

	Experiment title: <i>In operando</i> GISAXS studies of structural changes in Pt electrocatalysts	Experiment number: CH-3858
Beamline: ID03	Date of experiment: from: Nov 06, 2013 to: Nov 12, 2013	Date of report: March 5, 2014
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Report:

Structural changes due to oxidation-reduction processes in platinum electrocatalysts are of major interest for a broad field of applications. E.g., platinum is by far the most effective and most common electrocatalyst at the anode side in currently employed PEM fuel cells. Platinum nanoparticles in such fuel cells undergo great morphological alterations such as agglomeration or dissolution, especially when the anode is driven into the oxidation regime which cannot be completely avoided during practical fuel cell operation. Subsequent downsizing of reactive surface area (i.e., decreasing catalytic activity) is one substantial problem to circumvent in production and maintainability of cost-effective cells for commercialization. The formation of nanoscale islands induced by oxidation-reduction cycles is well known [1, 2], but no quantitative data on the morphological evolution and its time and potential dependence is published up to now. The experiment CH-3858 aspired to fill this gap of knowledge.

Recently at ID32 (SI-2282, [3]) and ID03 (SI-2524), we demonstrated in studies of homoepitaxial electrodeposition on Au(001) electrodes the feasibility of elucidating the evolution of nanoscale surface structures in an electrochemical environment with grazing incidence small angle x-ray scattering (GISAXS). The 3D platinum islands, which ripen upon successive oxidation-reduction cycles are an order of magnitude smaller than the surface structures, which had been observed on Au(001), but still in accessible range of GISAXS measurements.

As in former beamtimes we performed the *in situ* surface scattering measurements in our hanging meniscus transmission x-ray cell using a photon energy of 22.5 keV. As a working electrode we employed a hat-shaped, polished Pt(111) single crystal, as electrolyte we used 0.1 M HClO₄ prepared from Suprapur HClO₄ and MilliQ water (18.2 MΩcm). The two-dimensional scattering patterns were recorded with a Dectris Pilatus 300K-W, which was placed at a distance of ≈ 0.6 m behind the sample in beam direction.

The preparation of smooth and clean platinum surfaces was a challenging task and severely hampered by the poor AquaFlame device, which provided an adequate hydrogen flame, sporadically. In case of an operational AquaFlame, the crystal was transferred immediately after annealing into an inert argon atmosphere for cooling and was subsequently covered with a droplet of oxygen-free electrolyte inside the argon atmosphere. The freshly prepared and by a droplet of electrolyte protected crystal was then mounted in the EC cell and a potential of 0.05 V_{RHE} (i.e., in the regime of hydrogen adsorption) was established. Cleanness and morphology of the platinum surface, as well as a shift of the reference electrode was initially checked by at most five potential cycles within the range of the hydrogen evolution and 0.8 V_{RHE}, i.e., the upper limit of the butterfly peak, which is assigned to hydroxyl (OH[−]) formation. Furthermore, the scattered intensity as a reference scan had been recorded initially with the Pilatus for 100 s. In order to minimize beam influence, all x-ray measurements were performed at E = 0.05 V_{RHE}, which seems to be more favorable for illuminating the Pt surface than a potential in the double layer region.

Subsequently, an electrolyte exchange in the meniscus and a potential cycle in the range 0.05 V_{RHE} to E_f (E_f = 0.9 to 1.4 V_{RHE}) had been performed. After each cycle the scattered intensity had been recorded with the 2D detector for 100 s. The intensity maps show distinct intensity peaks, which indicate the formation of lateral structures with preferential size $\xi = 2\pi/q_r$. Fig. 1 shows ξ plotted against the number of potential cycles for six selected potentials E_f. Obviously, lateral structures grow smaller for higher values of E_f with the exception of E_f = 1.1 V_{RHE}. A possible reason for this exceptional behavior might be the transition from reversible to irreversible electrode reactions, when adsorbed OH converts to O and an initial Pt oxide layer forms [4].

Data analysis particularly with regard to intensity of diffusely scattered intensity and rms-roughness of the platinum surface is still in progress. The results of this experiment will provide an insight into the formation of nanoscale islands induced by oxidation-reduction cycles and its potential dependence.

References

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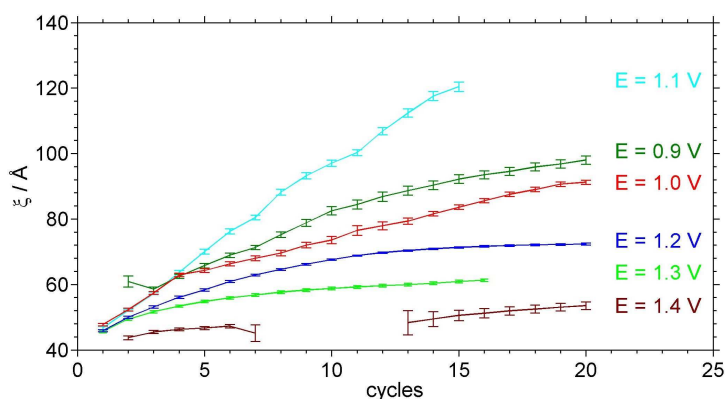


Figure 1: Evolution of the characteristic lateral structure size for various potentials E_f. A refill between the 7th and 8th cycle, while performing the measurements at E_f = 1.4 V, impeded the following evaluation of the peak position of the diffusely scattered intensity.