



Experiment title: Development and application of transmission surface diffraction: Au dissolution and iron group (hydro)oxide structure during oxygen evolution		Experiment number: MI-1277
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Report:

1) Introduction: Transmission Surface Diffraction is a novel technique for in situ XRD studies of spatially heterogeneous interfaces between solids and liquids or high-pressure gas phases. It uses high photon energies (40-70 keV) with a transmission geometry for single-shot projection of the in-plane atomic structure onto a large 2D detector. Recently published proof-of-principle studies conducted during experiments IHCH-1022 and IHCH-1063 have demonstrated surface sensitivity down to partial monolayers and the capability for operando monitoring of surface phase transitions. [1] Further studies during MI-1251, for which a publication is in preparation, have explored the combination of TSD with Bi electrodeposition in a microfluidic flow cell. In this experiment, TSD was used (a) for the investigation of different Co (hydro)oxides during oxygen evolution, (b) for studies of the Au(100) surface reconstruction and the PdCl₄ adlayer deposition on Au(111), (c) for measurements on scratched Si(111) wafers carrying various electrodeposited films using a 2×8 μm² focused beam. All experiments were performed at a photon energy of 70 keV in the 4×2×0.6 mm³ thin layer flow cell developed for MI-1251 in combination with a remote-controlled electrolyte exchange system. Parts (a) and (b) were performed on disc-shaped Au and Ir single crystals, for which a sample thickness of 0.2 mm has been achieved by partial spark erosion from the backside. Part (c) was performed on Si(111) wafers with an electrodeposited 8 nm epitaxial Au(111) film. [2] A pattern of controlled scratches with a width between 10 and 30 μm was then created with a motorised needle.

2a) Investigation of Co (hydro)oxides on Au(100) and Ir(100) during oxygen evolution: Building on previous studies conducted by our group in experiments MI-1251 and MA-3074, various cobalt (hydro)oxides grown on metal electrodes were investigated for potential-induced structure changes.

Depositing a Co film from CoCl₂ on Au(100) or Au(111) and then oxidising this film to Co₃O₄ at positive potential in Co-free, basic electrolyte yielded a disordered surface oxide, which is in agreement with our previous experiments.

As an alternative approach, Co_3O_4 was deposited directly on Au(100) from 2 M NaOH + 1 mM $\text{Co}(\text{NO}_3)_2$ + 1.2 mM tartrate acid using a reflux cell at 100 °C in Ar at -0.5 V vs. MSE, which yielded, as expected, a crystalline (111) deposit. [3] When scanning the potential between -0.2 V and +0.6 V vs. Ag/AgCl, we observed an 8 % decrease in intensity, a 13 % increase in FWHM, and a 0.5 % increase in in-plane compressive strain measured at the (440) diffraction peak. These changes were reversible and reproducible over several cycles (Fig. 1). After the onset of oxygen evolution at +0.6 V, no further structural changes were observed. By stepping the potential to -1.1 V for several seconds, the oxide could be completely removed.

Using different electrodeposition solution chemistries in the reflux cell, $\beta\text{-CoOOH}(001)$ was grown on Au(100). These films did not show any structural changes prior to and during OER and their electrochemical dissolution was not possible even with exposure to -1.1 V for several minutes.

$\text{Co}_3\text{O}_4(111)$ was also grown on Ir(100) by reactive deposition of Co in UHV under oxygen flux at 50 °C and subsequent annealing, yielding thicknesses between 2 and 6 nm. [4] With lowered O_2 supply during deposition, $\text{CoO}(111)$ films with a 2 % expansive lattice strain could be grown instead. Intermediate O_2 flow settings produced samples with simultaneous presence of Co_3O_4 and CoO . Although the structure of the $\text{Co}_3\text{O}_4(111)/\text{Ir}(100)$ deposit was confirmed to be identical to the films grown electrochemically on Au(100) and showed similar behaviour during cyclic voltammetry, we could not observe any peak shifts or other structural changes in the potential region between -0.2 and 0.7 V, neither with or without additional presence of CoO . The same results were gained for the (exclusive) CoO structure.

2b) Monolayer diffraction from PdCl_4 and Au(100) surface reconstruction: The electrochemically induced surface reconstruction of Au(100) in 0.1 M HCl was measured by observing the intensity difference in images taken before and after the lifting of the reconstruction with a counting time of 300 s. We also attempted to observe a PdCl_4 adlayer deposited on Au(111) to demonstrate diffraction from weaker scatterers, but did not succeed with this.

2c) Microdiffraction from Pd deposited on Au(111)/Si with scratch patterns: An array of 238 Al compound refractive lenses was used to focus the beam to a size of $2 \times 8 \mu\text{m}^2$ with a transmission coefficient of 0.3 and a focus depth of several mm, presenting a significant improvement over the $10 \times 20 \mu\text{m}^2$ beam size available for our earlier experiments. This was demonstrated by producing ‘maps’ of a Au(111)/Si(111) sample modified with a scratch pattern and comparing the results with SEM images. Measurements of a Pd film subsequently electrodeposited in the microfluidic cell showed a very heterogeneous deposit with thicknesses of 300 ML near the channel inlet and <50 ML further downstream. Detailed measurements at the Au-free scratches showed, as expected, no Pd presence in the scratches as well as slightly increased azimuthal and radial Pd peak widths close to the scratch edges.

3) Outlook: Cobalt oxides are among the best precious metal free catalysts for water splitting, but the origin of their performance is unclear. To shed more light on the catalyst surface structure before and during OER conditions, we have demonstrated potential-induced structural changes in electrodeposited $\text{Co}_3\text{O}_4(111)/\text{Au}(100)$ films and the absence of any such changes for $\text{Co}_3\text{O}_4(111)/\text{Ir}(100)$ films prepared in UHV. A detailed data analysis of these experiments is in progress. We were also successful in further reducing the spatial resolution available for TSD experiments at ID31, which will be of great interest for future studies performed on heterogeneous interfaces.

References: [1] F. Reikowski et al.: *J. Phys. Chem. Lett.* **8**, 1067 (2017)

[2] P. Prod'homme et al.: *Appl. Phys. Lett.* **93**, 171901 (2008)

[3] J. A. Koza et al.: *Chem. Mat.* **24**, 3567 (2012)

[4] K. Biedermann et al.: *J. Phys. Cond. Matt.* **21**, 185003 (2009)

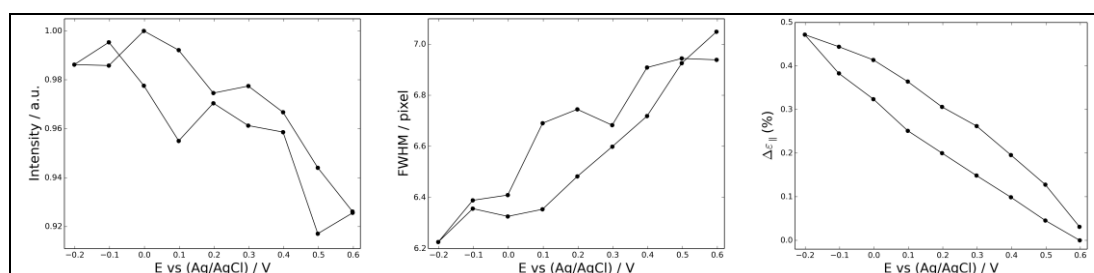


Fig. 1: Co_3O_4 structural properties (integrated intensity, FWHM, expansive strain) measured at the (440) diffraction peak in the potential range -0.2 .. +0.6 V vs. Ag/AgCl.