ESRF	**Experiment title:** Oxidation state of Sn at the Pt_3Sn surface in an electrochemical environment	**Experiment number**: 28-01-120
Beamline: BM28	**Date of experiment**: from: 11/5/02 to: 13/5/02	**Date of report**: 2/4/2003
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Report:

Introduction

The aim of this experiment was to determine the oxidation state of Sn atoms at the $Pt_3Sn(111)$/Electrolyte interface by the study of the near-edge energy dependence of the Crystal Truncation Rod (CTR) diffraction data. In a continuing experimental study of this catalytically important system by classical electrochemical techniques as well as *in-situ* FTIR and synchrotron x-ray scattering measurements, a detailed characterization of the surface has been obtained [1,2]. It has been shown that the presence of Sn at the interface greatly increases the catalytic reactivity for CO oxidation, as compared to pure Pt(111) for example. A likely cause of this is due to the oxyphillic nature of Sn. It was therefore the intention of this experiment to determine the oxidation state of Sn atoms in the surface atomic layer, during potential controlled reactions such as hydrogen and sulphate adsorption on the surface and the adsorption/oxidation of carbon monoxide (CO).

Experimental Details

The experiment followed the approach described by E.D. Specht and F.J. Walker in their experiment to determine the oxidation state of Cr atoms at the buried $Al_2O_3/Cr_2O_3(001)$ interface [3]. This involved measuring the diffracted intensity in the form of rocking scans at a series of reciprocal lattice positions along the integer and half order CTR's

(present due to the doubling of the conventional fcc unit cell size), as the energy was stepped through the Sn L_1 edge (4.465 keV). Measurements were taken at reciprocal space positions sensitive to the bulk of the Pt_3Sn crystal, (1, 0, 0.9) and (1/2, 0, 1.9), and at 'anti-Bragg positions' (0, 0, 1.55) and (0, 1, 0.55). The x-ray energy was stepped over the range 4.415 keV to 4.515 keV in increments of 0.005 keV. At these x-ray energies the experiment is rather demanding due to the increased absorption in the electrolyte and polypropylene layers which results in a significantly increased background signal. Using the tube slits on the XMaS beamline it was possible, however, to reduce this background scatter to a minimum.

Results

Fig. 1 shows a representative rocking scan taken at the (0.5 0 1.9) position and the associated fitted lineshape. This data was taken at an electrode potential where hydrogen is adsorbed on the surface, in CO-free electrolyte. This measurement was repeated over the range of energies and the integrated intensities calculated from the deduced fit parameters. Fig. 2 illustrates the change in the integrated intensity as a function of energy, displaying a distinct increase in the diffracted intensity as the energy is tuned through the Sn L_1 edge at 4.615 keV. These preliminary results are encouraging in that they confirm that this challenging experiment is without doubt feasible. However, we were unable to complete the study as desired, due to an unscheduled ESRF shutdown on 11/05/03, lasting around two days that covered the majority of our allocated beamtime.

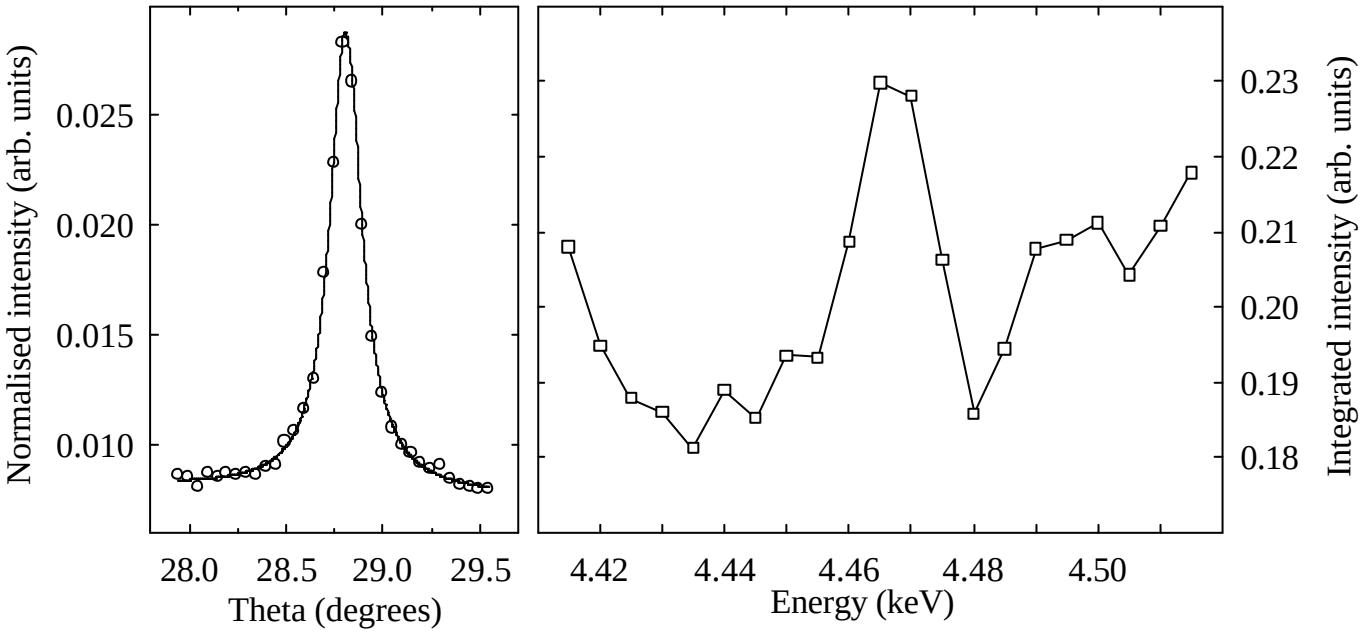

Fig. 1 **Fig. 2**

References

[1] V.Stamenkovic, M.Arenz, C.Lucas, M.Gallagher, P.Ross, N.Markovic, J. Am. Chem. Soc. 125 (2003) 2736

[2] M.Gallagher, C.Lucas, V.Stamenkovic, N.Markovic, P.Ross, submitted to Surface Science (2003)

[3] E.Specht and F.Walker, Phys. Rev. B, 47, (1993) 13743