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:** Structural effects on reactivity and deactivation of Pd (111) and Pd monolayer deposited on Au (111) toward the electrochemical oxidation of alcohols	**Experiment number**: MA-3338
Beamline: ID-03	**Date of experiment**: from: 26/04/2017 to: 02/05/2017	**Date of report**:
Shifts: 18	**Local contact(s)**: Raja Znaiguja **(ID-03)**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

***Enrico Berretti, *Francesca Russo,** Massimo Innocenti (University of Florence – Chemistry Department)

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

Report:

Aim:

The final aim of this experiment was the determination of the structural changes of palladium during electrochemical stimulus in the half cell of a direct alcaline ethanol fuel cell. It is in fact well known that palladium incurs into deactivation processes during alkaline fuel cells duty cycles. Previous experiments (MA-3173, as an example) performed on BM-08 enabled us to live follow changes into the speciation of palladium during duty cycles, but no previous study on structural modifications on these catalytical surfaces was previously been performed.

Experiment frame:

The experiment was conducted by depositing various thicknesses of Palladium on an Au (111) monocrystal working electrode, using the beamline electrochemical flow cell. This flow cell avoids the contamination of the studied surface, and can be mounted directly in the EXP hutch sample holder, enabling operando SXRD experiments. For each deposited Pd film, a series of maps, l-scans, crystal Truncation Rods profiles and XRR scans were acquired, in order to detect changes along characteristic directions. Sample characterization was performed in three steps for each Pd deposit:

1) Prior to the Pd deposition (bare surface characterization)
2) After Pd deposition (pristine palladium surface)
3) After voltammetric stress cycles in NaOH + EtOH

Experimental Set-up:

The experiment was performed in the hutch EH1 of the ID03 beamline, using the six circle diffractometer equipped with the ID03 electrochemical flow cell setup, already used in previous experiments MA-2082, MA-2251, MA-2636 and MA-3071. The experimental set up included the Maxipix detector mounted on the diffractometer arm and a Pilatus 300k-w detector used for fast acquisition of in-plane powder diffraction pattern

(covering a 2θ range between 10 and 20 with one single images at the energy of 24 KeV) and the XIA detector (for XRF) from the instrument pool.

Samples:

The first sample, constituted by a monolayer of Pd on Au (111) surface, was prepared using the underpotential deposition (UPD) of copper on gold, and Cu substitution by Surface Limited Redox Replacement (SLRR), as visible in Figure 1. The other palladium thicknesses were obtained by timed potentiostatic deposition from a Pd solution

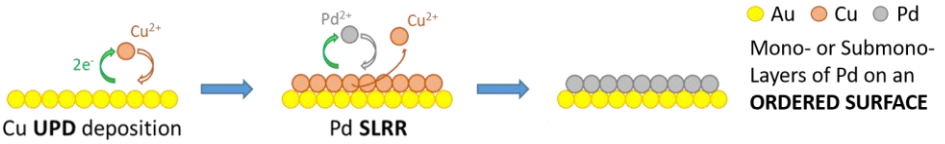

Figure 1 –The Cu UPD and Pd SLLR used to obtain 1 monolayer of Pd on Au (111)

Results:

XRR data analisys showed a Pd film roughness comparable to its thickness. On the other hand, we were able do notice, as a conseguence of the oxidative stress cycles, an enlargement of the Pd peaks, together with a shift of their position toward the gold ones. We were also able to detect an increase of the surface electrochemical activity (figure 2) after the oxidative cycles.

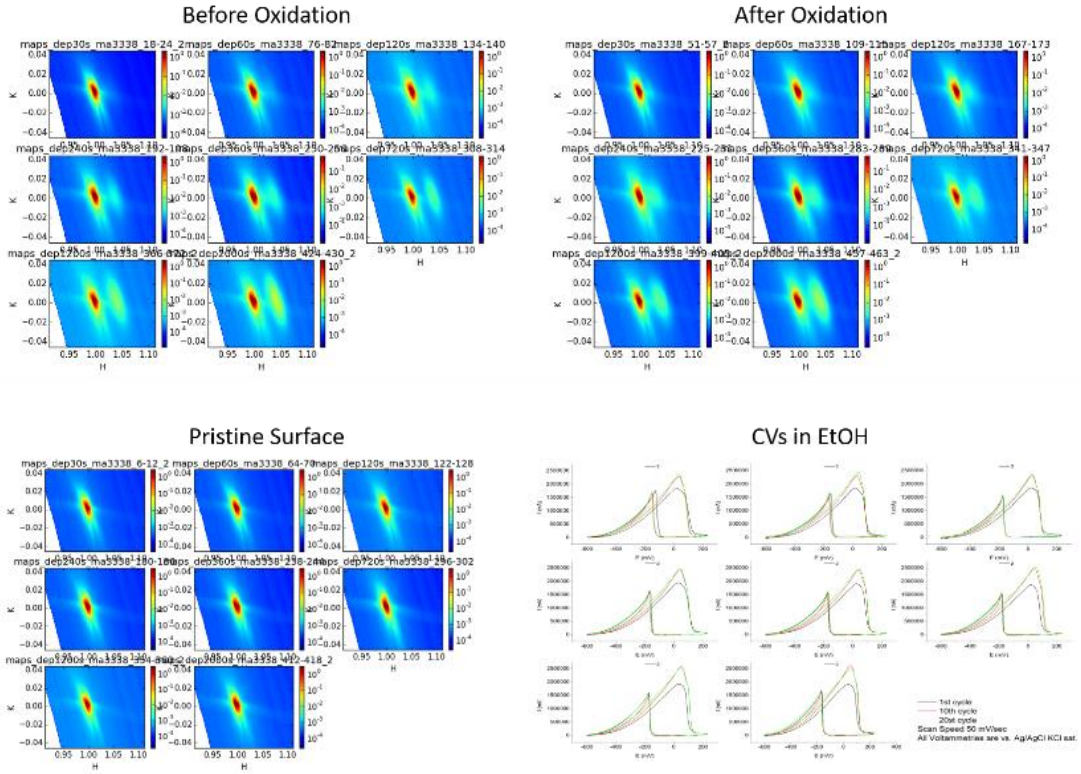

Figure 2 – HK maps of different thicknesses of Pd before (top left) and after (top right) oxidative cycles, Bare surface (Bottom left) and voltammetric scans