



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

- 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.



	Experiment title: In situ operando Fixed Energy X-ray Absorption of Pt-free direct liquid fuel cells	Experiment number: MA-3431
Beamline: BM-08	Date of experiment: from: 28/06/2017 to: 03/07/2017	Date of report: 01/02/2020
Shifts: 12	Local contact(s): Giovanni Orazio Lepore (BM-08)	<i>Received at ESRF:</i>

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**, Massimo Innocenti (University of Florence – Chemistry Department)

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

***Giordano Montegrossi** (CNR-IGG, Italian National Research Council, Institute of geosciences and earth resources)

Report:

Aim:

The proposal was focused on the acquisition of a complete set of data regarding Pd deactivation during direct alcohol fuel cell cycling. The beamtime permitted us to study this phenomenon using the Fixed Energy X-Ray Absorption Voltammetry, both in an half fuel cell and in a full fuel cell setup.

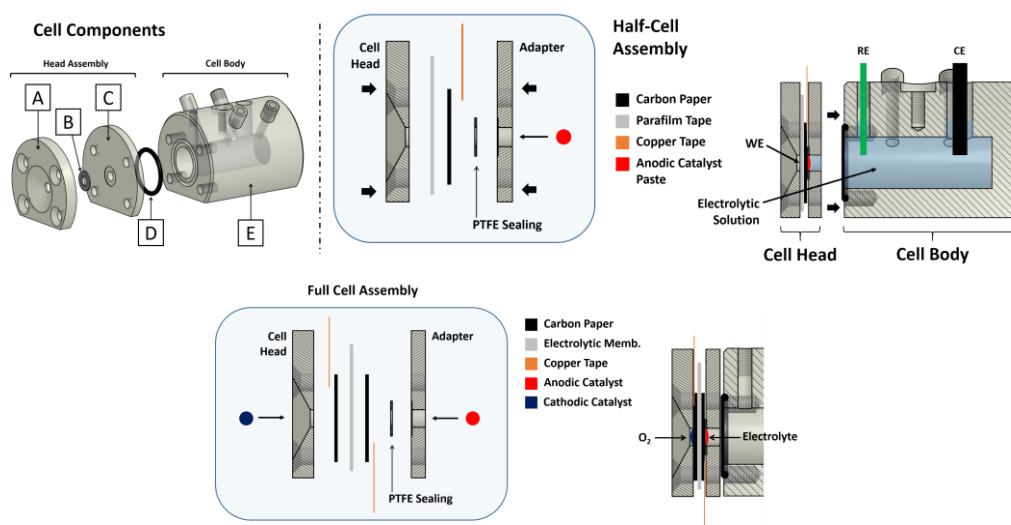


Figure 1 – The modified electrochemical cell, explaining the differences between Half-Cell set-up (top-right) and the Full-Cell set-up (bottom row)

Experimental Set-Up:

Experiments were performed in the Exp Hutch 2 of the BM-08, using the same experimental set-up of previous experiments (MA-2936). The Electrochemical cell was upgraded in respect to the previous

experiments enabling an easier switch between half-cell and full-cell configuration (as visible in figure 1), and an higher signal to noise ratio.

Samples:

Experiments were performed using Pd and Pd/CeO₂ inks as working electrodes, and NaOH and NaOH + EtOH solutions as electrolytes, simulating the alkaline solution and alkaline solution + fuel modes.

Results:

The new set of data acquired highlighted a difference between FEXRAV cycles performed in electrolyte and electrolyte + fuel (Figure 2), permitting to acquire a better understanding on the role of ethanol in the palladium oxidation.

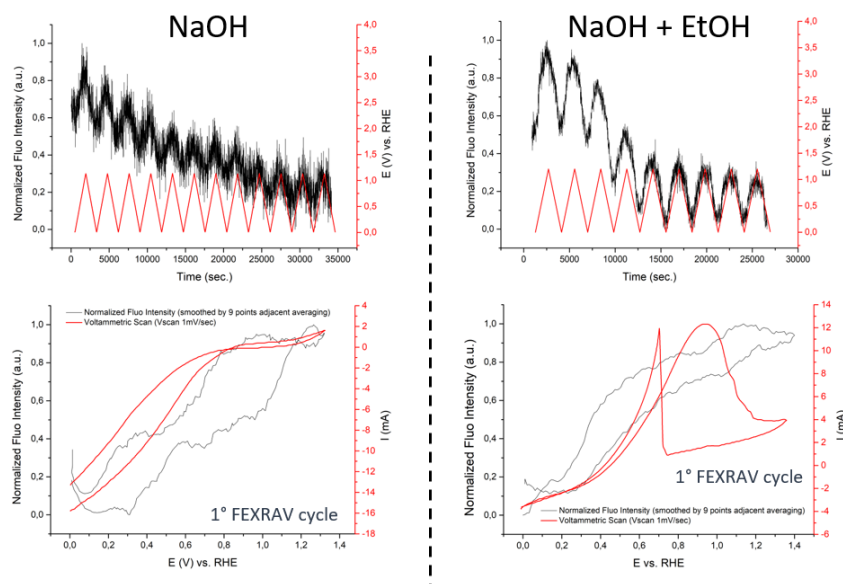


Figure 2 – An example of the Potential/Fluorescence signal vs. time graph (top row) for a Pd catalyst used in alkaline electrolyte (left column) and alkaline electrolyte + fuel (right column)

The set of measures obtained at the end of this experiment enabled the publication of two articles on the fundamentals of palladium electrooxidation in alkaline media (half-cell set-up):

- 1) G. Montegrossi, A. Giaccherini, E. Berretti, F. Di Benedetto, M. Innocenti, F. D’Acapito, A. Lavacchi, Computational speciation models: A tool for the interpretation of spectroelectrochemistry for catalytic layers under operative conditions, *J. Electrochem. Soc.* 164 (2017) 3690–3695. doi:10.1149/2.0711711jes.
- 2) E. Berretti, A. Giaccherini, G. Montegrossi, F. D’Acapito, F. Di Benedetto, C. Zafferoni, A. Puri, G.O. Lepore, Miller, Giurlani, Innocenti, Vizza, Lavacchi, In-situ Quantification of Nanoparticles Oxidation: A Fixed Energy X-ray Absorption Approach, *Catalysts*. 9 (2019) 659. doi:10.3390/catal9080659.

Also, another article on the behaviour of palladium during full fuel cell duty cycles is under completion.