

## 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.



	<b>Experiment title:</b> An in-situ FEXRAV investigation of the electrochemical oxidation of nanostructured palladium	<b>Experiment number:</b> 08-01-996
<b>Beamline:</b>	<b>Date of experiment:</b> from: 23/06/2015 to: 30/06/2015	<b>Date of report:</b> 31/07/2015
<b>Shifts:</b> 18	<b>Local contact(s):</b> Alessandro Puri	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> * LAVACCHI Alessandro - CNR/ICCOM (Italy) - <a href="mailto:alessandro.lavacchi@iccom.cnr.it">alessandro.lavacchi@iccom.cnr.it</a> * DI BENEDETTO Francesco - Dip. Scienze della Terra Univ. Firenze (Italy) ZAFFERONI Claudio, INNOCENTI Massimo, * GIACCHERINI Andrea - Dip. Chimica – Univ. Firenze (Italy) * MONTEGROSSI Giordano - CNR/IGG (Italy)		

## Report:

### Introduction and aims

The aim of the experiment was the study of the electrochemical oxidation of nanostructured Pd catalysts by Fixed Energy Ray Absorption Voltammetry (FEXRAV). FEXRAV provides fundamental information on the valence states and the coordination environment of Pd as a result of the application of an external applied voltage, during cyclic voltammetry experiments. This is essential to understand the behaviour of palladium catalysts for the exploitation of biomass in electrochemical energy conversion and storage. These palladium-based electrodes are particularly promising for alkaline Direct Alcohol Fuel Cells (DAFCs) and for the hydrogen production by electrochemical reforming.

### Experimental set up and optimisation of the methods

The whole assigned beamtime was approximately divided by two between *ex situ* XAS measurements, operated according the conventional procedures suggested by the beamline scientists, and in situ FEXRAV and Fixed Potential XAS measurements (FPXAS), all operated with the use of a specifically designed electrochemical cell, adapted and tested (see the report of the MA2051 experiment) on the BM08 Beamline. We have realized the cell to allow the FEXRAV detecting simultaneously Fluorescence and Transmission. The signal has resulted ideal to track the evolution of the Pd samples through, during cyclic voltammetry experiments. The FPXAS measurements are operated in the same set up, simply combining a chronoamperometric control (potential is fixed and a time dependant current is recorded) by the potentiostat, and simultaneously registering the XAS spectrum.

For this experiment, a novel arm for coupling the electrochemical cell to the Vpos1 motor of the 1<sup>st</sup> analytical chamber of the beamline was designed, provided and tested. This allows an easier control of the cell during its alignment under the X-ray beam. The electrochemical *in situ* operations were controlled by a PARSTAT 2273 Potentiostat (Princeton Applied Research), provided by the team, and installed into the beamline. The

Parstat was coupled to the Wago connector installed in the beamline, while remote control was operated through VNC connection.

During the set-up of the *in situ* instrumentation, some problems occurred in realising the VNC remote control, problems that were not completely solved during the whole experiment. Taking into account the simultaneous occurrence of an important failure of the ring (about 4 hours), about three shifts were necessary to be operative in the *in situ* operation mode.

### Analysed samples

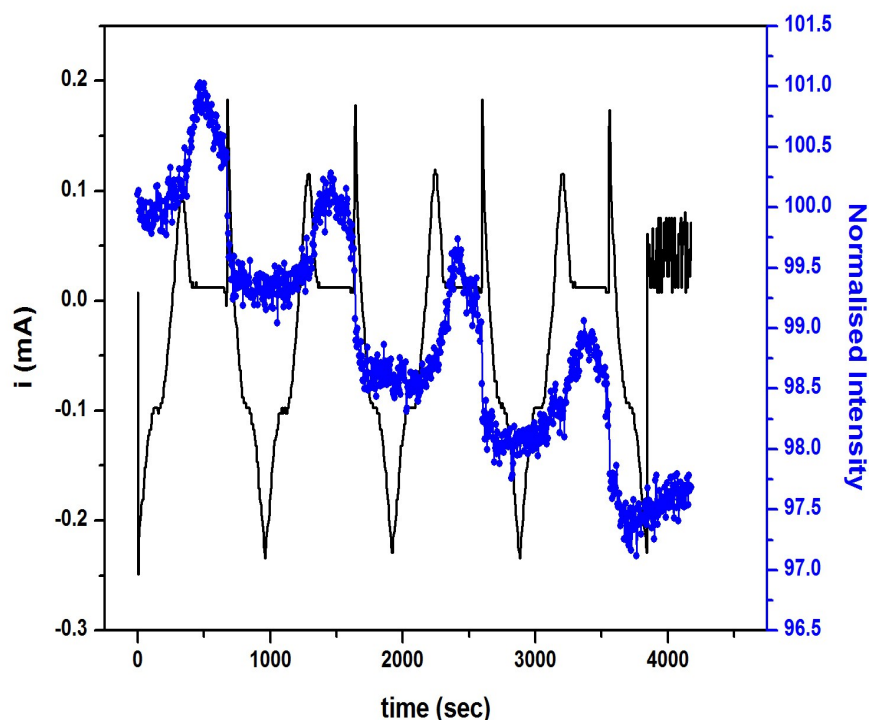
During the *ex situ* measurements, five catalyst classes were investigated (all of them in the Fluorescence mode): i) Pd nanoparticles on carbon (pure and doped with CeO<sub>2</sub>), ii) Pd-Co alloy thin films, iii) Pd nanoparticles dispersed in polymer, iv) Pd coatings on carbon paper and on carbon cloth. On the whole, more than 15 samples were investigated.

During the *in situ* measurements, FEXRAV measurements were operated with bare alkaline electrolytes (KOH) and electrolytes containing alcohols (EtOH). FEXRAV measurements were always operated at two different energy values, to monitor the evolution of the edge position and of one of the XANES features. Moreover, FPXAS measurements were operated at, at least, 4 different applied voltages, to verify the details and the evolution of the EXAFS and XANES features during the chronoamperometric measurements.

Finally, preliminary measurements on formate oxidation were carried out.

### Preliminary results

In the Figure 2, an exemplar FEXRAV is shown. The Figure clearly reveal the good quality of the data. Following the trend of the current in the cell, one can easily identify the onset of the Pd oxidation immediately after the end of the oxidation of the electrolyte (i.e. ethanol).



**Figure 2** – FEXRAV (in blue) and current (in black) data versus time, registered during a four-cycle voltammetry measurement. Voltage varied between -1 and 0.2 V vs. sat. Ag/AgCl. The electrolyte consisted of KOH and EtOH 2M.

The second relevant feature is that the pathways for the oxidative and reductive processes involving Pd are not identical. From the difference in intensity of the plateaux relative to the reduced state (Pd<sup>0</sup>), e.g. at 1000 seconds, and to the oxidized state (Pd<sup>II</sup>), e.g. at 1500 seconds, one can esteem the total amount of Pd involved in the process, with respect to the bulk amount. There is a third relevant feature: at every cycle the overall

intensity of the FEXRAV signal decreases by a constant amount (about 1 %). This effect was checked by verifying eventual drifts of the total intensity of I0 or I1, where a reference Pd foil was monitored, and by repeating the same FEXRAV measurement by leaving the cell in an open circuit configuration. Apparently, no effects due to the beamline set up were observed, and this decrease is tentatively attributed to the loss of catalyst. This fact has been attributed to the anodic stress of the catalyst. This fact only affects the intensity of the XAS signal, but has a negligible effect on the electrochemical activity. Hence we conclude that such phenomenon has no negative implication on the quality of the acquired data. At the time of the submission of the report a paper including the data acquired in the experiment is in preparation.

### **Conclusion and perspectives**

The results of the present experiment can be considered as very successful, both on the procedural and of the scientific point of views, and FEXRAV, as expected, could be implemented as an high powerful method to characterise *operando* the catalysers. Moreover, the electrochemical cell allows to extend the technique to several elements in the field of the hard X-rays ( $E > 20$  KeV). Future planned activities will include the following aspects: i) design and realization of a complete fuel cell for monitoring the fixed energy XAS signal in the course of the acquisition of a power density curve and ii) the design of an experimental set up to operate at intermediate energy values ( $10 < E < 20$  KeV).