



Experiment title:

In-situ SAXS Investigation on the Morphological Stability of Platinum on Heteroatom Modified Carbon Supports for Oxygen Reduction Reaction

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Report:

In this project we investigated the structural and morphological stability of Pt nanoparticles on modified carbon supports by applying both *in situ* small angle X-ray scattering (SAXS) and high energy X-ray diffraction (HE-XRD). The studied materials are used as catalysts on the cathode site of hydrogen fuel cells and are tested with respect to their long term term stability under simulated working conditions. It is well known from literature that state-of-art carbon supported electrocatalysts suffer from several degradation phenomena under harsh conditions (low pH, high oxygen concentrations and potentials) leading to strong performance losses. Pt particle growth and agglomeration resulting in active surface area losses are known to be the prominent catalyst degradation mechanisms. By modifying the carbon support with heteroatoms a stronger anchorage of the Pt nanoparticles is anticipated leading to improved electrochemical stability. With the results from *in situ* SAXS and HE-XRD we aim for a better understanding regarding structural and morphological stability of our support-modified electrocatalysts.

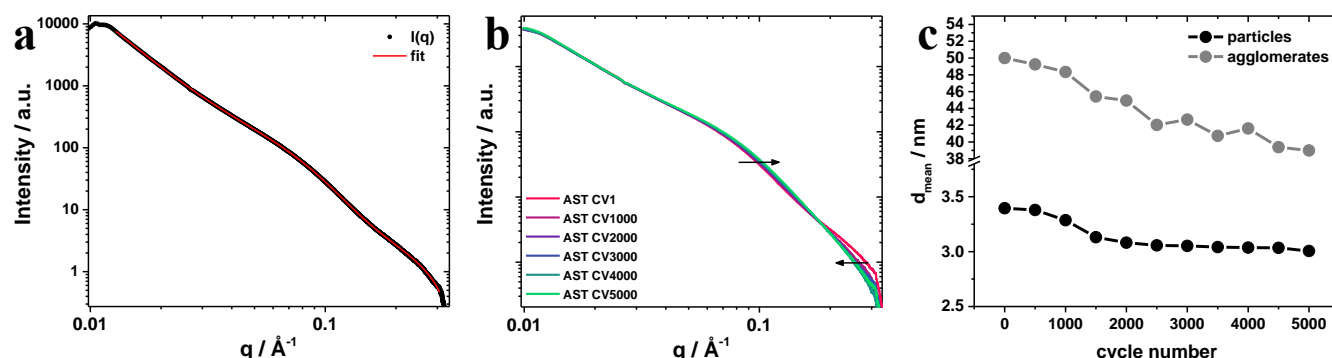


Figure 1 Results from *in situ* SAXS measurements for Pt/C-acid. (a) shows the transmittance-normalized and background-subtracted scattering curve (black dots) and the corresponding fit (red curve). (b) shows the evolution of the scattering curves of the course of 5000 potential cycles of the AST. (c) depicts the evolution of bimodal particle size (particles and agglomerates) from SAXS fits as a function of mean diameter over cycle number of the AST (5000 CVs, 0.6-0.95 V vs RHE).

Figure 1 shows the results from *in situ* SAXS measurements on Pt/C-acid. In this catalyst system we applied a step-by-step acid treatment to the carbon support (Vulcan XC 72r) to modify the mesoporous carbon with O- and N-species which are likely to provide anchorage points for the small Pt nanoparticles that are deposited on this support in another step by thermal reduction of a Pt precursor. In an previous *ex situ* accelerated stress test (AST; 5000 potential cycles between 0.6 - 0.95 V vs RHE) we were able to successfully proof the superior stability of Pt/C-acid compared to a untreated Pt/C catalyst with similar particle size and weight loading. After the applied AST the catalyst Pt/C-acid shows almost no loss in catalytic activity and active surface area while the reference system degrades by ca. 30 % in both descriptors.

The corresponding *in situ* SAXS results for Pt/C-acid are in agreement with Pt particle sizes obtained from TEM with around 3.5 nm and also the fitted model of the scattering curve is in good agreement with the data (see Figure 1 a). Our fit results give a bimodal particle size distribution with a major particle fraction in the size of ca. 3.4 nm and a very small fraction (ca. 0.002%) of relatively big agglomerates. The evolution of scattering curves over the AST reveals slight changes at around 0.1 \AA^{-1} to higher q and at 0.25 \AA^{-1} to lower q , see Figure 1 b. Fits of these scattering curves indicate a stable Pt particle size with a small decrease over the first 1500 CVs whereas the size of the agglomerates steadily decreases (Figure 1 c). This proofs the superior morphological stability of the Pt nanoparticles on this support and excludes any particle growth during the AST.

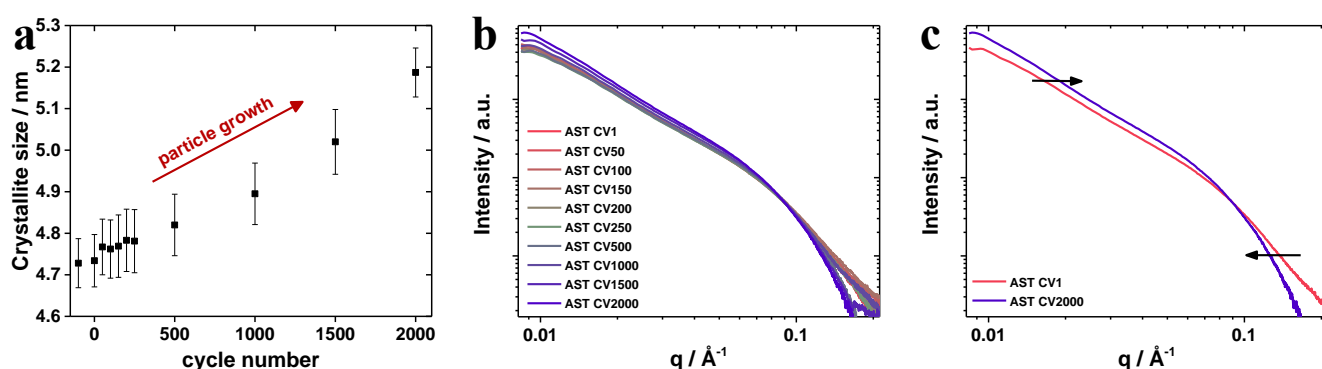


Figure 2 Results from *in situ* HE-XRD and SAXS measurements on Pt/C-acid in an AST of 2000 CVs with an upper potential limit of 1.2 V. (a) shows the evolution of crystallite size from Rietveld refinement over the cycle number, (b) the evolution of transmittance-normalized and background-subtracted scattering curves over the 2000 cycles and (c) the scattering curves of the first and last cycle of the stability test.

By applying a stress test with an upper potential limit of 1.2 V to this kind of material we wanted to investigate the stability of the Pt nanoparticles under such harsh conditions. In *ex situ* electrochemical measurements the catalyst showed a bigger loss in catalytic activity than in the AST with an upper potential limit of 0.95 V suggesting some kind of material degradation. From single crystal and dissolution studies it is known that Pt performance loss can additionally be caused by reductive oxide dissolution which is favoured at potentials higher than 1 V. In the *in situ* experiments of 2000 potential cycles a clear increase in crystallite size from 4.7 to 5.2 nm was observed from Rietveld refinement of the HE-XRD patterns. This means that the observed performance decrease is caused by Pt particle growth also leading to surface area losses as measured by the decreased electrochemical active surface. Additionally, the scattering curves as shown in Figure 2b,c change during the cycling and these changes are more pronounced than in the milder stability protocol as seen in Figure 1. These changes are most distinctive in the region of lower q values (Figure 2c) indicating a higher fraction of larger particles and thus, Pt particle growth. The evaluation and fitting of the SAXS curves for this stability test are ongoing work but the observed changes in the scattering curves are in good agreement with the results from Rietveld refinement.

In summary, we can say that *in situ* SAXS and HE-XRD are powerful tools to investigate the morphological and structural stability in a catalyst system. By applying two different stability protocols to a support-modified Pt electrocatalyst, we were able to show that the catalyst exhibits great stability when cycled below 1 V and little particle growth in a harsher oxidizing protocol.