



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title:

Influence of Carbon Support Modification on the Morphological Stability of Pt Nanoparticles in Electrochemical Environments: Combined in situ SAXS and HE-XRD Investigation

Experiment number:

CH-5350

Beamline: ID31	Date of experiment: from: 09 May 2018 to: 14 May 2018	Date of report: <i>Received at ESRF:</i>
Shifts: 15	Local contact(s): Jakub Drnec, Raphael Chattot	

Names and affiliations of applicants (* indicates experimentalists):

*Henrike Schmies, TU Berlin

*Malte Klingenhof, TU Berlin

*Thomas Merzdorf, TU Berlin

*Elisabeth Hornberger, TU Berlin

Peter Strasser, TU Berlin

Report:

In this project, we studied the structural and morphological stability of Pt nanoparticles supported on undoped and N-doped carbon supports under applied potential cycling using both *in situ* high energy X-ray diffraction (HE-XRD) and (anomalous) small angle X-ray scattering ((A)SAXS) simultaneously. We aimed for a better understanding regarding the structural and morphological stability of our support-modified electrocatalysts under potential cycling.

To study our catalysts, we used our custom designed grazing incident cell filled with 0.1 M perchloric acid as electrolyte and equipped with PEEK foil acting as X-ray window. The samples were prepared by drop-casting the catalyst ink on a glassy carbon (GC) cylinder aiming for an RDE-like Pt loading of $12.5 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$. X-ray attenuation due to the electrolyte film was reduced significantly thanks to the high-energy X-ray radiation. For each sample, we measured HE-XRD and SAXS scans in the dry state, after filling the cell with electrolyte (wet state) and after activation with cycling voltammetry (CV) of 50 times cycling between 0.05 and 1.0 V vs RHE at 100 mV s^{-1} . Finally we measured HE-XRD and SAXS scans while applying an accelerated stress test (AST) protocol every 250 cycles.

Table 1: Sample list indicating the performed electrochemical protocols and problems during the beamtime.

	LP (“Pt stability”) MP: 1 s holding time; 10k cycles; 0.6 V & 0.95 V	HP (“Carbon stability”) CV: 500 mV/s; 5k cycles; 1.0 – 1.5 V
Reference: HISPEC 20% Pt/C	✓	No time to measure
WSR07: Pt/Vulcan	✓	✓
WSR11: Pt/N-V 400°C	Only data for before and after AST → error in macro loop	ECLab aborted after cycle 4188
WSR12:Pt/N-V 800°C	ECLab aborted after cycle 5251 (restart) and 9749	ECLab aborted after cycle 4209

Table 1 indicates the investigated samples and the performed electrochemical protocols, which were adapted from the US Department of Energy 2020 targets, and arising electrochemical problems during the beamtime (likely due to the capability of the counter/reference electrode or the limitations of the potentiostat). A reference material (HISPEC3000, 20% Pt/C, Alfa Aesar) and three catalysts prepared in our lab (Pt/(unmodified) Vulcan, Pt/(N-doped Vulcan) N-V 400°C and Pt/N-V 800°C) were measured. The low potential “LP”-AST is investigating the Pt stability and the high potential “HP”-AST is investigating the carbon stability.

After performing the experiments and integration of the data, we noticed that the background scans measured for the subtraction of other diffraction and scattering responses (e.g. GC substrate, PEEK foil, electrolyte/water, cell body) were not beneficial for further analysis of the data as the background scans would overcorrect and tamper the data. Therefore, HE-XRD scans were background-corrected using a polynomial function and analyzed with the Scherrer approach on basis of the Pt (220) reflex as this reflex is mostly free of any interfering background reflexes. The Pt (220) reflex was fitted best when using two Pt phases, one for a major phase with smaller crystallite size, one minor phase with a larger crystallite size. This is supported by TEM images of the pristine powder. Figure 1a shows the resulting crystallite sizes of Pt phase 1 as extracted using the Scherrer equation. The results for the crystallite sizes of the *ex situ* pristine powder measured at our lab XRD and the *in situ* thin catalyst film dry state on the GC substrate measured at the ESRF show acceptable values. The results from the *in situ* after 50 CV and after LP-/HP-AST state show some variation. So far, the catalysts appear to show for both AST protocols a high structural and morphological stability. But using the simple Scherrer equation here, it is unclear yet if the results show a true trend of catalyst stability or are biased due to poor background subtraction. Finding an acceptable analysis procedure is ongoing work.

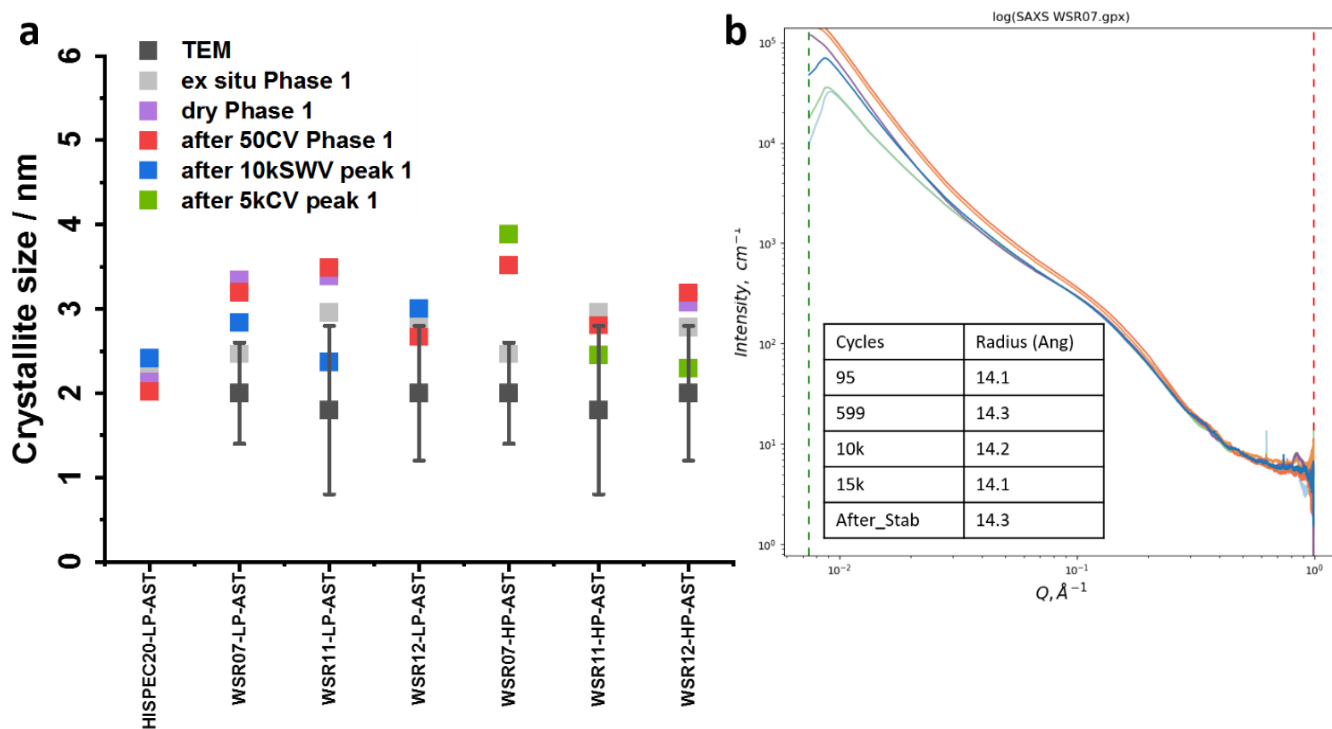


Figure 1: (a) Crystallite sizes for HISPEC20, WSR07, WSR11 and WSR12 extracted from TEM images, *ex situ* lab-based XRD and *in situ* synchrotron-based HE-XRD of the Pt phase 1. (b) *In situ* SAXS curves of WSR07-LP-AST. The inset table shows the resulting radii during potential cycling.

Because the background subtraction and the anomalous contrast failed, SAXS data was analyzed without any further correction. This is acceptable because the background interference is neglectable for SAXS. SAXS scans were analyzed using a combined model of spheres and the power law. Figure 1b shows the *in situ* SAXS curves during potential cycling for WSR07-LP-AST. Changes are observed only at low q values due to larger background objects, not due to the smaller Pt particles. The extracted radii of ~14.1-14.3 nm are in agreement with the HE XRD results (which itself are under debate). For WSR07-LP-AST no massive degradation is observed. The evaluation and fitting of the SAXS curves are ongoing work.

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. But an adequate background subtraction is essential for the correct analysis of such delicate measurements.