



## 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

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> 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.



<b>Experiment title:</b> <b>Dependence of Pt oxidation and oxygen-reduction reaction on surface-adsorbing species</b>		<b>Experiment number:</b> CH-5523
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 26/09/2018 to: 2/10/2018	<b>Date of report:</b> 20/02/2020
<b>Shifts:</b> 18	<b>Local contact(s):</b> R. Chattot, J. Drnec	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): *D.A. Harrington, University of Victoria *N. Stubb, University of Victoria *J. Drnec, ESRF *T. Fuchs, Universitaet zu Kiel Institut fuer Exp & Angewandte Physik O. Magnussen, Universitaet zu Kiel Institut fuer Exp & Angewandte Physik		

## Report:

In these experiments, we studied the differences of the initial stages of platinum oxidation using SXRD. A comparative study was undertaken on Pt(100) and Pt(111) surfaces in HClO<sub>4</sub> (a non-adsorbing electrolyte) and H<sub>2</sub>SO<sub>4</sub> (adsorbing). This was a continuation of earlier work on Pt(111) in HClO<sub>4</sub>[1-5]. For each of the two surfaces, we performed a series of cyclic voltammograms in both deaerated and oxygenated 0.1 M HClO<sub>4</sub> and 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolytes, while simultaneously measuring the intensity at an anti Bragg position.

Figure 1 shows CVs of **(B)** Pt(111) and **(C)** Pt(100) at 20 mV/s. Platinum oxide formation through place exchange, indicated by the intensity drop at the peak label O<sub>ads</sub>, is initially fully reversible on Pt(111), whereas for Pt(100) it always results in irreversible surface restructuring. We also conducted potential step experiments in the oxidation region of both surfaces, returning to a lower hold potential between each step, to probe the potential at which surface restructuring becomes irreversible for each surface.

Figure 2 shows the reversibility of the PE process, determined by potential step experiments, where the potential was changed for 20 s from a potential in the double layer range to a potential in the oxidation regime and then moved back to the lower potential. The relative changes in X-ray intensity indicate that irreversible platinum surface restructuring starts at higher potentials on Pt(111) than on Pt(100) by about 150 mV.

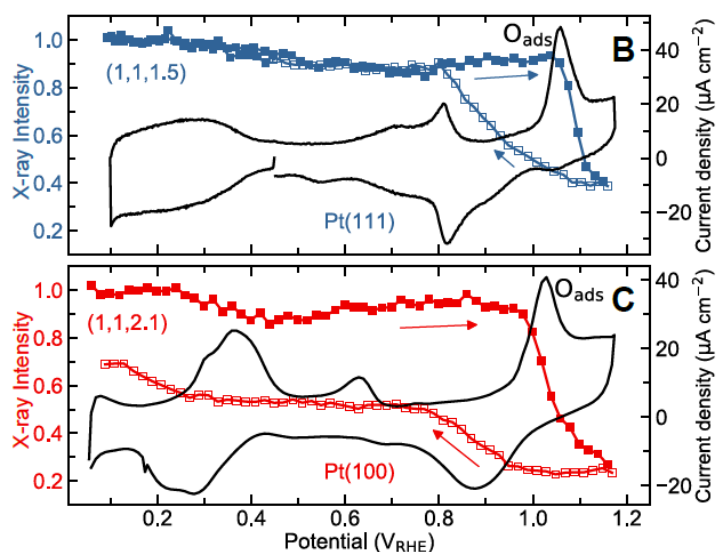


Figure 1. CVs of Pt(100) and Pt(111) overlaid with x-ray intensity to show the place exchange

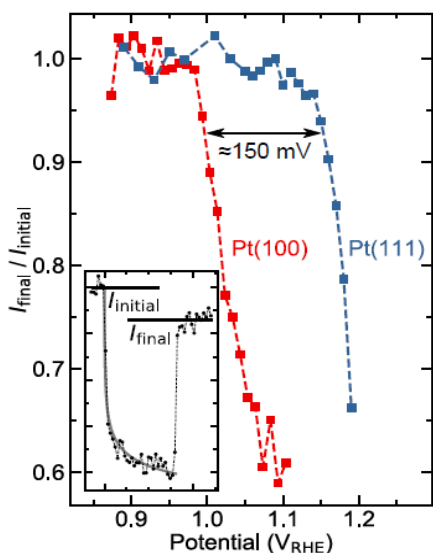


Figure 2. X-ray intensity for Pt(100) and Pt(111) at various potentials.

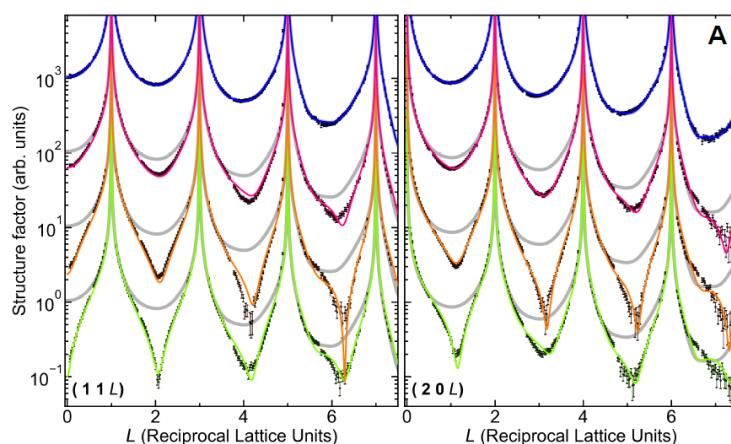


Figure 3. CTRs of Pt(100) at at 0.95 V, 1.07 V, 1.12 V and 1.17 V showing that at higher potentials, more surface atoms undergo “place

exchange” process. Analysis of the CTRs shows that the location of the oxidized Pt atoms on Pt(100) are very different from on Pt(111) and can no longer be considered a simple exchange of the Pt atom with an oxygen atom.

Figure 4 shows the dependence of coverage (determined from the CTR analysis) on potential for both surfaces. Not only are the atom locations very different on Pt(100) and Pt(111), the oxidation initiates much earlier in the Pt(100) case, which agrees with the reversibility differences presented in Figure 2. We collaborated with Federico Calle-Vallejo (University of Barcelona), who carried out DFT calculations. These correlated well with the x-ray and electrochemical data and gave a detailed understanding of the differences of the initial stages of oxidation on both surfaces at an atomic level, and explained the differences in their stability. For Pt(100) a second and third atom extraction becomes more energetically favorable after the first extraction, which can lead to formation of a stripe structure, which is a not energetically possible on Pt(111).

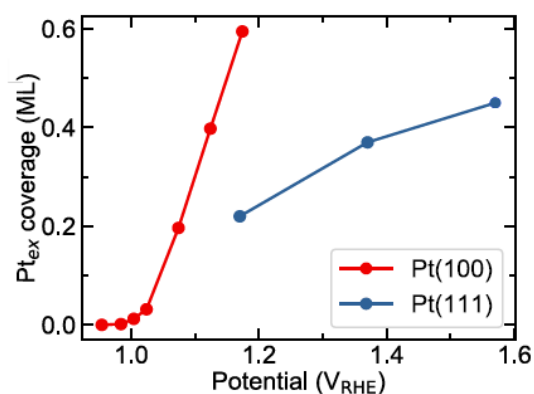


Figure 4. An illustration of how the coverage of place exchanged platinum atoms varies by potential and between the two surfaces.

The dissolution of Pt catalysts is a key reason for degradation of activity in hydrogen-oxygen fuel cells. We collaborated with Serhiy Cherevko and his group (IEK-11, Forschungszentrum Jülich), who carried out parallel dissolution measurements on the Pt(100) and Pt(111) surfaces, and we were able to explain the differences in dissolution with the using the differences in the oxidation behaviour on the two surfaces. A joint paper presenting the X-ray, DFT, and dissolution results is currently under review in *Nature Catalysis* [7].

The detailed differences between results in the two electrolytes with and without oxidation are under analysis and yet to be published. A publication is also under preparation on the detailed differences in the oxidation kinetics of Pt(100) and Pt(111) during potential step and sweep–hold experiments undertaken during this beamtime.

References:

- [1] J. Drnec, D.A. Harrington, O.M. Magnussen, *Current Opinion in Electrochemistry*, (2017),
- [2] J. Drnec et al, *Electrochim. Acta*, **224**, 220 (2017).
- [3] M. Ruge et al, *J. Am. Chem. Soc.*, **139**, 4532 (2017).
- [4] M. Ruge et al, *J. Electrochem. Soc.*, **164**, H608 (2017).
- [5] J. Drnec et al, *Electrochem. Comm.*, **84**, 50 (2017).
- [6] J. Gustafson et al., *Science* **343**, 758 (2014).
- [7] T. Fuchs et al, *Nature Catalysis*, under review.