ESRF	**Experiment title:** Development and application of Transmission Surface Diffraction: Investigation of heterogeneous Pt(111) thin film electrodes during electrooxidation	**Experiment number**: MI-1320
Beamline: ID31	**Date of experiment**: from: 2018-07-18 to: 2018-07-24	**Date of report**: 2019-02-27
Shifts: 12	**Local contact(s)**: Dr. Jakub Drnec	*Received at ESRF:*

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Introduction

Pt is the electrocatalyst of choice for many reactions such as hydrogen and oxygen evolution and the surface science of the Pt(111) electrode during these processes is thus a subject of great interest in electrochemistry. We proposed to use *in situ* high-energy Transmission Surface Diffraction (TSD) [1] to study the oxidation behaviour of Pt(111) deposited on Au(111) in a microfluidic flow cell. By modifying the deposition procedure, the electrolyte flow rate and the geometry of the flow channel, heterogeneous Pt thin film electrodes with different 2D gradient of thicknesses and step densities can be created, which can then be mapped with high spatial resolution using the TSD scattering geometry (vertical beam incidence). On a method development level, the aim of the study is to demonstrate the coupling of TSD with *in situ* sample preparation in a microfluidic channel.

Experimental details

All experiments were performed at 70 keV. Pt electrodeposition was performed from K_2PtCl_4 on a smooth 8 nm Au(111) film epitaxially deposited on an H-terminated Si(111) wafer, which contributes very little background. We employed an improved version of the thin layer flow cell already used in previous TSD experiments. The experiment was controlled using a remote-controlled rapid electrolyte exchange system and a *BioLogic* potentiostat. The beam was focused using the T1 transfocator installed in ID31's OH1 and an additional array of 250 compound refractive lenses installed in the experimental hutch, yielding a beam size of about $8\times2\ \mu m^2$.

Results

Pt(111) electrodeposition from K_2PtCl_4 was performed by sequential pulsing of the potential from 0.4 V to -0.8 V vs. Ag/AgCl for 5 s. In the TSD geometry, the emergence of a Pt diffraction signal was observed from the 2nd deposition cycle onwards, confirming the (almost) monolayer sensitivity of the technique. We initially observed the growth of epitaxial Pt layers with a notable lattice strain. At around 3 ML thickness, we observed a discrete transition to relaxed layer growth, with scattering data from the first layers and from subsequent layers discernible as two separate peaks. We prepared Pt electrodes with thicknesses between 3 ML and 15 ML and scanned the focused beam over the sample surface to create real-space maps of the Pt deposit in the flow channel (example in Fig. 2, left). Some heterogeneity in the Pt diffraction intensity along the flow channel is observed as a function of sample position, which, due to the self-terminating nature of the pulse-based deposition process, should probably be assigned to a difference in island coverage rather than the vertical size of islands. Oxidation of Pt was induced by stepping the potential from 0.2 V to 1.2 V. This resulted in the decrease of the Pt diffraction intensity and also in a shift of the Pt Bragg peak to lower q values, indicating tensile strain. For thin films (below 6 ML), the Pt Bragg peaks completely disappeared during oxidation and new epitaxial diffraction spots were observed, which we assign to a crystalline PtO_2 phase. Thicker Pt films did not show this behaviour, indicating that they are only partially oxidized. By scanning *theta*, we obtained a scan over the Pt Bragg peak along the *L* direction (Fig. 1). We observed that the peak profile changed very reproducibly and reversibly during oxidation. This reproducible shape allows us to use the diffraction at only a single value of *theta* as a qualitative indication of the magnitude to which the sample is oxidised. By scanning the sample position, a real-space map of the film in its oxidised state can thus be created (Fig. 2, right). Comparing the sample maps in the reduced and the oxidised state (Fig. 2) shows that there is some heterogeneity in the oxidation process, i.e. the amount of oxidised material is not directly proportional to the island coverage. Sample regions closer to the electrolyte outlet (where island coverage and/or size is lower) are oxidised to a larger degree. We also observe some irregularities in the shape of the oxidised film on length scales of 0.2 .. 0.8 mm. As a general observation, the oxidised sample is not as "smooth" as the reduced one. We also performed a fine mesh scan of a 60×20 μm² region of the sample (with spatial resolution equal to the beam size), but observed no systematic structuring of the oxidised sample on this length scale. Diffraction data from the maps of the reduced and oxidised sample is also analysed for spatial dependences of other lattice parameters (strain, grain size). This is still in progress.

Conclusion

We succeeded in preparing Pt(111) electrodes of various thicknesses with a gradual decrease in island coverage along the flow channel and mapping them with TSD in both the reduced and the oxidised state.

References

F. Reikowski et al.: J. Phys. Chem. Lett. 8, 1067 (2017)

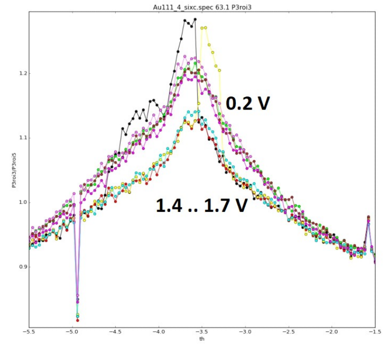

Fig. 1: Scan along *L* over the Pt Bragg peak shown as a function of potential at 0.2 V (several scans), 1.4 V, 1.5 V, 1.6 V, 1.7 V (single scans each). The Pt peak changes reproducibly and reversibly during oxidation. Potentials higher than 1.4 V have no effect.

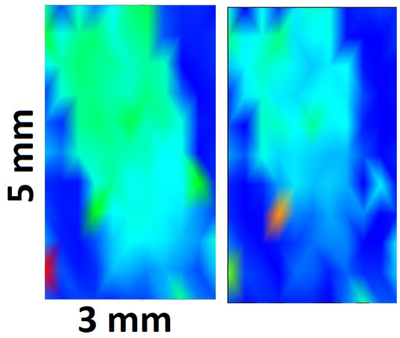

Fig. 2: Pt Bragg peak intensity (in arbitrary units) shown as a function of position on the sample before (left, 0.2 V vs. Ag/AgCl) and after (right, 1.2 V) Pt oxidation. Electrolyte flow in the cell was from top to bottom. The thickest parts of the sample corrospend to 15 ML of Pt.

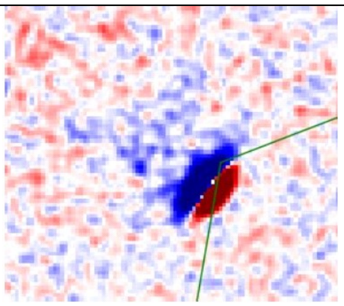

Fig. 3: Difference in diffraction intensity (blue: decrease, red: increase) by Pt oxidation from 0.2 V to 1.2 V. The peak shifts to lower values of *q*, indicating the formation of tensile strain.

Commissioning of *in situ* optical microscopy for TSD experiments

A small part of the experiment was spent on the commissioning of *in situ* optical microscopy for the TSD setup at ID31. In the future, we aim to employ this technique for the study of transition metal dichancogenides (TMDCs) such as TaS_2 and MoS_2. These meterials are relevant as electrocatalysts, but are most efficiently used as small, single-layer nanoflakes, which makes their study with SXRD difficult. While the TSD geometry with its small beam footprint is ideal for obtaining diffraction data from these small flakes, the alignment can be a major challenge. We developed and commissioned a procedure in which TMDC flakes were prepared on glass slides covered with Indium Tin oxide, which was then mounted in the flow cell. An optical microscopy with a *Basler* camera was installed at ID31, which was aligned to the position of the X-ray beam with μm precision. This allows us to use the optical microscope to find and align desired TMDC flakes on the already installed sample, estimate their thickness by their optical transmission, and then study their behaviour with XRD.

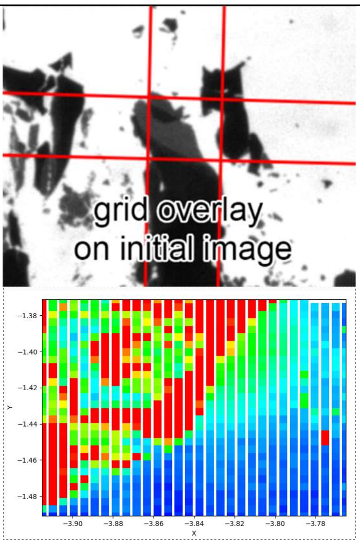

Fig. 4: *In situ* optical microscopy of TaS_2 flakes installed on ITO in the flow cell (top) and corresponding XRD data (bottom), revealing the flake's internal structure.