



	Experiment title: On the morphological stability of supported Pt nanoparticle ensembles in electrochemical environments: In situ SAXS investigation	Experiment number: CH 4623
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Report:

In this beamtime, we applied in-situ (anomalous) small angle X-ray scattering and high energy X-ray diffraction to study the morphological and structural evolution of platinum nanoparticles and its metal oxide support during electrochemical potential cycling. These materials are used as electrocatalysts for the oxygen reduction reaction at the cathode side of polymer electrolyte fuel cells (PEFCs).

This project aimed to provide fundamental insight into the structural parameters that control the structural and morphological (in)stability of Pt nanoparticles under electrocatalytical conditions. We analyzed two different catalyst systems: Pt supported on Indium Tin Oxide (Pt/ITO) [1] and on Ruthenium Titanium Oxide (Pt/RTO). These materials were investigated during potential cycling between 0.6 and 0.95 V vs RHE mimic fuel cell operating conditions and between 1.0 and 1.5 V to mimic start/stop cycles for 5000 times.

Prior to the in-situ studies, we investigated carefully the beam sensitivity of the ITO and RTO by the evolution of the structural properties as function of X-ray radiation under electrochemical resting conditions. We identified that the structure did not change for RTO whereas for ITO we had to choose the experimental conditions carefully to rule out the beam damage of the ITO.

In case of Pt/ITO, we identified that the ratio of peak intensities of Pt and the In_2O_3 alters from the dry state until the end of the stability test in the lower potential range (Figure 1). Rietveld refinement revealed that the fraction of In_2O_3 decreases from 79% to 61% during 5k cycles. Simultaneously, the Pt coherence length does not increase from the initial value of 4.3 nm whereas the crystallite size of In_2O_3 increases from 14 to 16 nm. These results indicate that the support material ITO is partially dissolved during potential cycling and the remaining ITO crystallites grow in size via Ostwald ripening.

In the upper potential range the catalyst composition and structural coherence length of Pt and ITO was significantly more stable as revealed by in-situ X-ray studies which is in agreement with the electrochemical characterization showing a better stability of the catalytic activity compared to the lower potential range.

The results from HE-X-ray diffraction are in agreement with the recorded anomalous SAXS scattering curves recorded at the Pt K-edge which indicate the stability of the Pt nanoparticles on the oxide support in terms of number of particles and particle size distribution. In combination with the results from electrochemical experiments and ex-situ electron microscopy allowed us to explain the determined loss of electrocatalytical activity towards oxygen reduction reaction.[1]

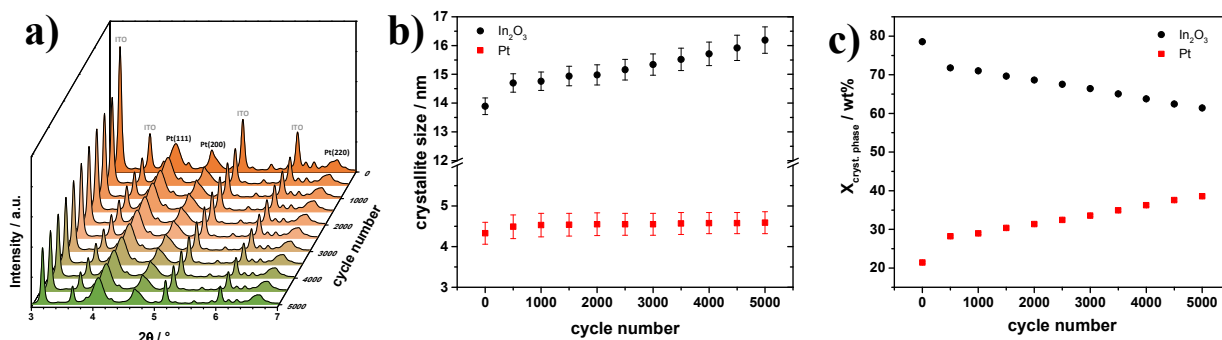


Figure 1: Results of in in-situ HE XRD measurements for Pt/ITO. a) showing the evolution of diffraction pattern from 0 to 5000 potential cycles. b) showing the Pt and In_2O_3 crystallite size as function of potential cycles. c) showing ratio of crystallite phases of In_2O_3 as function of potential cycles obtained from rietveld refinement.

Figure 2 shows the results from *in-situ* HE-XRD for Pt nanoparticles supported on mixed Ruthenium Titanium Oxide (Pt/RTO). The diffraction patterns during the 5000 potential cycles show the strong stability of the nanoparticles and of the oxide support (Figure 3). By analyzing the diffraction patterns in more detail, we obtain the presence of three different oxide phases: TiO_2 in anatase and a Ti-rich and a Ru-rich rutile phase. Rietveld refinement revealed that both rutile phases are present in a fraction of around 10 wt%. The anatase phase has a higher fraction with around 45 wt% and Platinum ~38 wt%. During the electrochemical potential cycling, the rutile phases remained constant whereas the fraction of anatase increased and the fraction of metallic Platinum decreased by 5 wt%. We explain this by the partial detachment of Pt nanoparticles (Figure 3b) during the potential cycling. The coherence length of all 4 phases remained constant. Pt has a crystallite size of around 5 nm what is also in good agreement with TEM analysis. The Ru-rich rutile phase shows small crystallites with around 10 nm, whereas the anatase and the Ti-rich rutile phase show sizes of around 20 nm (Figure 3c). Compared to Pt on ITO, this sample shows a much higher stability in terms of loss in mass activity. This can now be explained by these *in-situ* X-ray studies where no dissolution or crystallite growth can be assigned.

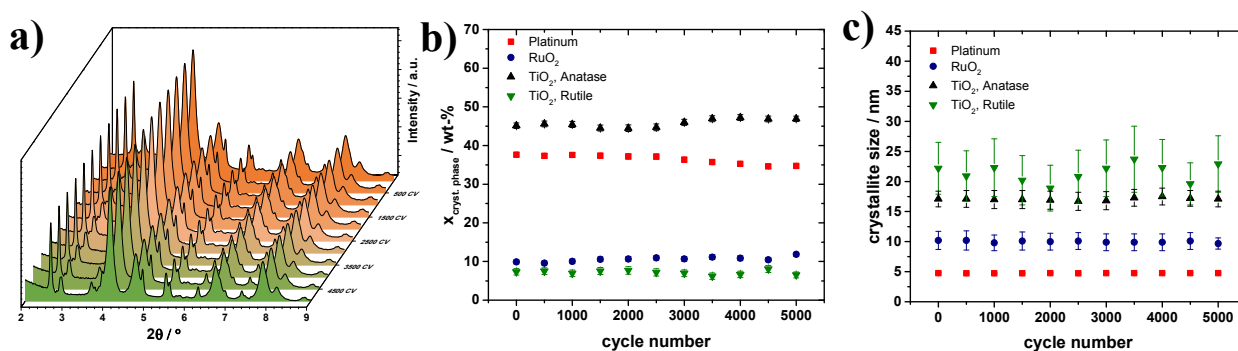


Figure 3: Results of in in-situ HE XRD measurements for Pt/RTO. a) showing the evolution of diffraction pattern from 0 to 5000 potential cycles. b) showing ratio of crystallite phases of In_2O_3 as function of potential cycles obtained from rietveld refinement. b) showing the Pt and In_2O_3 crystallite size as function of potential cycles.

In conclusion, we can say that *in-situ* HE-XRD and anomalous SAXS are powerful tools to analyze the morphological and structural changes in electrocatalysts under reaction conditions. We were able to successfully show the reasons for electrocatalytic (in)stability in terms of crystallite growth due to Ostwald ripening and agglomeration as well as detachment from the oxide support.

Literature:

[1] H. Schmies, A. Bergmann, J. Drnec, P. Strasser, et al., in preparation.