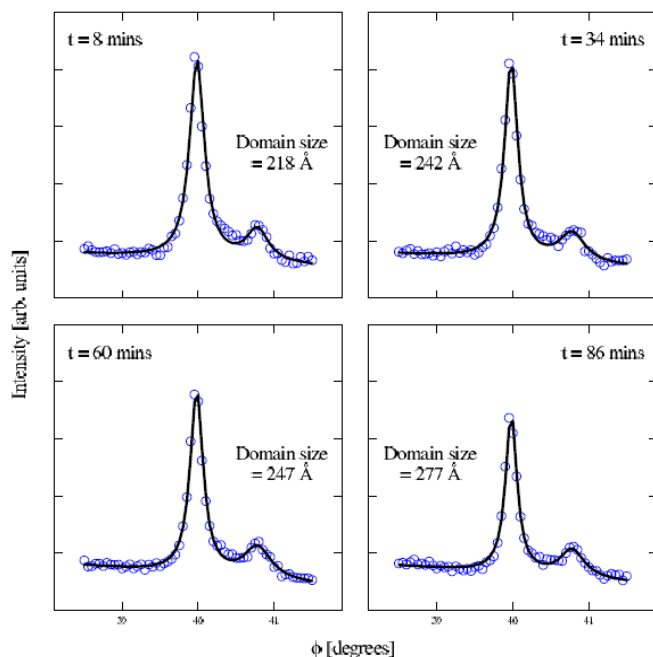
	Experiment title: A surface x-ray diffraction study of ordered water layers at the Pt(111)-electrolyte interface	Experiment number: SI-1077
Beamline: BM28	Date of experiment: from: 16/3/05 to: 21/3/05	Date of report: 1/2/2007 <i>Received at ESRF:</i>
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Report:

The interaction of water with solid surfaces plays a crucial role in many areas of science. The water structure at well-defined metal surfaces is of particular importance in catalysis and electrochemistry as the activation of water is the crucial step in many surface reactions. Despite this importance, at the electrified interface numerous experimental and theoretical studies have yet to provide a detailed picture of the atomic-scale structure of water and its behaviour remains poorly understood. Although water structures can be observed by LEED on metal surfaces under ultra-high vacuum (UHV) conditions, the electrochemical interface is much harder to study due to the presence of the bulk electrolyte. In order to understand the role of hydration water molecules on the electrochemical double layer, it is imperative to reveal the structure under control of the electrode potential. In electrolyte solutions free of strongly adsorbing anions, e.g. KOH, the electrochemical interface offers the opportunity of controlling the surface coverage by hydrogen, H₂O and OH species simply by controlling the applied electrode potential. The aim of this experiment was to probe, *in-situ*, the structure of the water layer at the Pt(111)/electrolyte interface. This was a technically challenging experiment as the scattering signal from the ordered oxygen atoms is relatively small compared to the diffuse scattering from the bulk of the electrolyte solution. We performed a detailed search for ordered water structures at the Pt(111)-electrolyte interface. This involved scans along high symmetry reciprocal lattice directions at a variety of electrode potentials. No ordered structures were detected using this methodology. In a second attempt, we scanned the electrode potential while monitoring the diffracted intensity at key reciprocal lattice positions where scattering due to an ordered water structure would be observed (based on previous UHV LEED experiments). Again no ordered structures of water could be detected. In order to confirm that the Pt(111) surface was well ordered, i.e. to rule out the possibility that ordered structures could not be detected due to surface preparation issues, we performed a series of experiments looking at the ordered structures formed by a monolayer of CO adsorbed on the Pt(111) surface in electrolyte. Results are summarized in the figure below which shows rocking scans through the ($\frac{1}{2}$, $\frac{1}{2}$, 0.2) reciprocal lattice



position where the scattering from a $p(2 \times 2)$ CO structure is observed. The results shown are taken after the electrolyte was saturated with nitrogen gas and show the disappearance of the structure due to slow displacement of the CO molecules from the surface. This indicates that an overpressure of CO is required in order to maintain the CO adlayer. Studies of the order-disorder transition of this CO adlayer were performed and have been incorporated in a publication that has recently been submitted to the Journal of the American Chemical Society. The abstract is attached.

The results indicate that the surface is well ordered with the structure having a coherent domain size of 200-300 Å. The scattering from a CO monolayer is weak and the signal from an ordered water layer could be expected to be similar in scattering

strength. It is thus concluded that any ordering in the water layers at the Pt(111)-electrolyte interface is too small to be detected using surface x-ray scattering. An interesting follow-up experiment would be to study the formation of ordered water layers under UHV conditions and then transfer the ordered interface to the electrochemical environment. Such experiments could be feasible using the newly developed UHV-electrochemistry chamber on ID32 at the ESRF.

Abstract of paper submitted to the Journal of the American Chemical Society:

Nano-holes as active sites for CO and hydrogen oxidation reactions

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The model concept of an ensemble of nanoelectrodes with active and inactive areas is introduced to account for the fact that diffusion limiting currents for CO oxidation and the hydrogen oxidation diffusion reactions are observed on a macroscopic electrode with $\leq 10\%$ of active sites. The appearance of both the CO diffusion limiting current on the Pt(111) surface covered by a stable “ $(\sqrt{19} \times \sqrt{19})R23.4^\circ - 13\text{CO}$ ” structure ($\Theta_{\text{CO}} = 0.685$ ML per surface Pt atoms) and the diffusion limiting current for hydrogen oxidation on Pt(111) modified by a template of bromide, forming a (3×3) hexagonal structure ($\Theta_{\text{Br}} = 0.44$ ML per surface Pt atom), are explained within this model. It is proposed that on these surfaces the active sites for the CO and hydrogen oxidation reactions are an ensemble of nano-holes of small “islands” (defect sites with a diameter of ≤ 100 nm) embedded in an “ocean” of closely packed spectator adsorbates. Analytical methods are used to demonstrate that, with only 10 % of active surface area the separated diffusion fields established on an ensemble of nano-holes can merge into a single larger field spread over the whole geometric area of the macroscopic electrode and, thus, the theoretical diffusion limiting currents, characteristic for the rotating disk electrode, are observed. In the kinetically controlled region, however, the number of active holes is reduced below the number required to produce the diffusion limiting current.