.8) (Figure 2) the results are essentially identical, which is expected since the measurement is probing the bulk Cu environment. At (1, 1, 0.2), however, the scattering from the bulk is cancelled and the signal arises from the surface Cu atoms and the adsorbed halide adlayer, Due to the differences in the atomic form factors for Cl and Br the changes in the atomic form factor either lead to a descrease in the scattering through the resonance (Cl) or an increase (Br). What is clear, however, that for Br (Figure 3) there is no shift in the edge compared to Cl. This data is currently being analysed both using a simple interpretation (in terms of shifts in the oxidation states of the surface Cu atoms) together with a more sophisticated approach using density functional theory to calculate the surface density of states with subsequent input into the resonant x-ray intensity calculations.

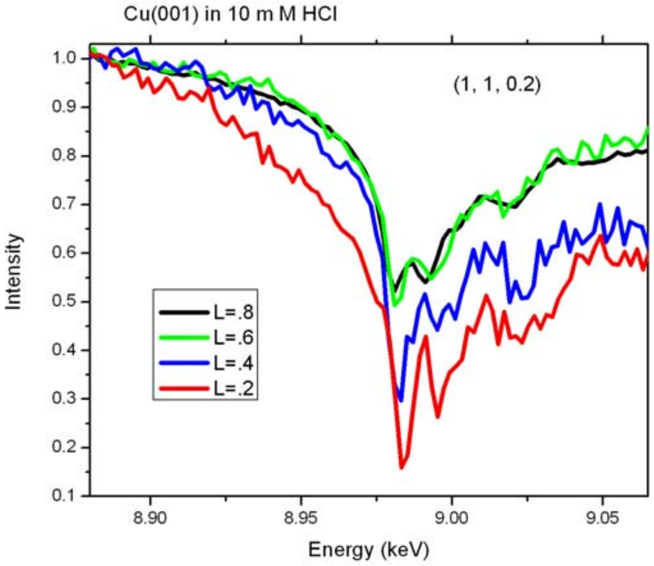

Figure 1

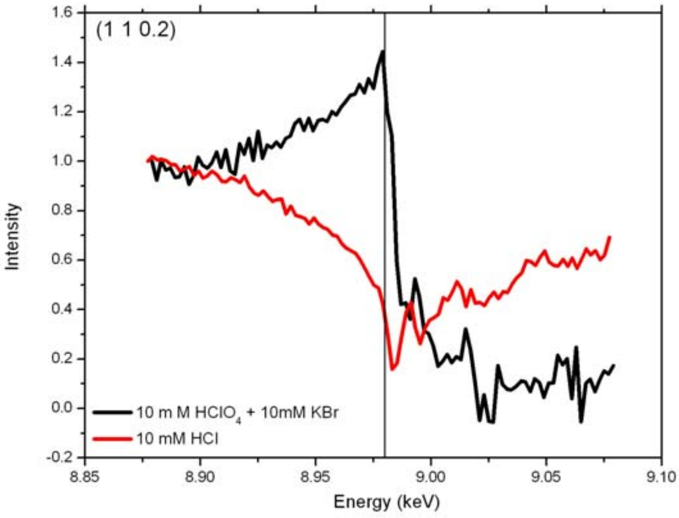

Figure 2

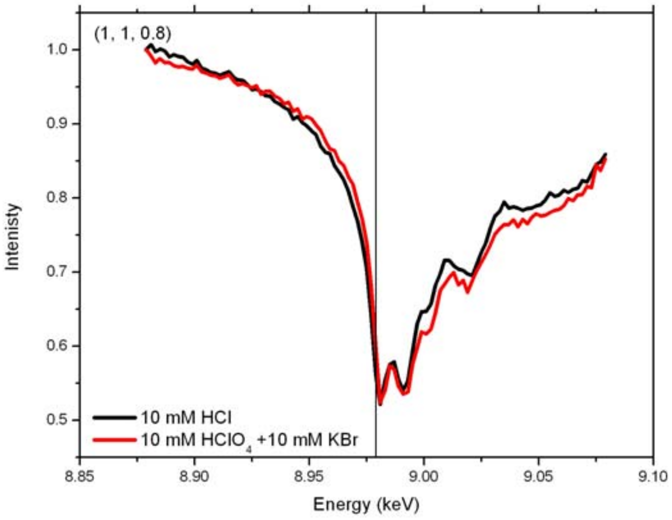

Figure 3