



Experiment title:

Anion structure at the gold/perchloric interface

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Report:

With our experiment "Anion structure at the gold/perchloric interface" (ESRF grant CH126) we studied the anion-water structure at the metal/perchloric acid solution interface as a function of solution composition using X-ray surface diffraction (XRSD) under in-situ conditions.

The results obtained from electrochemical studies suggest that the Au/HClO<sub>4</sub>.5.5H<sub>2</sub>O interface with the electrolyte in its liquid state has a similar structure as in the case of the solid electrolyte which is known to possess a clathrate structure. In the liquid state the anions do not get in direct contact with the charged metal surface, however, they are supposed to be in fixed positions with a cubic symmetry, inside water cages as in the solid clathrate.

After flame treatment the Au(100) 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 the experiment of grant SI61 in 1995 with excellent success. The single crystal was aligned using the (002) and the (111) bulk reflections. So-called hkl-scans were performed parallel to the surface in order to detect the ordered adlayer structure expected close to the electrode surface.. The hkl assignment is based on the surface LEED coordinates (choosing h, k in the surface plane and l perpendicular to the surface). Scans were recorded in perchloric acid solutions of different concentrations ( $\approx 7M$ , corresponding to HC10<sub>4</sub>.5 .5H<sub>2</sub>O, 1M and 0. 1M) and at two potentials (-1V and 0V vs AuOx).

The hkl scans obtained in water and in  $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$  exhibit two significant differences:

- a wide peak at low h and k values, which was found to increase with increasing perchloric acid concentration,
- and two small peaks at  $h = k$  values equal to 1.46 and 1.95 observed only in  $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ .

Both of these effects could be caused by a structure existing in  $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$  and not in pure water. Atypical M-scan at  $l=0.3$  is shown in the figure below. The arrows indicate the peak positions in the  $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$  solution.

Despite the reference data recorded in pure  $\text{H}_2\text{O}$  the quality of the data was not good enough for a significant determination of the effects observed in the hkl scans.

Several difficulties arose during the measurements such as problems in aligning the single crystal due to uncertainties of the spec software.

In order to improve the signal-to-noise ratio we replaced the kapton foil (thickness:  $12.5\mu\text{m}$ ) covering the electrochemical cell which was used in previous experiments by a thinner prolene foil ( $4\mu\text{m}$ ). Although the integral background signal was reduced the new polymer foil exhibited an unexpected high X-ray diffraction signal at very localized positions, disturbing the weak signal coming from the double layer.

Due to a lack of time we did not manage to record rocking scans along the (00L) and (11L) CTRs giving essential additional information on the existence of an ordered electrolyte structure.

For the next proposal round we therefore suggest an experiment for measuring these CTRs in order to complete our data on this system.

