



Beamline: ID-32	Experiment title: In-situ structural studies of hydrogen adsorption on Pt(111) electrodes prepared under UHV conditions	Experiment number: SI-1639
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Report:

Hydrogen adsorption, evolution, and oxidation at Pt electrodes are electrochemical processes of major importance, relevant to electrolysis and fuel cell reactions. In previous surface x-ray scattering (SXS) studies of flame annealed Pt(111) electrodes we had observed an interesting, previously not reported structural hysteresis in the hydrogen adsorption regime. Unfortunately, Pt electrodes are extremely sensitive to impurities and rigorously clean electrochemistry could not be ensured in those experiments. We therefore performed in this project similar studies on Pt(111) prepared by sputtering and annealing in the UHV system of the ESRF surface preparation laboratory and investigated those in-situ in H_2SO_4 electrolytes using the transfer cell of ID32. Although UHV analytic techniques (LEED, AES) indicated clean Pt surfaces after the preparation, only strongly contaminated electrochemical behavior could be observed after the transfer, which prohibited detailed structural studies. We attribute these contamination problems to the very long times required for the transfer from UHV into electrochemical environment in this setup (≈ 30 min.) and to details of the cell construction.

As a backup experiment and to efficiently use the large time periods for the renewed UHV preparation of the Pt single crystal sample, the electrochemical dissolution of Au in Cl-containing solution was studied by in situ SXS. Elucidating the dissolution mechanism of noble metals is important for both industrial applications and fundamental understanding. Employing the same time-dependent surface x-ray scattering methods used in our previous studies of Au electrodeposition [1], we investigated the atomic-scale dissolution behavior as a function of electrode potential. As shown in Fig. 1, pronounced x-ray intensity oscillations are found at the (0, 1, 0.1) reflection upon increasing the potential into the regime of active dissolution, indicating a layer-by-layer dissolution mechanism. This is in agreement with in situ STM studies where anisotropic monolayer etch pits were observed during Au dissolution [2]. The difference between Au(111) dissolution and homoepitaxial electrodeposition on Au(111), where 3D growth is observed, may be related to an enhanced Au surface mobility at the more positive potentials required for dissolution (e.g. due to the presence of Cl⁻ adsorbates) or to a different Ehrlich-Schwöbel barrier for adatoms and vacancies, respectively. Interestingly, the growth oscillations not only manifest in the SXS intensity, but also in the current density (Fig. 1, blue

line) or, in the case of galvanostatic dissolution, in the electrode potential. This behavior can be attributed to the different number of active (i.e. step) sites in different stages of a growth period, which is substantially higher for a surface layer with a coverage of 0.5 ML than for an almost completed surface layer. Based on existing models, developed for growth under UHV conditions [3], we are currently developing a kinetic growth model that allows to describe quantitatively both the SXS and the electrochemical data. Fitting of the data by this model should provide detailed information about mass transport and local step dissolution rates at this interface.

Au dissolution can be studied in Au-free solution and allows simple and fast regeneration of an atomically smooth surface by keeping the potential in the double layer potential regime. It is a particularly simple process and was therefore employed as a model system to further develop the technique of time-dependent in situ SXS studies of electrochemical interfaces. Specifically, we demonstrated in our experiments that kinetic growth mode studies are possible up to growth rates of 1 ML/s, which is much higher than the rates used in previous (UHV) SXS studies and only one order of magnitude lower than rates used in technological processes. Furthermore, by employing complex sequences of potential steps or mixed potentiostatic/galvanostatic programs “digital” etching in 0.5 ML steps (i.e. controlled stepwise alternating between an atomically smooth surface and a surface covered by half a monolayer of Au islands) could be realized and directly verified by SXS.

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- [2] S.Ye, C.Ishibashi, K.Uosaki, *Langmuir* 15, 807 (1999).
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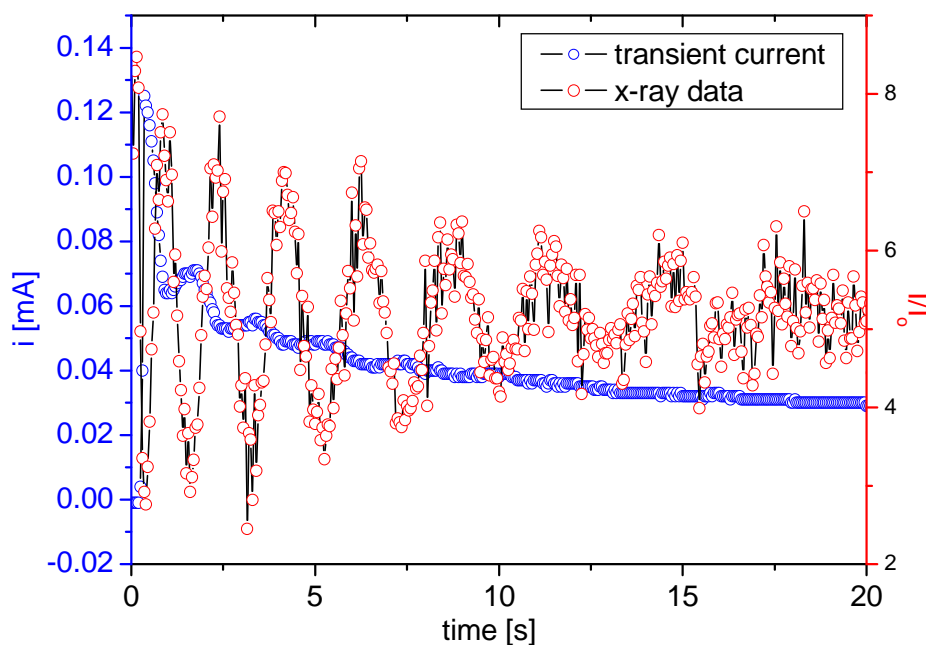


Figure 1. Dissolution of Au(111) surface at constant potential of 1.2V. Red points indicate x-ray intensities scattered from the surface at (0, 1, 0.1), blue points represent the simultaneously recorded dissolution transient current.