



THE UNIVERSITY of  
LIVERPOOL

# Surface Structure and Relaxation at the Pt<sub>3</sub>Sn(111)/Electrolyte Interface



M. E. Gallagher<sup>1</sup>, V. Stamenkovic<sup>2</sup>, N. M. Markovic<sup>2</sup> and C. A. Lucas<sup>1</sup>

<sup>1</sup>Department of Physics, University of Liverpool, Oliver Lodge Laboratory, Liverpool, L69 7ZE, UK

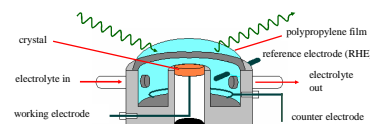
<sup>2</sup>Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720, USA

## Introduction

- Platinum is a ubiquitous catalyst, however in electrocatalysis Pt is prone to poisoning by organic molecules such as carbon monoxide.
- Recent studies have shown that bimetallic alloy surfaces can enhance the oxidation of CO and small organic molecules due to a combination of bifunctional and electronic (or ligand) effects.
- Pt<sub>3</sub>Sn(111) is a model bifunctional electrocatalyst, where the oxidation of CO is enhanced by the presence of OH species adsorbed onto the inactive Sn surface atoms.
- A detailed *in-situ* Surface X-ray Scattering study of the Pt<sub>3</sub>Sn(111)/Electrolyte interface has been performed on the XMaS beamline at the European Synchrotron Radiation Facility (ESRF).
- X-ray diffraction data has been combined with electrochemical measurements to explore surface reactions at the interface and how they govern the surface structure.

## Experimental Details

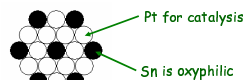
- The Pt<sub>3</sub>Sn(111) single crystal is prepared in UHV by repeated cycles of sputtering and annealing. The sample is then transferred to the x-ray electrochemical cell (below) and immersed in 0.5M H<sub>2</sub>SO<sub>4</sub>.



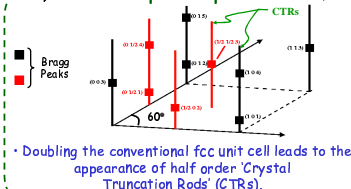
- The cell is mounted at the centre of a four circle diffractometer and the film is deflated, trapping approximately a 10 μm layer of electrolyte. This allows transmission of x-rays to the surface if using a synchrotron source.
- The cell is maintained in a nitrogen atmosphere during the measurements protecting the surface from oxygen. For measurements of CO adsorption and oxidation the outer chamber of the cell is purged with CO.

### Real Space

- UHV preparation leads to a p(2 × 2) surface structure where the unit cell contains 3 Pt atoms and 1 Sn atom.

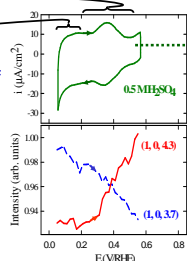


### Reciprocal Space



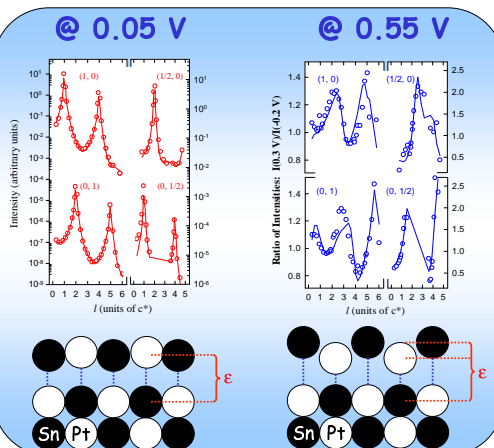
## Cyclic Voltammetry

- 'Butterfly' feature in the CV corresponds to adsorption/desorption of sulphate species on the surface



- adsorption/desorption of hydrogen on Pt
- onset of Sn dissolution occurs at higher potentials (>0.6 V)
- The change in diffracted intensity at reciprocal lattice positions of interest is monitored as the applied potential is cycled. The mirror like increase of intensity above the Bragg peak with decreasing intensity below is consistent with a changing expansion of the surface atomic layer.

## CTRs and Structural Model



- Variable structural parameters included in the CTR fit are the surface atomic layer expansion ( $\epsilon_{Sn, Pt}$ ), surface coverage ( $\theta_{Sn}, \theta_{Pt}$ ) & surface roughness ( $\sigma_{Sn}, \sigma_{Pt}$ ).

- Fits to the CTR data at 0.05 V indicates a hydrogen adsorption induced expansion of the surface atomic layer of ~ 2% of the (111) layer spacing.

- The ratio of the diffracted intensity of the CTR data set at 0.55 V to that at 0.05 V is shown on the right. The asymmetry around the position of the Bragg peaks visible on the plot is indicative of changes in the surface expansion. The best fit to the ratio data set indicates that the expansion of Pt atoms in the surface layer is reduced to 0.6%, in contrast to the surface Sn atoms which become expanded by 6.5%.

- There are no other significant changes to the fit parameters (summarised below).

	$\epsilon_{Pt}$ (%)	$\epsilon_{Sn}$ (%)	$\theta_{Pt}$	$\theta_{Sn}$	$\sigma_{Pt}$ (Å)	$\sigma_{Sn}$ (Å)	
N	0.05 V	2.3	1.8	0.60	0.20	0.10	0.31
	0.55 V	0.6	6.5	0.62	0.22	0.12	0.33
CO	0.05 V	1.5	1.6	0.59	0.20	0.13	0.29
	0.55 V	1.5	5.1	0.61	0.18	0.14	0.24

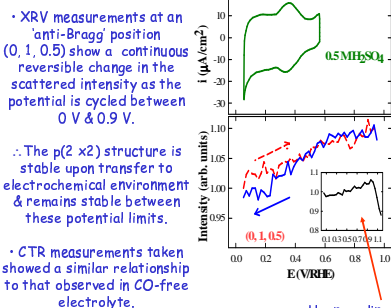
## 'X-Ray Voltammetry'

$\epsilon_{Pt} = 2.3\%$   $\epsilon_{Sn} = 1.8\%$        $\epsilon_{Pt} = 0.6\%$   $\epsilon_{Sn} = 6.5\%$

Expanded state of Sn is a precursor to dissolution

## Oxidation of CO on Pt<sub>3</sub>Sn(111)

- With a constant overpressure of CO in the cell, CO displaces hydrogen from surface Pt adsorption sites.
- As CTR measurements are sensitive to the termination of the Pt<sub>3</sub>Sn lattice it is possible to examine the stability of the surface during the adsorption and oxidation of CO.



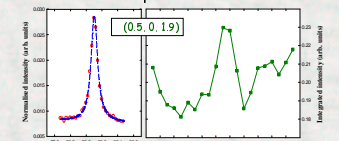
- XRV measurements at an 'anti-Bragg' position (0, 1, 0.5) show a continuous reversible change in the scattered intensity as the potential is cycled between 0 V & 0.9 V.
- The p(2 × 2) structure is stable upon transfer to electrochemical environment & remains stable between these potential limits.

- CTR measurements taken showed a similar relationship to that observed in CO-free electrolyte.

### Oxidation State of Sn?

- Possible to monitor change in diffracted intensity at surface/bulk sensitive positions on the CTRs as the x-ray energy is tuned through the Sn L edge (anomalous diffraction).

- Can determine the oxidation state of Sn atoms in the surface atomic layer during potential controlled reactions such as hydrogen and sulphate adsorption and the adsorption/oxidation of CO.



- Preliminary measurements at the bulk sensitive position (0.5, 0.19) show an increase in the scattered intensity as the energy is tuned through the L edge at 4.465 keV.

- Upon cycling to more positive potentials (> 1.0 V) the diffracted intensity reduces greatly due to dissolution of Sn from the surface leading to irreversible roughening of the surface.

## Summary & Outlook

- The UHV-prepared Pt<sub>3</sub>Sn(111)-p(2 × 2) surface is stable upon transfer to the electrochemical environment and remains stable upon potential cycling from the limits of hydrogen adsorption up to the onset of Sn dissolution.

- At positive potential (0.55 V), with sulphate adsorbed on the surface, the surface becomes increasingly buckled with the surface Sn atoms moving outwards by 6.5% of the lattice spacing. This expanded state is a precursor to Sn dissolution.

- In CO saturated solution the Pt<sub>3</sub>Sn(111) surface is stable up to 0.95 V. Above this Sn dissolution causes irreversible roughening of the surface

- Experiments are underway to determine the oxidation state of the surface Sn atoms in the electrochemical environment.