ESRF	**Experiment title: Temperature-dependent x-ray scattering studies of the solid-liquid interface**	**Experiment number**: SI-934
Beamline: ID03	**Date of experiment**: from: 07/11/03 to: 14/11/03	**Date of report**: 2/3/2005
Shifts: 21	**Local contact(s)**: Ernesto Paiser	*Received at ESRF:*

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Report:

In studies of electrochemical systems it is evident that there is an important role played by the mobility of solution species in determining reaction rates and even the potential stability of structural effects. Electrochemical reactions and surface structures/reconstructions are extremely sensitive to the temperature of the electrolyte solution. In these experiments we aimed to extend previous *in-situ* studies of the electrochemical interface to incorporate control of the electrode/electrolyte temperature. The x-ray cell for the temperature studies was modified as follows: Basically a ceramic body with electrolyte and electrical feedthroughs comprises the traditional x-ray electrochemical cell and is mounted on top of a Peltier device. One side of the Peltier is water-cooled. A thermocouple embedded in the wall of the cell allows temperature control. The aim of the experiments was to gather an understanding of the changes in interface structure as the temperature was varied from –5 °C to 60 °C in a selection of model electrode/electrolyte systems.

This experiment was one of a series of experiments at the ESRF in which we have examined the effect of temperature on the surface electrochemistry of Au(*hkl*) electrode surfaces in simple electrolyte solutions. Crystal truncation rod (CTR) measurements for the Au(111) and Au(001) surfaces in both acid electrolyte (0.5 M H_2SO_4) and alkaline electrolyte (0.1 M KOH) are described in the report for experiment 28-01-610. In this experiment we performed a detailed study of the effects of temperature on the deposition of Ag onto the Au(111) electrode. The key results are summarized in figures 1-4. Figure 1 shows the specular CTR for the Au(111) surface at three potentials; 0.7 V (surface free of Ag), 0.1 V (after one monolayer of Ag

deposition) and –0.2 V (after 2 monolayers of Ag deposition). We note here that it is possible to deposit 2 monolayers of Ag in the underpotential region, i.e. at electrode potentials that are positive of the Nernst potential where bulk Ag deposition occurs.

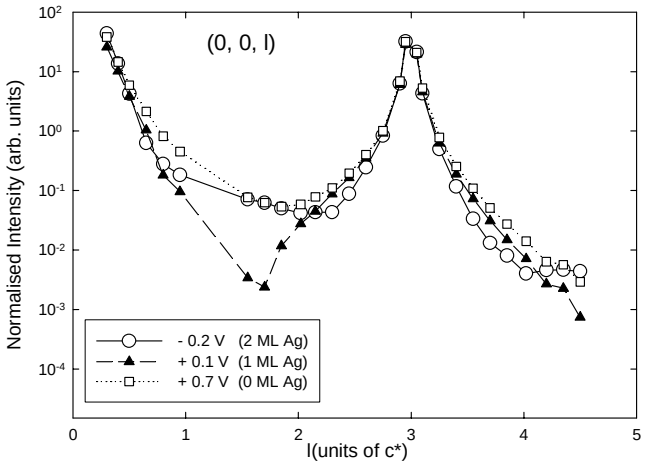

Fig. 1 Specular CTR measured at potentials corresponding to stages of Ag_{UPD}

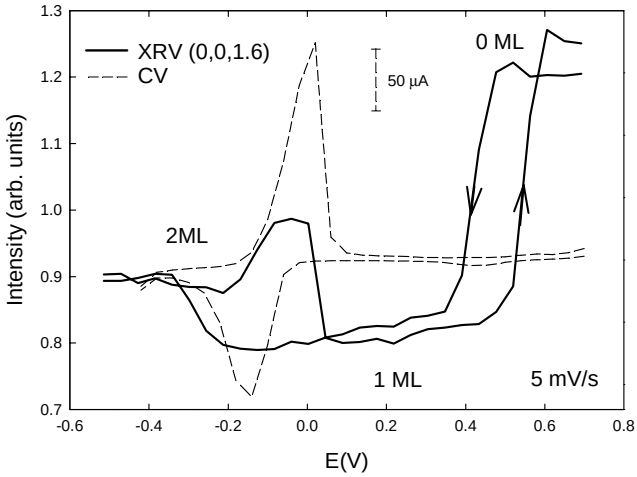

Fig. 2. XRV and CV for the Au(111) surface in 0.05 M H_2SO_4 + 1mM Ag_2SO_4

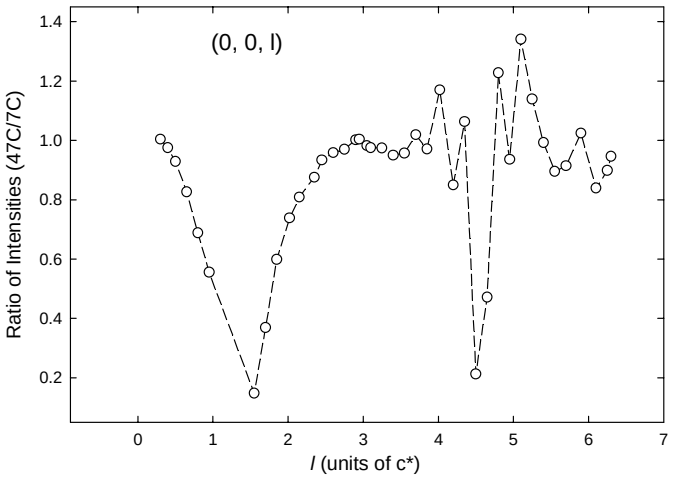

Fig. 3 Ratio of (0, 0, *l*) CTR data sets (47°C / 7°C)

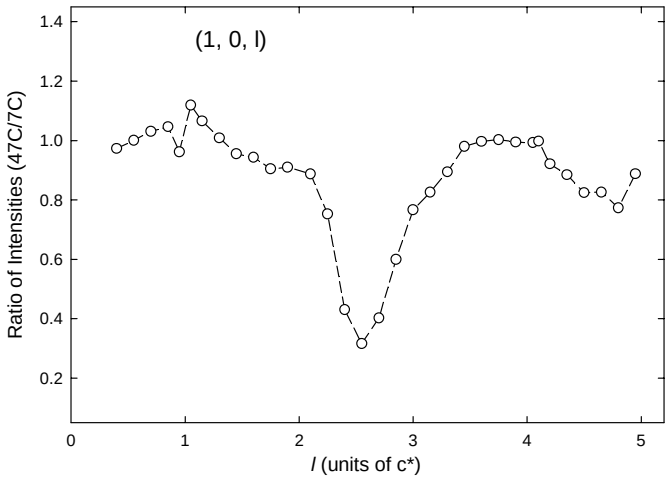

Fig. 4 Ratio of (1, 0, *l*) CTR data sets (47°C / 7°C)

Figure 2 shows the correponding x-ray voltammetry (XRV) for this system, measured with the sample/electrolyte temperature lowered to ~7 ºC. Also shown as the dotted curve is the corresponding cyclic voltammetry as measured simultaneously in the x-ray electrochemical cell. It can be seen that deposition of the Ag monolayer causes a large decrease in intensity (at ~0.5 V) although the current features are rather small. The increase in x-ray intensity coincides with the large current peak in the CV and this is due to the deposition of the second Ag monolayer. Measurements of the XRV and CV were performed at room temperature, 7 ºC and 47 ºC. Although there are differences in these results it is impossible to determine if these differences are intrinsic to the surface reaction or dependent on the kinetics in the thin layer configuration of the electrochemical cell that is required to perform the x-ray measurements.

The most exciting results that were obtained are shown in figures 3 and 4. After deposition of the Ag monolayer and with the potential held at +0.1 V, CTR measurements were performed at both low (7 ºC) and high (47 ºC) temperature. The ratios of the 2 data sets for the (0, 0, *l*) and (1, 0, *l*) CTR's are shown in figures

3 and 4 respectively. Increasing the temperature has a dramatic effect at the ‘anti-Bragg’ positions, i.e. midway between the Au Bragg reflections, where the scattering is sensitive to the surface Ag layer. The results shown are fully reversible as the temperature is changed and indicate that the sample temperature has a dramatic effect on the structure at the electrochemical interface. Analysis of this data to quantify the structural changes is currently in progress and it is anticpated that a paper summarizing these results will be submitted shortly. This will be the first *in-situ* structural study of the effect of temperature changes on the atomic structure at the electrochemical interface.