EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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

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 form 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.

ESRF	**Experiment title:** In-situ electrochemical REFLEXAFS of Palladium Electrocatalysts for Electrochemical Energy Conversion and Storage	**Experiment number**: MA-3173
Beamline: BM-08	**Date of experiment**: from: 02/11/2016 to: 08/11/2016	**Date of report**: 02/02/2020
Shifts: 18	**Local contact(s)**: Giovanni Orazio Lepore	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

***Alessandro Lavacchi** (CNR-ICCOM, Italian National Research Council, Institute for the chemistry of OrganoMetallic Compounds)

***Andrea Giaccherini, *Enrico Berretti**, (University of Florence – Chemistry Department)

***Francesco di Benedetto** (University of Florence, Earth Sciences department)

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Report:

In the experiment we have tested a new cell for the in-situ Grazing Incidence X-ray Absorption Spectroscopy (GI-XAS) of Pd ultrathin films. Fig. 1 describes the cell in detail. The basic concept is that at grazing incidence the spot of the beam on the sample is spread over a few cm in length. Considering the energy of the Pd Kα edge, a significant part of the spot is effective in producing the XAS signal. To achive the required flatness the samples were obtained onto glass microscopy slides. The slides where coated with a thin (100-150 nm) gold layer subsequently annealed to a chieve a iso-oriented polycristalline Au (111) surface. We pursued the controlled deposition of Pd by Cu underpotential deposition followed by displacement with $PdCl_2$ electrolytes. This allowed us to get coverage from 0.66 ML up to 10 ML.

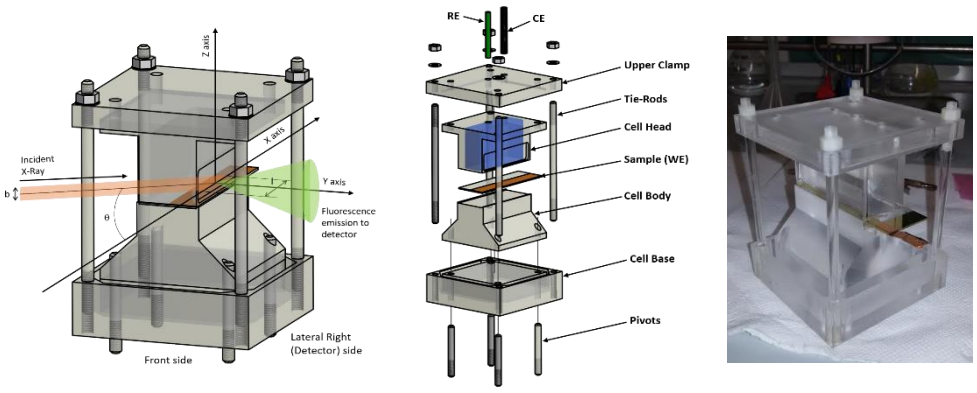

Figure 1: 3D rendering of the electrochemical GI-XAS cell: a) assembled view and b) exploded view. The cell assembled and ready to fit the the GI-XAS cradle of the XAS measurment chamber at BM08.

In the first part of the experiment we perdformed ex-situ experiments, expoiting the possibility of the cell to work in this configuration. Figure 2 a shows the spectrum of a bulk palladium foil and a corresponding Pd oxide acquired during the experiment. Figure 2b report the XAS acquisition performed on Pd layer corresponding to 0.66 ML. In this, we recognize all the features of Pd, showing the effectiveness of the set-up, especially due to the flatness of the electrode and the cell and the accurate control on Pd deposition.

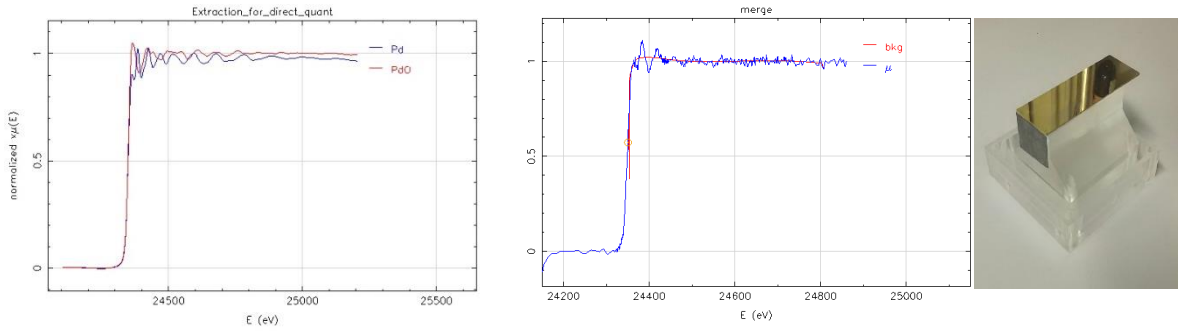

Figure 2: Ex-situ XAS of a Pd foil at the Pd Kα line (a); ex-situ XAS of a 0.66 ML film of Pd on iso-oriented polycristallyne on Au(111) (b); c) the cell described in fig.1 in the configuration for ex-situ measurments (c).

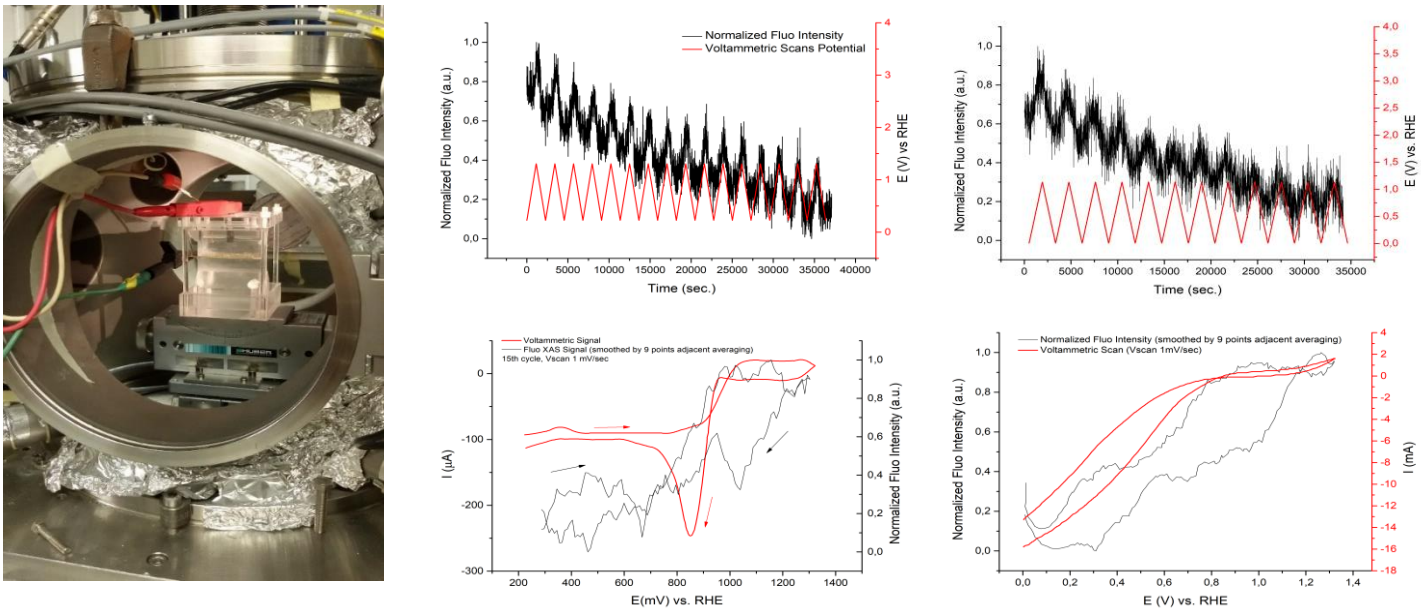

Figure 3: [Left] The Cell assembly inside the exp. Chamber, [center] FEXRAV spectrum (top) and voltammetric scan (bottom) of 10 ML of Pd on poly isooriented Au (111) in 2M KOH, [Right] FEXRAV spectrum (top) and voltammetric scan (bottom) of a Pd/C catalysts in 2 M KOH

In the last part of the experiment we have tested the cell for the acquisition of Fixed Energy X-ray Absorpion Voltammetry. Figure 3 (left) report the cell assembled for Grazing Incidence FEXRAV experiments inside the measurment chamber of BM08. Figure 3 (center & right) shows a comparison between FEXRAV cycles performed using a Pd nanoparticle paste as working electrode (right, results from EXP MA-2936) and 10 monoloayers of palladium deposited on policrystalline isooriented Au (center). The FEXRAV pattern in the GI-XAS is much more resolved than in the FEXRAV experiments performed on conventional nanoparticles Pd catalysts; even the quality of the electrochemical data is much better in the grazing incidence set-up as this mallow a significant reduction of the catalyst surface area. Is worth mentioning that this are high quality data and that if completed with measurements performed in electrolytes that simulate fuel cell fuels (e.g. KOH + ethanol) will lead to high impact dissemination. For this reason we plan to apply for beamtime to extend the dataset to Pd ultrathin film of various thickness in electrolytes conaing renewable fuels for direct ethanol fuel cells.