



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: Temperature dependence of the electrooxidation on Pt(111)	Experiment number: CH-6392	
Beamline: ID31	Date of experiment: from: 24/01/2023 to: 30/01/2023	Date of report: 28/04/2023
Shifts: 18	Local contact(s): Jakub Drnec	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Jan Ole Fehrs* , University of Kiel, Germany Jing Tian* , University of Kiel, Germany Finn Schröter* , University of Kiel, Germany Olaf M. Magnussen , University of Kiel, Germany Jakub Drnec* , ESRF, France Andrea Sartori* , ESRF, France Olvido Irrazábal Moreda* , ESRF, France Valentin Briega-Martos* , Forschungszentrum Jülich, Germany David Harrington , University of Victoria, Canada		

Report:

It was the aim of our experiment to investigate the influence of temperature on the oxide structure and oxidation kinetics of Pt(111). Therefore, it was planned to study the oxidation and reduction process at different elevated temperatures in Ar- and O₂-saturated electrolytes (0.1 M HClO₄ and 0.1M H₂SO₄). The performed experiments were a continuation of our previous efforts on understanding the oxidation/reduction process on platinum single crystals.[1-7]

To perform the proposed experiments a new HESXRD-setup was advertised, that unfortunately could not be finished on time due to heavily delayed part deliveries. These circumstances forced us to use a modified version of our previously used cell, but without the ability to re(-prepare) the sample on the diffractometer. Because additional time was needed to perform the foreseen experiments with this different setup, we were not able to finish all of proposed experiments. Therefore we focused on the experiments in Ar-saturated 0.1 M HClO₄ at the highest temperature (343 K) as a model system.

We started our experiments on Pt(111) oxidation/reduction kinetics by measuring the X-ray intensity at the anti-Bragg position during potential cycling at elevated temperature (X-ray voltammetry, XRV). We performed this experiment at multiple potential sweep rates to compare with already published data of our group.[7] The preliminary results in figure 1 show, that we were able to reproduce the temperature dependent potential shifts of the oxidation/reduction, as they were discussed in literature.[8] Surprisingly, the observed X-ray intensity, which is a measure of the extraction of Pt atoms out of the surface, shows almost no difference during the anodic sweep/oxidation of the surface. Only during reduction there is an observable difference, specifically a lower hysteresis of the Pt extraction at higher temperatures. This behaviour is in accordance to our recently published results on platinum oxidation/reduction kinetics.[7] There, it was found that the Pt

extraction during the anodic sweep is a fast process, that is driven by potential and not directly coupled to the slower electrochemical formation of surface oxygen species.

After this, we performed similar measurements at increasing upper potential limit to investigate the temperature dependence of the onset of the irreversible place-exchange process. This process is of special interest for understanding the degradation of the platinum surface. The analysis of these data is still in progress.

Furthermore, we performed crystallographic studies of the Pt(111) surface by CTRs at different potentials to study the effects of the elevated temperature on the formation and structure of the ultra-thin oxide layer upon the surface. A preliminary analysis of these CTR data suggests similar Pt oxide structures as measured at room temperature. Since the kinetic of oxide formation seems to be almost unchanged according to the XRV measurements, it is anticipated that the oxide structure itself does not depend on the temperature. Detailed fits of the CTR datasets with our most recent model still have to be done to fully confirm that the atomic structure of the surface is actually identical.

In summary, we succeeded in studying the oxide formation/reduction kinetics on Pt(111) in HClO₄ solution at 70 °C and found the structural change due to Pt extraction independent of the temperature, in contrast to the temperature-dependent kinetics of the accompanying charge transfer. Furthermore, we obtained full CTR datasets of this system at different potentials within the double layer and oxidation range, which will allow to assess the influence of the temperature on the precise Pt oxide structure.

Due to the additional time needed for the reparation of the samples in the modified setup, unfortunately no experiments within O₂-saturated electrolyte or in 0.1 M H₂SO₄ could be performed within the assigned time.

References:

- [1] T. Fuchs et al, Nat. Cat.,3 (2020) 754
- [2] J. Drnec et al, Electrochim. Acta, 224 (2017) 220
- [3] M. Ruge et al, J. Am. Chem. Soc., 139 (2017) 4532
- [4] M. Ruge et al, J. Electrochem. Soc., 164 (2017) H608
- [5] Drnec et al., Current Opinion Electrochem., 4 (2017) 69
- [6] J. Drnec et al, Electrochem. Comm., 84 (2017)
- [7] T. Fuchs et al., J. Phys. Chem. Lett., 14 (2023) 3589
- [8] N. Marković et al., J. Phys. Chem. B, 103 (1999) 8568

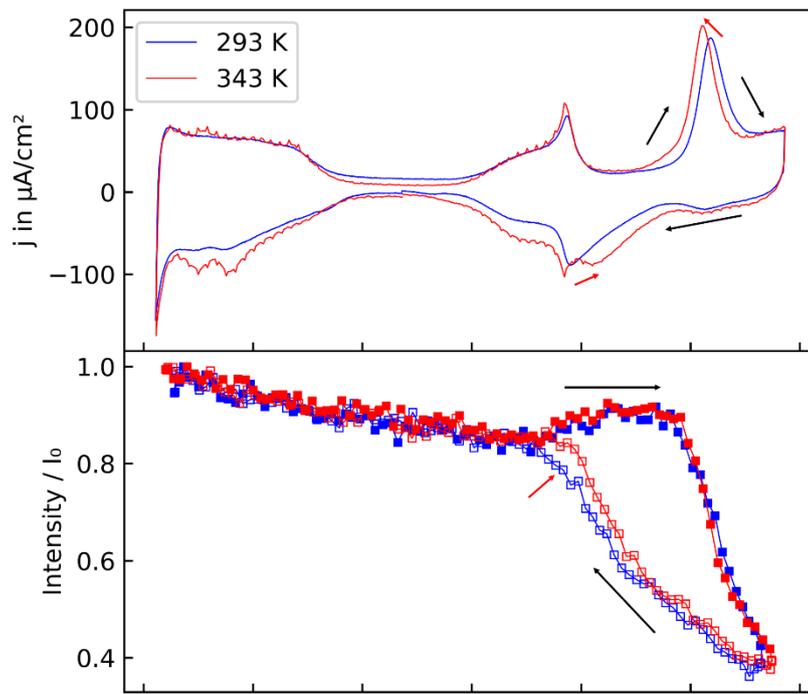


Figure 1: Preliminary results of the XRV measurements. Top: Cyclic voltammograms of Pt(111) in 0.1 M HClO₄ at different temperatures (100 mV/s sweep rate). Bottom: Corresponding X-ray intensity measured at 1 1 1.5 anti-Bragg.