ESRF	**Experiment title:** **Towards operando electrochemical X-ray diffraction of supported, electrochemically grown high-index faceted Pt nanoparticles as catalysts for the electrolysis of water** **Keywords:** electrocatalysis, nanoparticles, surface X-ray diffraction, gracing incidence small angle X-ray scattering, operando studies	**Experiment number**: MA2086
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1. Pt nanoparticles supported on Si(100)

The initially proposed system Pt tetrahexahedral (THH) nanoparticles (NP) supported on glassy carbon (GC) substrates was shown to be not suitable for GISAXS characterization already during beamtime MA1891 (Dec 2013). This was largely due to the diffuse scattering of the GC substrate. Therefore, it was decided to produce Pt NPs electrochemically on single crystalline Si(100) substrates. By doing that, we could reduce scattering background significantly. However, as shown in Fig. 1a, the shape of the Pt particles is not well defined – THH particles could not be prepared on Si(100). From GISAXS analysis in this beamtime we concluded that these quasi-spherical particles consist of polycrystalline randomly oriented domains.

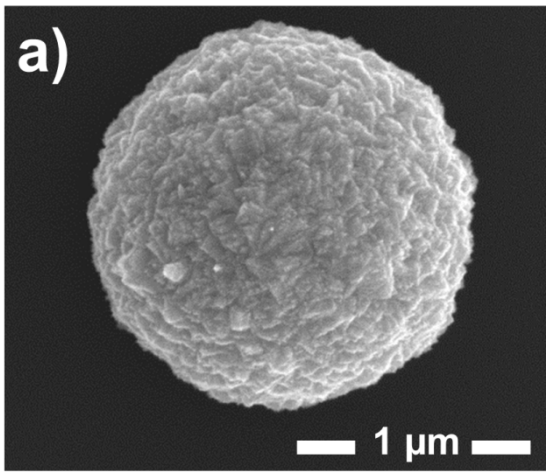

Figure 1. SEM image of Pt particles electrodeposited onto Si(100)

2. Combination of mass spectrometer with electrochemistry cell – towards operando EC-SXRD/XRR/GISAXS

The modified in-situ EC cell of ID03 [1] was extended by an on-line electrochemical mass spectrometry (OLEMS) setup [2] connected to a mass-spectrometer via a differential pumping system. Approaching of the tip has been done by piezo-stage driver with feedback loop. The whole system was tested for polycrystalline Pt foil at TU/e in advance (see Fig. 2). At ID03 a UHV prepared Pt(111) was mounted and characterized electrochemically.

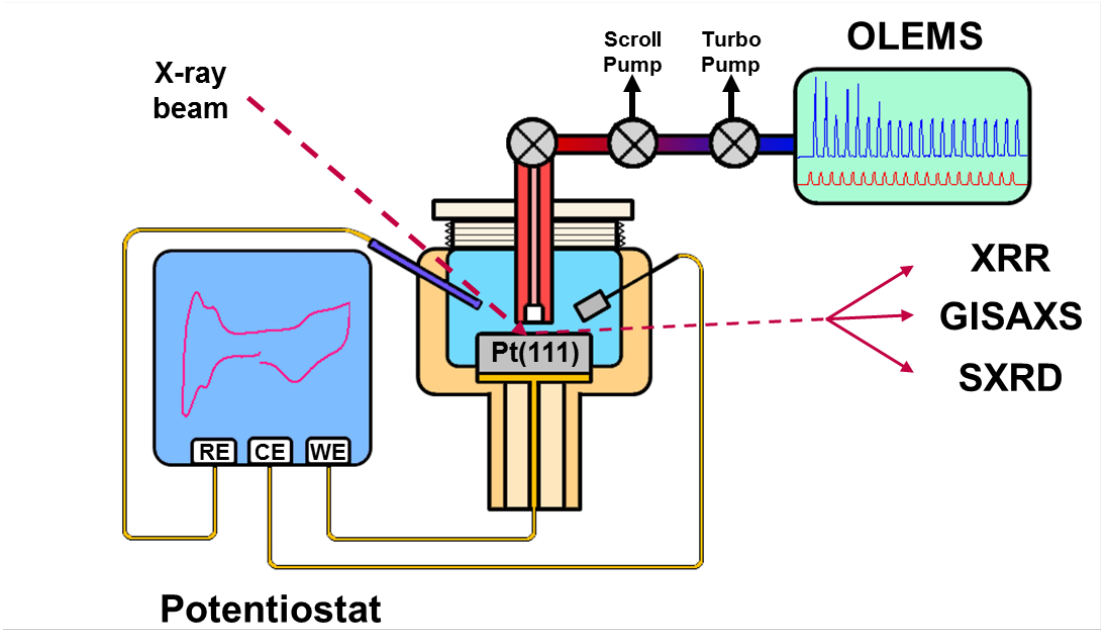

Figure 2. Scheme of the operando EC-OLEMS-SXRD/GISAXS/XRR setup.

As showcase and to validate the combined OLEMS–[SXRD/GISAXS/XRR] setup for *operando* studies of electrode reactions, we chose the hydrogen evolution (HER) reaction and oxygen evolution reaction (OER) on Pt(111). The HER activity was monitored by OLEMS (on-line electrochemical mass-spectrometry) and the structural evolution after several electrochemical treatments was assessed by SXRD (crystal truncation rods), GISAXS (Grazing-incidence small-angle scattering) and XRR (X-ray reflectivity). We could show a relation between the rate of H_2 production with an increased roughening of the Pt(111) electrode induced by potential cycling. Potential cycling by CV (cyclic voltammetry) in the range of [0.9 .. E_N, 50 mV/s], where E_N is upper potential, which was altered from 1.0 V till 1.5 V with 0.1 V step, was used to induce roughening, which relates to an increase in activity of H_2 evolution.

A real *operando* experiment could be conducted during stepping the potential on the Pt(111) electrode between OER (+1.6 V) and HER (-0.4 V). Simultaneously, XRR was continuously measured at 1 point (mu =1, gam = 1) at which intensity change was shown to be maximal. The obtained data set can be further used to derive structure-activity relationships for Pt(111) single crystal electrode in the OER and HER reactions (Fig. 3).

Further data analysis and manuscript preparation is currently ongoing.

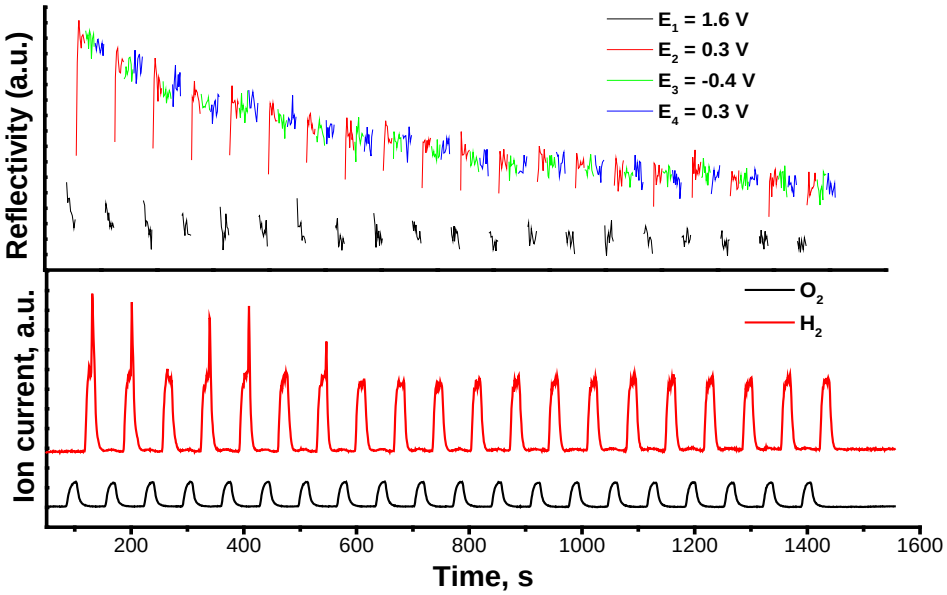

Figure 3. a) Simultaneously recorded XRR as well as O_2 and H_2 mass spectrometer signal data during potential switching (1.6 V for OER and -0.4V for HER).

References

[1] M. L. Foresti, A. Pozzi, M. Innocenti, G. Pezzatini, F. Loglio, E. Salvietti, A. Giusti, F. D'Anca, R. Felici, and F. Borgatti, "In situ X-ray analysis under controlled potential conditions: An innovative setup and its application to the investigation of ultrathin films electrodeposited on Ag(111)," *Electrochim. Acta*, vol. 51, no. 25, pp. 5532–5539, Jul. 2006.

[2] A. H. Wonders, T. H. M. Housmans, V. Rosca, and M. T. M. Koper, "On-line mass spectrometry system for measurements at single-crystal electrodes in hanging meniscus configuration," *J. Appl. Electrochem.*, vol. 36, no. 11, pp. 1215–1221, Aug. 2006.