ESRF	**Experiment title: Resonant x-ray scattering studies of charge transfer at the solid-liquid interface**	**Experiment number**: 28-01-710
Beamline: BM28	**Date of experiment**: from: 14/12/04 to: 20/12/04	**Date of report**: 10/05/2005
Shifts: 18	Local contact(s)**: David Paul**	*Received at ESRF:*

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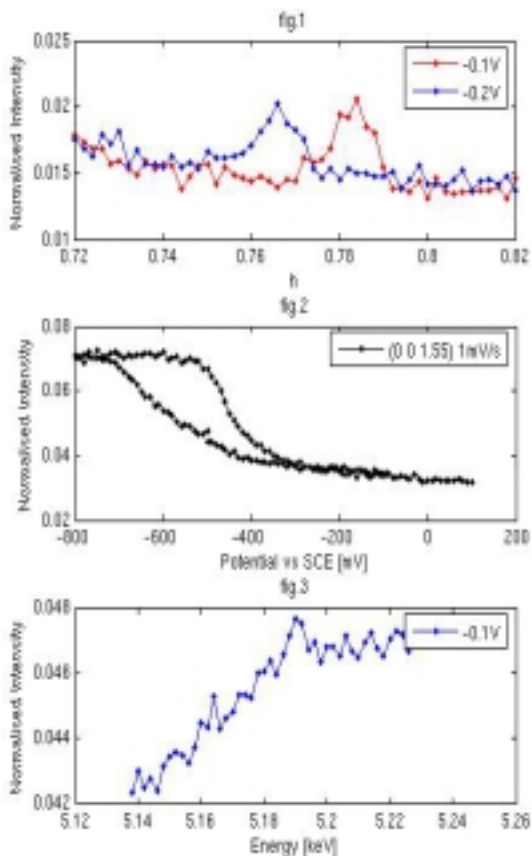**Paul Thompson* (XMaS beamline)**

Report:

   Central to all electrochemical reactions is the issue of charge transfer at the interface between a metal electrode and the electrolyte solution. In fact, charge transfer at interfaces is a phenomenon common to many scientific disciplines ranging from chemical technology to biomaterials and biophysics. In the case of the specific adsorption of anions it is known that by tuning the electrode potential it is possible to change the character of the atomic bonding from ionic to covalent up to the onset of anion desorption. For halide adlayers on Au(111), e.g. chloride, bromide and iodide it has been determined that, in the ordered adsorbed layers that are formed, the adsorbed species is almost completely discharged, i.e. the electrosorption valency, γ, is −1. At lower potentials, however, where the anion adlayer is disordered, electrochemical results indicate that γ is considerably lower and in the solution the anion species is negatively charged.

   In this experiment we attempted to measure resonant x-ray diffraction from the iodide structure on the Au(111) electrode surface. Iodide forms an incommensurate hexagonal monolayer on the Au(111) surface that becomes disordered as the potential is swept cathodically prior to desorption. The experiment on BM28 focussed on the use of resonant x-ray scattering at the iodine L_I edge (5188 eV) as the electrode potential was stepped over the region of the order-disorder transition and the desorption process. This was a challenging experiment as there was considerable x-ray adsorption in the liquid overlayers at these relatively low energies. This experiment was followed up by an experiment at the APS where resonant x-ray scattering measurements were performed in the region of the Au L_{III} adsorption edge (11919 eV) and a detector was

used which allowed the separation of the elastically scattered and fluorescent x-ray signal. The same potential region was examined in both experiments. In both cases the electrolyte solution contained 0.1 M KI.

Figure 1 shows the scattered x-ray intensity (incident energy = 5.088 keV, below the Iodine edge) along the <2 -1 0> reciprocal lattice direction at l=0.25. The peak is due to the uniaxially incommensurate (px$\sqrt{3}$) iodide structure. As the potential is stepped negatively (in this case from -0.1 V to -0.2 V, measured versus a saturated calomel (SCE) reference electrode) the peak shifts towards the commensurate (3x$\sqrt{3}$) position at (0.75, -0.5, 0.25). As the potential is stepped more negatively the peak eventually disappears as the structure disorders, there is a small potential range where a disordered iodide layer is present on the surface and then, at more negative potentials the iodide desorbs. In order to measure the resonant scattering signal throughout the entire potential region of interest it is necessary to choose a reciprocal lattice position which is sensitive to the iodide layer over the entire potential range. The (0, 0, 1.55) position on the specular crystal truncation rod (CTR) is insensitive to the surface plane structure of the adsorbed iodide. Figure 2 shows the x-ray voltammetry measured at this recipocal lattice position as the potential was swept at 1 mV/sec (a positive and negative sweep are shown) and clearly shows the iodide adsorption/desorption.

Figure 3 shows a fixed Q energy scan, at (0, 0, 1.55), measured at an electrode potential of -0.3 V (where the ordered iodide structure is still present on the surface). The data is taken is steps of 2 eV with a count time of 30 secs per point. At (0, 0, 1.55) the scattering from the iodide layer causes a decrease in the overall scattering due to interference with the scattering from the surface Au atomic layer. As the energy is scanned over the iodine edge (at 5.188 keV) there is a peak in the scattered signal due to the decrease in the real part of the atomic form factor at the iodine edge. Figure 3 demonstrates the experimental difficulty of this measurement. In order to improve the counting statistics, rather than just a fixed Q energy scan, we performed rocking scans at each energy. This was time-consuming as it meant that for each electrode potential a set of ~60 rocking scans was necessary to cover the energy range. Preliminary analysis of this data, however, indicates that there was a dramatic change in the near-edge resonant region, as the electrode potential was stepped over the order-disorder transition in the iodide monolayer, i.e prior to desorption of iodide from the surface. Further measurements with improved counting statistics are required to confirm this effect and to cover the entire

potential region of interest (unfortunately this was not possible during this preliminary experiment). The results can then be combined with the data obtained at the APS (a much easier experiment as the Au edge is at 11.9 keV!), which showed that the electronic state of the surface Au atoms remained relatively unperturbed (perhaps due to screening in the Au surface) during the iodide desorption.