

Introduction

- The *in-situ* study of the electrochemical interface is possible using the technique of synchrotron x-ray diffraction (XRD). Synchrotron radiation is needed to penetrate the overlying electrolyte and measure changes in the surface atomic structure of the electrode under potential control. Using this technique it is possible to detect single monolayers at the surface, such as water, oxide species and carbon monoxide.

- Some recent examples are:

- CO/Pt(111)

- I/Au(111)

- Ag UPD on Au(111)

- Au(001) and Au(111) interface structures

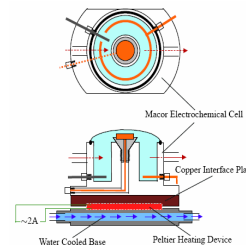
- Recently the x-ray electrochemical cell has been redesigned to incorporate temperature control over a range of 0 - 70°C.

Experimental Details

- An electrochemical cell has been designed, which allows the temperature to be controlled over a range of 0-70°C.

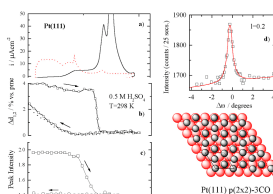
- The cell is mounted at the centre of a four circle diffractometer allowing *in-situ* x-ray scattering experiments to be carried out.

- The Prolene film can be deflated, trapping approximately 10 µm of electrolyte across the surface of the crystal. X-rays from a synchrotron source are able to penetrate the film and electrolyte through to the crystal surface.



- The cell is maintained in a nitrogen (or CO for the relevant experiments) atmosphere in order to protect the surface from contamination.

CO Structure On Pt(111)



- At a sufficiently negative applied electrode potential, a p(2x2) CO structure can be observed on Pt(111).

- In reciprocal space these surface rods are observed at the (1/2 1/2 l) position.

- The potential dependence of the CO structure can be measured (known as x-ray voltammetry, XRV). The intensity is measured at the (1/2 1/2 0.2) position over a suitable potential range.

- The CO structure is shown to be lifted by the drop in intensity as potential is increased.

- The disappearance of the p(2x2) CO structure is caused by a small pre-oxidation wave (surface coverage of CO changes from 0.75 to ~0.68). The structure changes to √19. With a constant supply of CO the structure reforms on the negative sweep.

Temperature Effects on the CO Structure

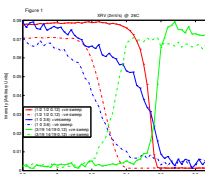
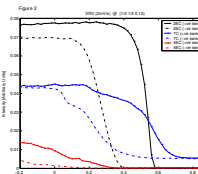


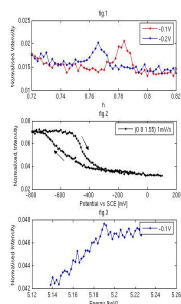
Figure 1 shows room temperature XRV data for three reciprocal lattice positions. The measured intensity at the (1/2, 1/2, 0.12) and (3/19, 14/19, 0.12) positions shows the disappearance of the p(2x2) CO structure and the appearance of the √19 CO structure respectively, with increasing potential. With a constant over pressure of CO the opposite effect is seen on the negative sweep. The (1, 0, 3/6) position is sensitive to the expansion of the Pt(111) surface. A decrease in the surface expansion can be seen as the potential is swept positively, and is again reversible on the negative sweep.

Figure 2 shows the XRV data of the p(2x2) structure at three different temperatures. At low temperature p(2x2) to √19 transition is frustrated by the slow kinetics of OH_{ad} nucleation and CO₂ diffusion. Conversely at high temperature the √19 structure is present even at -200mV implying that there is continuous CO oxidation. The p(2x2) to √19 transition is shifted negatively by 400mV



Iodine on Au(111)

Figure 1 shows the scattered x-ray intensity along the <2 -1 0> reciprocal lattice direction at l=0.25. The peak is due to the uniaxially incommensurate (px√3) iodine structure. As the potential is stepped negatively the peak shifts towards the commensurate (3x√3) position at (0.75, -0.5, 0.25). As the potential is stepped more negatively the peak will eventually disappear as the structure disorders, there is a small potential range where a disordered iodine layer is present on the surface and then, at more negative potentials the iodine desorbs.



The (0, 0, 1.55) position on the specular crystal truncation rod (CTR) is insensitive to the surface plane structure of the adsorbed iodine. Figure 2 shows the x-ray voltammetry measured at this reciprocal lattice position as potential was swept at 1 mV/s (a negative and positive sweep are shown) and clearly shows the iodine adsorption/desorption.

Figure 3 shows a fixed Q energy scan, at (0, 0, 1.55) measured at an electrode potential of -0.3V (where the ordered iodine structure is still present on the surface). At (0, 0, 1.55) the scattering for the iodine layer causes a decrease in the overall scattering due to the 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.

Summary and Acknowledgments

- A new electrochemical cell has been designed that allows temperature control of the electrode/electrolyte during *in-situ* x-ray diffraction measurements.

- Preliminary studies are:

- CO/Pt(111) - a dramatic effect seen in the p(2x2) to √19 CO structure transition
- I/Au(111) - it is possible to investigate the charge transfer at the solid-liquid interface
- Au(001)/0.1M KOH
- Surface oxidation of Au(111)

- Temperature effects have been seen in all systems studied thus far.