

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>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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: Pt Oxidation: Structure, Dynamics and Role in ORR Electrocatalysis	Experiment number: CH4977
Beamline: ID31	Date of experiment: from: 20.7.2017 to: 26.7.2017	Date of report: 12.9.2017
Shifts: 18	Local contact(s): Francesco Carla	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Jakub Drnec, ESRF, France Olaf M. Magnussen, University of Kiel, Germany * David A. Harrington, University of Victoria, Canada		

Report:

The aim of this experiment was to determine the atomistic model for oxidation behaviour of Pt(100) and Pt(110) surfaces. Furthermore, we wanted to compare the oxidation for both orientations in Ar and O₂ saturated electrolytes and to assess the irreversible reconstruction dynamics upon the extensive potential cycling. This experiment was a continuation of our previous work on Pt(111) surface which was well received by the community (3 published papers, 2 submitted papers).

Unfortunately given the problems with the stability of the beam, we were able to finish only part of the foreseen experiments. We focused on Pt(100) surface and characterized the oxidation only in Ar saturated electrolyte.

We started with the thorough crystallographic determination of the surface structure at different potentials (Fig. 1). We measured large datasets of 6 CTR's for 8 different potentials to find the structural evolution for progressively higher potentials. The data show clear trend in the CTR's shape and can be fitted with the place-exchange model developed recently by our group [1-2]. The fitting is in progress and will allow us to understand the oxidation process with atomic resolution.

The next step was to understand better the oxidation dynamics. For this experiment we performed several cycles between 0.1 V and 1.17 V while measuring the intensity at antibragg position, which is very sensitive to the extent of oxidation (Fig 2). To our surprise, the oxidation of Pt(100) surface has significantly different behaviour when compared to the same experiment at Pt(111). First, on Pt(100) the oxidation starts at lower potential and, second, it is irreversible even for lower cycling potentials. This suggests that the oxidation process is faster on Pt(100) and the place-exchanged atoms lose their register with the substrate for lower potentials. This results in an irreversible structural change. Such a result has wide consequences. It will be difficult to stabilize shaped fuel cell nanoparticle catalysts as the (100) facet will dissolve at a higher rate and at lower potentials. This will lead to a loss of the shape and therefore the activity of the catalyst.

To further clarify this point we performed potential step experiments. These gave us further details about the processes taking place during the oxidation, mostly the place-exchange kinetics. The comparison of these results with the one obtained on Pt(111) surface is shown in Fig. 3. On the left are plotted the slopes of the lines fitted to the F vs $\ln(\text{time})$ curves for each step experiment. Preliminary analysis showed that the activation energy of the place-exchange process is lower for Pt(100) while the rates can be higher for Pt(111) for higher potentials.

The right side shows the ratio of initial and final intensities during one cycle. This is a quantitative marker for the reversibility of the process as a function of potential. While the oxidation is reversible to 1.13 V for Pt(111), the Pt(100) is much less stable and the process is irreversible after the first signs of the place-exchange process. Therefore the stability of the real fuel cell catalyst would be very dependent on the shape of the nanoparticle and how much of the total surface area is composed of each different facet.

Unfortunately all experiments with longer acquisition time (e.g. long cycling GISAXS experiment) will need to be remeasured due to the beam instability. The beam instability is also responsible that we did not finish the measurements on Pt(110) surface and measurements with O_2 saturated electrolytes.

As a conclusion we summarize the expected results which were mentioned in the experimental proposal:

1. Find the structure of electrochemically formed Pt oxide on Pt(110) and Pt(100).
 - Done for Pt(100)
2. Understand the differences of the oxidation behavior for different Pt faces by determining the state of the surface at different electrochemical potentials.

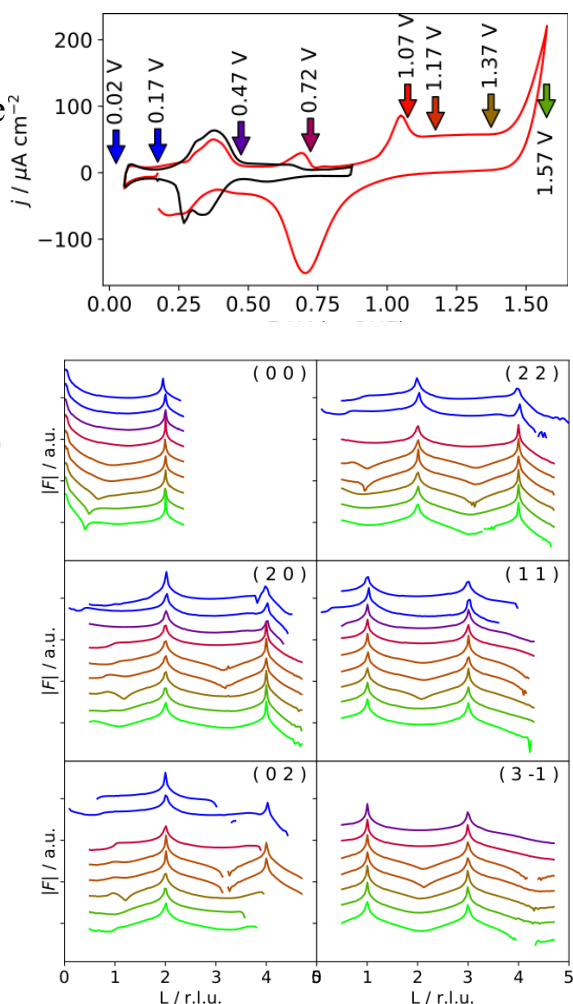


Fig 1. CTR's measured at different potentials on Pt(100) surface (bottom) and different potentials (top).

- Done for Pt(100), compared to previous results measured on Pt(111)
3. Determine the potentials for O adsorption and place exchange (the onset of quasi-3D oxidation) in both deaerated and O₂ saturated electrolytes.
 - Not done due to the beam instabilities
 4. Understand the structural dependence of the processes leading to irreversible roughening and Pt dissolution.
 - Not done due to the beam instabilities

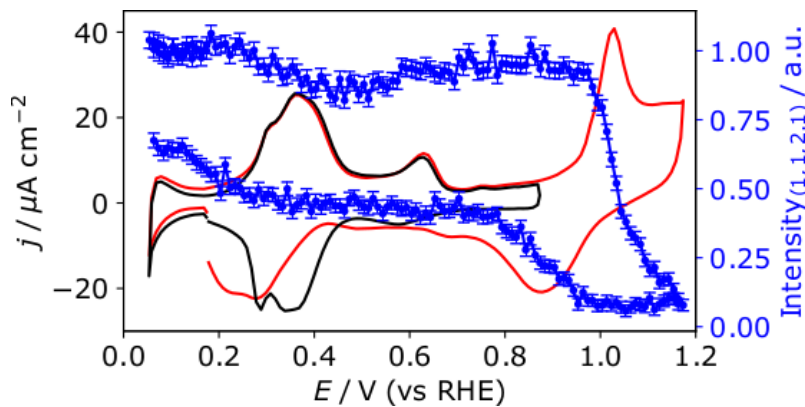


Fig. 2 Cyclic voltammogram plotted together with antibragg position intensity showing the dynamics and irreversibility of the oxidation process.

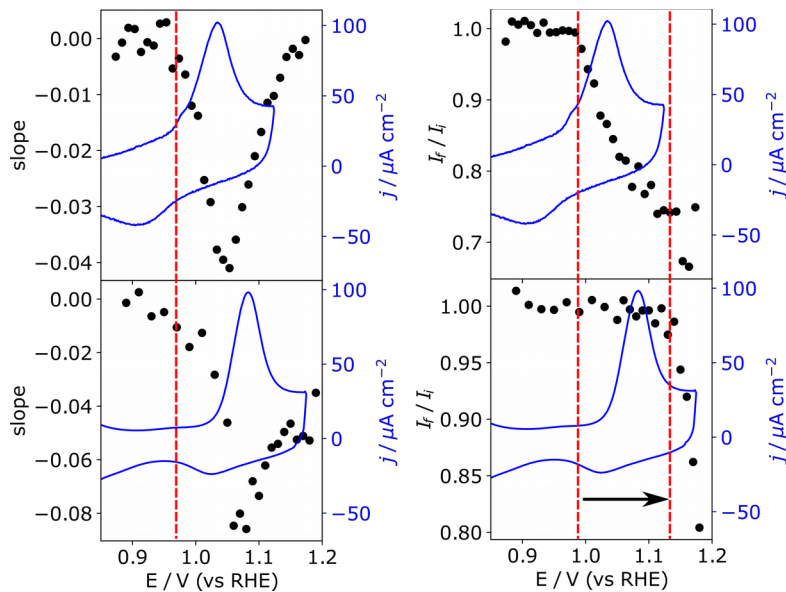


Fig. 3 Preliminary results of the potential steps analysis.

References:

- [1] J. Drnec et al, *Electrochimica Acta*, 224(2017),
- [2] M. Ruge et al, *J. Electrochem. Soc.*, 164(2017)