	Experiment title: Determining the Oxidation State of Sn at the Pt ₃ Sn(111) Surface in an Electrochemical Environment	Experiment number: SI-1032
Beamline: BM28	Date of experiment: from: 04/5/04 to: 11/5/04	Date of report: 03/02/2005
Shifts: 9	Local contact(s): Dr. L. Bouchenoire	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Chris Lucas, Dept. of Physics, University of Liverpool, UK *Mark Gallagher, Dept. of Physics, University of Liverpool, UK *Ben Fowler, Dept. of Physics, University of Liverpool, UK *Paul Thompson, XMaS Beamline (BM 28), ESRF. Nenad Markovic, Materials Science Division, Lawrence Berkeley Lab, CA, USA		

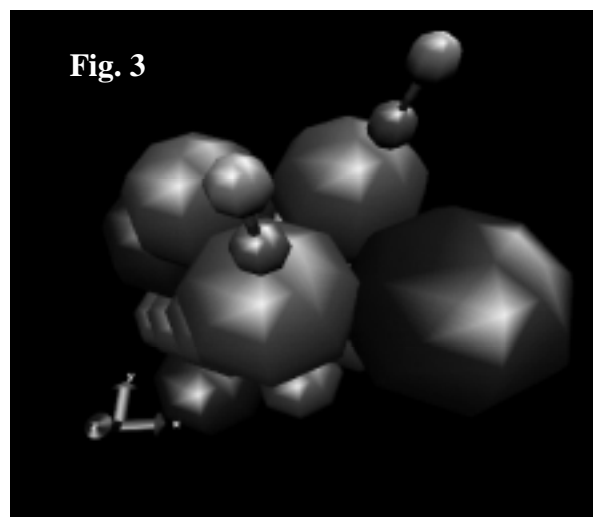
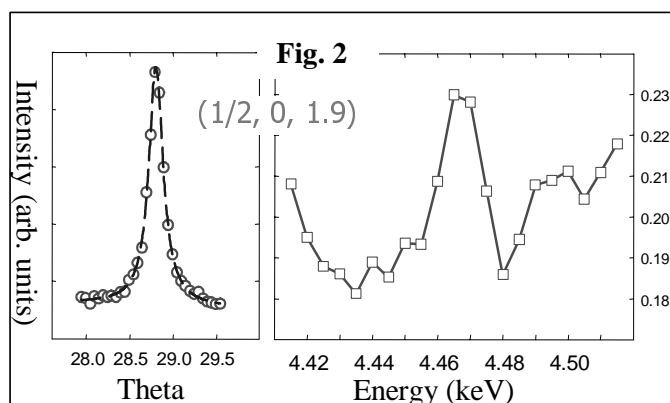
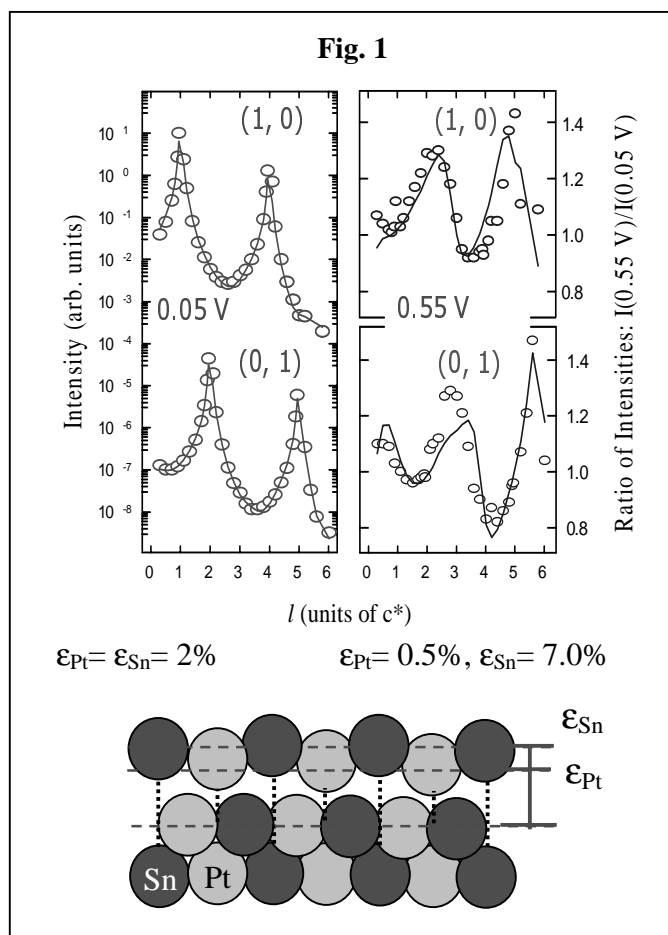
Report:

Bimetallic alloy surfaces enhance the oxidation of CO, due to a combination of bifunctional and electronic effects. The results highlighted here represent the fruits of a comprehensive experimental and theoretical investigation into the nature of the alloy-electrode/electrolyte interface. The surface x-ray scattering data shown is the first ever *in-situ* characterisation of the surface structure of an alloy, under reaction conditions. As the applied potential is cycled from the onset of hydrogen adsorption on the surface, at low potentials of $E < 0.2$ V, to the region corresponding to sulphate adsorption, $0.2 < E < 0.55$ V (data not shown), there is a decrease in intensity (1, 0, 3.7) with a corresponding increase in the intensity at (1, 0, 4.3). Such behaviour is consistent with a change in the expansion of the surface Pt and Sn atoms, which is fully reversible.

A detailed structural study by crystal truncation rod (CTR) analysis (figure 1) shows that the surface layer of Pt and Sn atoms undergoes an expansion of ~2% of the (111) layer spacing at low potential (0.05 V) in CO-free electrolyte. At 0.55 V the expansion of the Pt atoms is reduced to ~0.5% and the Sn atoms are expanded by ~7%. This buckling of the surface layer is also observed in CO-saturated electrolyte and is a precursor to Sn dissolution which occurs at ~1.0 V, causing irreversible roughening of the surface.

A likely cause of the increased catalytic activity, compared to Pt(111), is the oxyphilic nature of Sn. The oxidation state of Sn can be determined from the near-edge energy dependence of the CTR data. Figure 2

shows a representative rocking scan taken at (0.5, 0, 1.9) and the associated fitted lineshape, measured at an electrode potential corresponding to hydrogen adsorption on the surface. This measurement was repeated as the x-ray energy was stepped over the range 4.415 keV to 4.515 keV in increments of 0.005 keV and the integrated intensity is calculated from the deduced fit parameters. Figure 2 illustrates the change in intensity at (1/2, 0, 1.9), as the incident x-ray energy is stepped through the Sn L_1 edge (4.465 keV). A distinct increase is observed in the diffracted intensity at 4.615 keV revealing there is no shift in the edge at this position. This indicates that the surface Sn atoms are in the Sn^0 state at this potential (0.05 V), consistent with recent DFT calculations [1]. Figure 3 shows the results of DFT calculations at this potential in the presence of CO, where there are two tilted CO molecules adsorbed onto three surface Pt atoms (red spheres), whilst there is no adsorption onto the surface Sn atoms (blue spheres).



[1] W. Hofer, C. Lucas, M. Gallagher (unpublished)