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Report:

With our experiment "Anion structure at the metal/sulfuric acid interface" (ESRF grant SI194) we studied the anion adsorption from sulfuric acid solutions on Au (111) using X-ray surface diffraction (XRSD) under in-situ conditions.

The system metal/sulfuric acid has already been investigated by UHV structure sensitive methods (low energy electron diffraction (LEED), infrared reflection absorption spectroscopy (IRAS)) which reveal a $(\sqrt{3} \times \sqrt{3})R30^\circ$ anion adsorption structure. In contrast, in-situ scanning tunneling microscopy (STM) studies observe a $\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$ -structure on

Au(111), Pt(111) and Rh(111) in contact with sulfuric acid. Despite essentially identical experimental results different structural models - a centered adlattice of hydrogensulfate with an anion coverage of 40% of a monolayer on the one hand and a primitive adlattice of sulfate anions with coadsorbed hydronium ions with an anion coverage of 20% of a monolayer on the other hand - are derived from the STM images. As XRSD has proven to be sensitive to anion structures adsorbed on metal surfaces XRSD was used to get additional information concerning the adlayer structure as well as anion coverage on the surface. After a flame treatment the Au(111) single crystal was placed in a thin layer cell providing the in-situ electrochemical environment and which was especially designed for such XRSD measurements. The same cell was already used at ESRF during previous experiments (grant S16 1 and CH1 26).

After getting a typical voltammetric response of a well-defined Au(111) surface in a clean electrochemical environment the single crystal was aligned using the (003) and the (101) bulk reflections. Rocking scans were recorded along the (00L) and the (10L) crystal truncation rods (CTR) at two different potentials. The hkl assignment is based on the surface LEED coordinates (choosing h,k in the surface plane and l perpendicular to the surface). The cyclic voltammogram of Au(111) in contact with sulfuric acid solutions exhibits a sharp spike at 1070 mV vs. Reversible Hydrogen Electrode (RHE). The first set of rocking scans was recorded at 670 mV vs. RHE where no ordered anion structure is present at the surface. The second set of measurements was performed at 1170 mV vs. RHE being well above the potential at which the anion adlattice is formed.

The figure below shows a (10L) CTR obtained at 1170 mV vs. RHE. The data is geometry-, lorentz- and absorption-corrected. Although it is difficult to tell the exact anion adlayer structure from these measurements it might be possible to determine the adsorption site of the anions. The solid line corresponds to a fit assuming a $\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$ -structure with threefold hollow adsorption sites and an anion coverage of about 10% of a monolayer. The anions are approximated having a spheric symmetry with a scattering cross section of 34 electrons. The vertical distance between the anions and the Au surface is $(4.7 \pm 0.5) \text{ \AA}$. In contrast, assuming on-top adsorption sites with a distance of $(5.0 \pm 0.5) \text{ \AA}$ as indicated by the dotted line fits the data significantly worse in the region of the minimum being sensitive to the surface structure. The discrepancy between the fits and the data points for $L=3$ to $L=3.9$ is due to a non-perfect alignment of the sample and the maximum at $L=2$ has its origin in a stacking fault of the single crystal.

