	Experiment title: Temperature-dependent measurements of the atomic structure at the charged solid-liquid interface	Experiment number: SI-1006
Beamline: ID03	Date of experiment: from: 25/02/04 to: 02/03/04	Date of report: 2/3/2005
Shifts: 21	Local contact(s): Ernesto Paisier	<i>Received at ESRF:</i>
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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. From a technological point of view, such effects are key to developing a fundamental understanding of electrocatalytic reactions that occur at temperatures that are significantly above room temperature, for instance in low-temperature fuel cell applications. 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 $\text{Au}(hkl)$ electrode surfaces in simple electrolyte solutions. All three low-index single-crystal Au surfaces exhibit potential-dependent surface reconstruction although there is some disagreement over the driving force for the forming and lifting of the reconstructed surface. The experiments showed that the potential range over which Au surfaces are reconstructed is significantly extended by the presence of CO in solution, although there is no strong adsorption of CO onto

the Au surface. This implies that the mobility of species in the electrolyte solution, particularly in the diffuse layers adjacent to the electrode surface plays a key role in determining the surface behavior. X-ray measurements both of the structural changes (for example in surface relaxation) and the kinetics and potential stability of the reconstruction (from x-ray voltammetry) were performed. Negative potential regions (reconstruction/hydrogen adsorption) and positive potential regions (ORR, oxide formation) were studied. The results at room temperature have been written up and submitted as an article to Surface Science. The abstract is included at the end of this report.

The effect of changing the electrolyte/electrode temperature has been examined in detail for a number of systems. Crystal truncation rod (CTR) measurements for the Au(111) and Au(001) surfaces in both acid electrolyte (0.5 M H₂SO₄) and alkaline electrolyte (0.1 M KOH) are described in the report for experiment 28-01-610. A detailed study of the effects of temperature on the deposition of Ag onto the Au(111) electrode is described in the report for experiment SI-934. These results are all being prepared for publication. Potentiodynamic data were obtained for all three low-index Au crystal and typical results are shown in figure 1. The top panel shows the X-ray voltammetry (XRV) measured at (0, 0, 1.5), the ‘anti-Bragg’ position on the specular CTR for the Au(111) electrode in 0.5 M H₂SO₄. In the lower panel the cyclic voltammetry is shown which was measured simultaneously in the x-ray electrochemical cell. In each case the blue (dotted) curve was measured at a temperature of 4 °C and the red (solid) curve at 50 °C. The dramatic structural change,

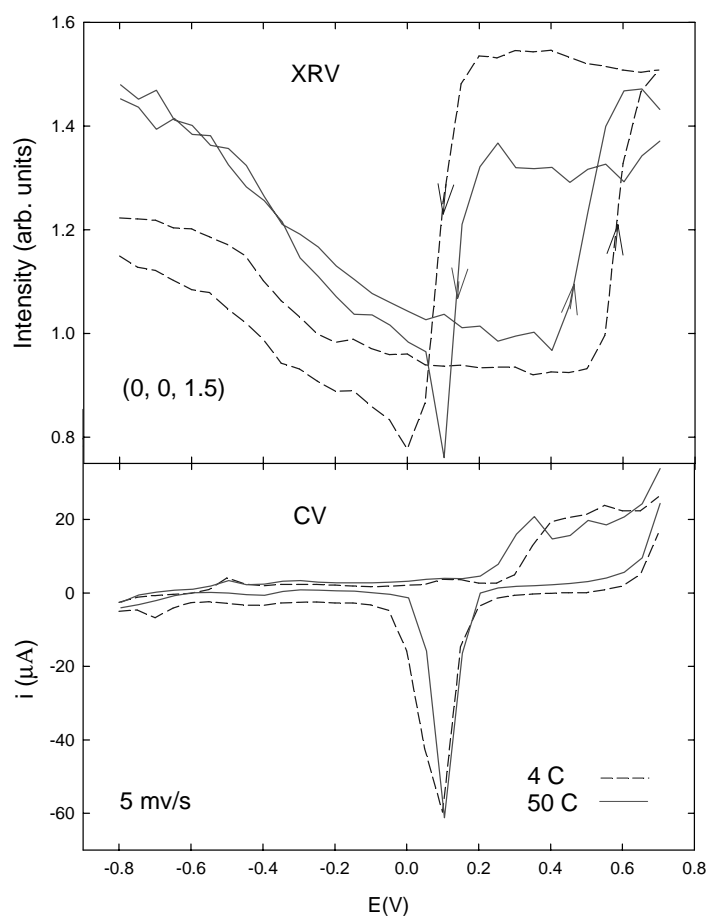


Fig. 1. XRV and CV for the Au(111) surface in 0.5 M H₂SO₄

signified by the increase in the scattered x-ray intensity, over the potential region 0.1 – 0.7 V is due to the reversible oxidation of the Au surface and this is signified in the CV by the current peaks (at ~0.3 V on the anodic sweep (oxidation) and the well-defined peak at ~0.1 V on the cathodic sweep (oxide reduction)). Increasing the electrode/electrolyte temperature narrows the potential window for the oxidation process, i.e. the increased kinetics at higher temperature mean that both the oxidation and reduction reactions are faster. A systematic study of the effect of temperature on the oxidation/reduction reaction on the three low-index Au(*hkl*) surface has been performed and the results are currently being prepared for publication.

Structure Sensitivity of CO Oxidation on Gold Single Crystal Surfaces in Alkaline Solution: Surface X-ray Scattering and Rotating Disk Measurements

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Abstract:

A combination of *in-situ* surface X-ray scattering (SXS) and cyclic voltammetry (CV) measurements have been performed to determine the effect that the surface atomic structure of the low-index faces of Au single crystals has on carbon monoxide (CO) oxidation in alkaline solution. For the (111), (100) and (110) surface orientations, potentiodynamic measurements of the scattered X-ray intensity at key reciprocal lattice points have been employed to determine the potential window of stability for the reconstructed surfaces. By saturation of the electrolyte with CO, the effect that adsorbed CO has on the stability of the reconstructed surfaces has been investigated. The presence of CO acts to stabilize the surface reconstructions over a wider potential range, causing a positive shift in the potential for the lifting of the Au(111) surface reconstruction of ~200 mV. In the case of the (100) and (110) orientations, the adsorption of CO stabilizes the reconstruction over the entire potential range studied. The oxidation of dissolved CO was found to be structure-sensitive, with the activity decreasing in the order Au(110)-(1x2) > Au(100)-"hex" > Au(111)-(23x√3). The structure-sensitivity is correlated with the surface density of low coordinated sites.
