

## IN-SITU X-RAY SCATTERING TECHNIQUES IN ELECTROCHEMISTRY

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Recent experimental developments have made it possible to investigate a number of interesting processes occurring at the solid-liquid interface. In particular a new *in-situ* x-ray electrochemical cell has been designed which allows control of the electrolyte temperature over the range 0-80°C. Between these limits the mobility of solution species varies greatly, yet little is known about the effects that this has on the atomic structure at the interface. Using this approach it is now possible to study the effect of temperature on reactions such as adsorption/desorption of anions, electrocatalysis and electrodeposition. Initial experiments have been completed on the XMaS beamline (BM 28) at the European Synchrotron Radiation Facility and on beamline 7-2 at the Stanford Synchrotron Radiation Laboratory. Some recent results are shown here.

The lower section of Figure 1 shows the cyclic voltammetry (CV) recorded for an Au(111) single crystal electrode surface immersed in acid solution, at 4 and 50°C. A simultaneous 'x-ray voltammetry' measurement of the potential dependence, at a reciprocal space position sensitive to the surface oxidation process, is shown in the upper part of Figure 1. A temperature dependent shift in the potential window of the reversible oxidation/reduction region is observed, corresponding to the shift in the surface atomic structure measured.

It is possible to extend this technique to study structural changes during electrodeposition. The reversible process of Ag under potential deposition (upd) on Au(111) has been investigated. Figure 2 shows the measured XRV at an 'anti-Bragg' position, sensitive to the surface termination of the crystal, together with the CV, in solution containing Ag. The transition from bare Au (+0.85V), to completion of the Ag monolayer (~+0.3V) and then upd of a second Ag monolayer (~-0.05V) has been studied in detail. The potential region of stability of these structures has been determined and detailed structural measurements completed at these fixed potentials of interest (Figure 3), in the form of Crystal Truncation Rod measurements. It is possible to change the temperature of the electrolyte and study the effect that solution mobility may have on the growth processes occurring at the electrode surface. The adsorption of OH on the Ag monolayer surface has been studied by exchange of the electrolyte to KOH following deposition.

Results will be presented on relevant systems of interest, displaying the importance of the application of these techniques, to advance fundamental understanding of electrodeposition on the atomic scale.

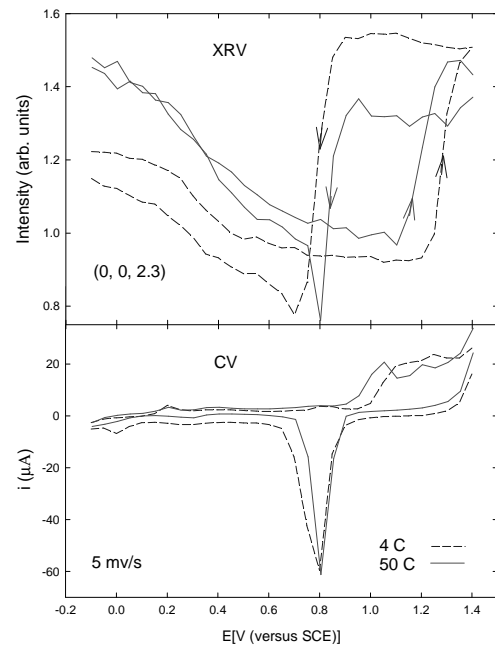


Fig. 1. XRV and CV for the Au(111) surface in 0.5 M H<sub>2</sub>SO<sub>4</sub>

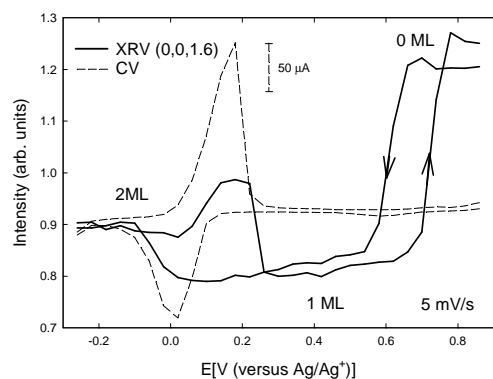


Fig. 2. XRV and CV for the Au(111) surface in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 1mM Ag<sub>2</sub>SO<sub>4</sub>

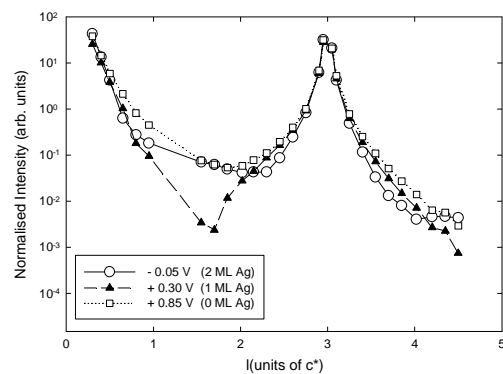


Fig. 3 Specular CTR measured at potentials corresponding to different stages of Ag<sub>UPD</sub>