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://wwws.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.

Report:

In this experiment detailed SXRD data and parallel single crystal voltammetry were obtained on Pt(111) electrodes in oxgen-free and oxygen-containing electrolyte. The CV measured in the *in-situ* cell (Figure 1) shows all the characteristic features of a clean, well-ordered surface.

The features below 0.4 V correspond to the underpotentially deposited H (H UPD) and the sharp "butterfly" peaks at 0.8 V are due to specific OH adsorption/desorption processes. In the positive-going scan, there is also an anodic peak around 1.06 V, traditionally associated with OH_{ads} to O_{ads} conversion and further OH adsorption. The corresponding reduction charge is spread out in potential and does not show as a sharp peak.

We first verified that there were no significant changes to the CV under X-ray irradiation levels used in our experiments (Figure 2). After, a large dataset of crystal truncation rods (CTRs) was then collected to enable us to make a definite model of the surface structure with significantly more detail than in previous studies. CTRs were collected in Ar-saturated 0.1 M $HClO_4$ in the double layer regime at 0.43 V and on the partially oxidized surface at 1.15 V (Figure 3).
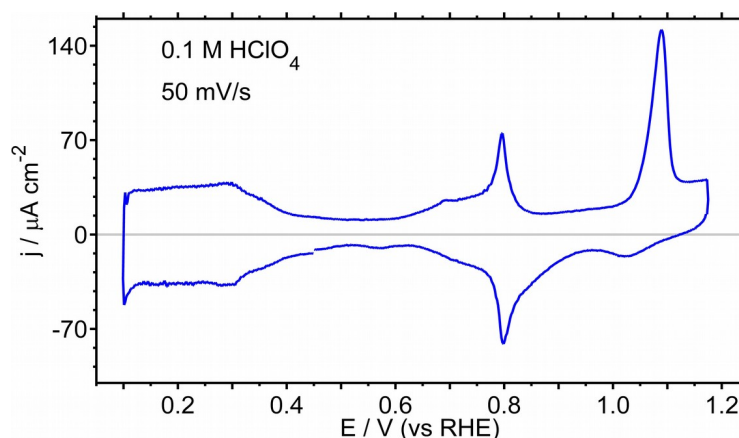

Figure 1: Cyclic voltammogram measured in the in-situ electrochemical cell in 0.1 M $HClO_4$ at 50 mV/s

Five independent CTRs were measured and used in the analysis. The models utilized to fit the data for each potential are depicted at the bottom of the same Figure. An unreconstructed surface model fits the data well at 0.43 V as expected. For the rod profiles measured at 1.15 V , the smallest χ^2 value was obtained with the place exchange model. The fit is very sensitive to the exact in-plane position of exchanged Pt atoms and for the best result the majority of exchanged atoms must be located directly above the original positions in the Pt(111) lattice. This finding further supports that the apparent surface roughness is caused by the site exchange exclusively. The surface has about 20 % of the surface sites already exchanged after the potential is held at 1.15 V .

Our model reveals that the intensity of the (1,1,1.5) reflection is a sensitive measure of the degree of place exchange but is insensitive to the structure of the double layer. Therefore, we measured this reflection during potential cycling and potential step experiments in Ar-saturated and O_2-saturated solutions, to clarify the effect of oxygen on the place exchange process (Figure 4).

During a CV in Ar-saturated $HClO_4$ the intensity shows a reversible increase in the H UPD region, due to the change of Pt surface interlayer spacing upon H adsorption. Upon OH adsorption in the "butterfly" region we also detect a slight intensity increase, followed by a sharp drop in intensity at
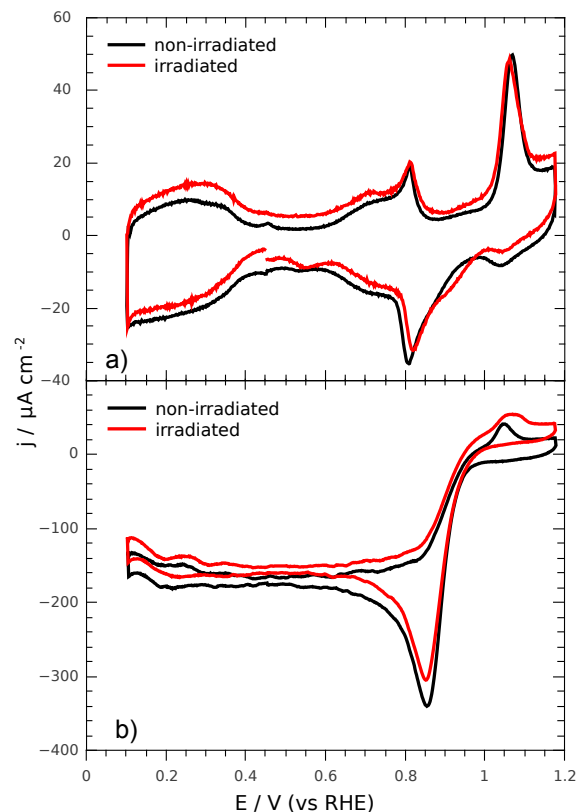

Figure 2: Radiated and non-irradiated cyclic voltammograms. Beam influence during the experiment in (a) Ar-saturated, (b) O_2-saturated electrolyte.

1.02 V , marking the onset of the place exchange process. In the negative-going sweep, the intensity slowly reverts back to the original values between 1.08 V and 0.78 V .

As in the static experiment, it is clear that the place exchange starts rather early at about 1.02 V, and is associated with the anodic peak around 1.06 V. The sudden structural change in (1,1,1.5) intensity is consistent with the sharp peak in the CV while the slower change on the reverse sweep is consistent with the spread out reduction charge. Although both the CV and the X-ray intensity curves exhibit significant hysteresis, the change is reversible over a cycle in the sense that the surface returns to its initial state, as evidenced by the return of the intensity to its initial value. In contrast to previous conclusions [1], we assign the hysteresis and quasi-reversible process to the place exchange with slow kinetics.

The same experiment was repeated in O_2-containing solution. The CV reproduces literature results. In the positive-going sweep, the reduction current drops between 0.80 V and 0.90 V and the oxidation peak around 1.06 V is clearly detected. Upon sweep reversal, there is a large reduction peak and then the current levels off to the diffusion-limited ORR current. The intensity of the (1,1,1.5) reflection follows very closely the behavior observed in the Ar-saturated electrolyte. The place exchange commences at exactly same potential of 1.02 V and similarly slowly reverts back to the original state between 1.08 V and 0.78 V . The lack of influence of O_2 on the place exchange contrasts some literature results [2].

During the positive-going sweep, the ORR current decreases at about 0.9 V on the ordered surface, well before the place exchange at 1.02 V. Therefore, the surface oxide or sub-surface oxygen cannot be responsible for the high ORR overpotential, which must be due to the mechanism of the ORR itself. On the reverse sweep the reverse place exchange process, resulting in a recovery of the smooth Pt surface, overlaps with the onset of the ORR. Here the influence of the place exchange is harder to establish, and exchanged species or sub-surface oxygen are likely present on the surface during the ORR.

Even though we do not observe any difference in the CV, it is possible that the kinetics of the place exchange differs when O_2 is present, and this could be responsible for the accelerated dissolution during potential cycling. To investigate this point, we stepped the potential to successively higher values and followed the intensity of the (1,1,1.5) reflection (Figure 5). For both Ar-saturated and O_2-saturated electrolytes, potential steps below 1.00 V show no significant intensity changes. As the potential is further increased to 1.05 V, the (1,1,1.5) intensity decreases as the place exchange occurs and then levels off. Further place exchange is induced by stepping to higher potentials, in this case 1.15 V. After reversal of the potential to 0.43 V, the intensity rapidly increases as the
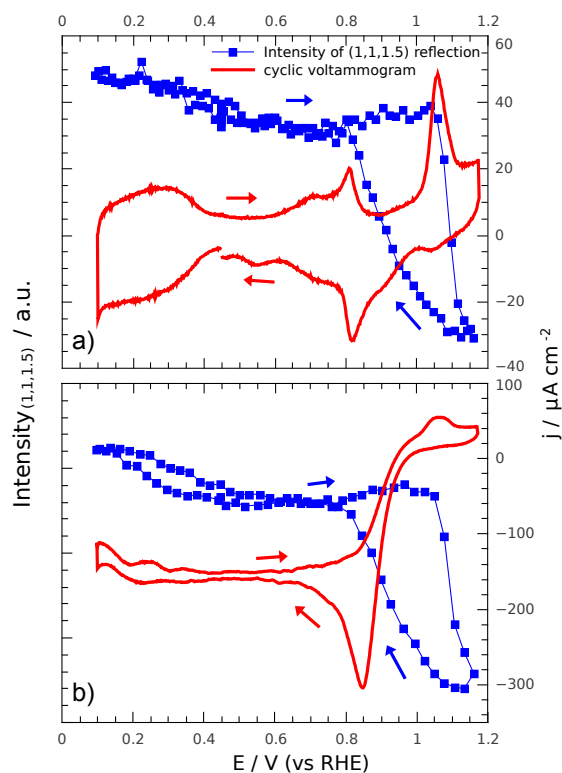

Figure 3: The SXRD measurement of five different crystal truncation rods, measured at (H,K) positions of (0,0), (1,0), (0,1), (1,1), (2,0), at 0.43 V (blue triangles) and 1.15 V (red squares). The fits, using the model depicted at the bottom of the figure, are shown as solid lines. Dashed and dotted lines are fits from the models with different in-plane position of exchanged atoms.

reconstruction is removed. However, its final value is less than the original value, indicating that the change is irreversible, consistent with the coverage of exchanged sites having exceeded the critical coverage.

For quantitative comparison, the intensities were converted to coverages of exchanged sites (θ_{ex}) and plotted as a function of the logarithm of time. The number of exchanged sites was determined from the structure factor of the (1,1,1.5) reflection and the model used to fit experimental curves in Figure 3. For each coverage, we calculated the rod profile and determined the relation between the θ_{ex} and the (1,1,1.5) structure factor. The linearity of θ_{ex} with ln(t) is consistent with the linear charge vs ln(t) plots previously attributed to place exchange kinetics [3]. Our results definitely rule out a significant influence of O_2 on the place exchange in $HClO_4$.

Figure 4: Cyclic voltammogram (red) and intensity of (1,1,1.5) reflection (blue) during cycling in (a) Ar-saturated, and (b) O_2-saturated 0.1 M $HClO_4$. Sweep rate 20 mV/s.
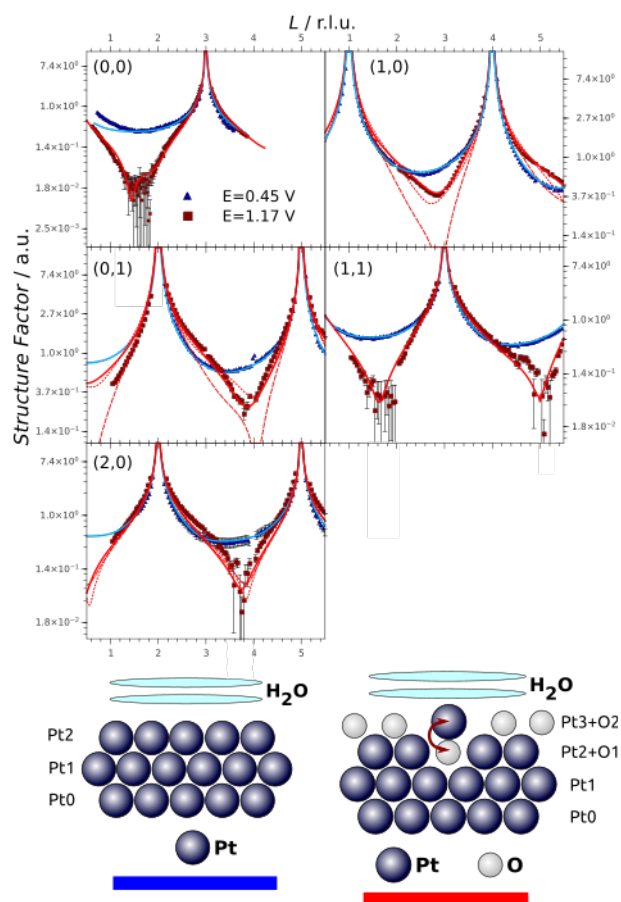
In conclusion, our *in-situ* SXRD studies provide detailed atomic scale data on the initial stages Pt(111) oxidation and are a significant step towards understanding structural behavior of Pt during ORR and the Pt degradation mechanism in fuel cells. Interestingly, the place exchange process commences at lower potentials than deduced from CV experiments, and is structurally fully reversible below a critical coverage of exchanged atoms. The inhibition of the ORR occurs before the place exchange, which is therefore not the limiting factor in the ORR. The presence of O_2 in the 0.1 M $HClO_4$ electrolyte has no detectable effect on the onset potential of the place exchange or on the kinetics of the process, contradicting some earlier suggestions. Further *in-situ* exploration of the oxidation behavior of different Pt single crystal faces in different electrochemical conditions is essential in order to better understand the role of surface structure on the oxidation behavior. In particular, such studies will be crucial for fully understanding the stability of Pt nanoparticles under ORR conditions and thus providing a link between the oxidation and dissolution that limits catalyst lifetime in fuel cell operation.

This work has been submitted to publication [4-6].

Figure 5: Potential step experiments in Ar- and O_2-saturated 0.1 M $HClO_4$. (a) (1,1,1.5) intensities vs time, (b) Corresponding coverage of exchanged sites obtained from the model vs ln(t).

References:
[1] A. M. Gómez-Marín, J. M. Feliu, *Electrochim. Acta*, **2012** , 82 , 558-569
[2] A. Kongkanand, J. M. Ziegelbauer, *J. Phys. Chem. C*, **2012** , 116 , 3684-3693.
[3] B. E. Conway, G. Jerkiewicz, *J. Electroanal. Chem.*, **1992** , 339 , 123-146.
[4] J. Drnec et al, *submitted*
[5] J. Drnec et al., *in preparation*
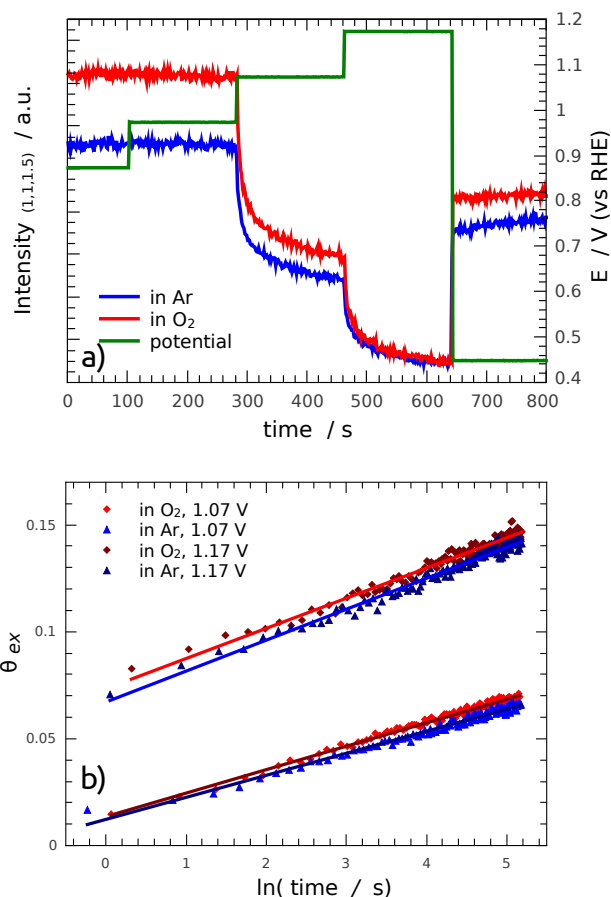[6] M. Ruge et al., *in preparation*