ESRF	**Experiment title:** In situ operando X-ray Absorption investigation of Palladium anodes in direct liquid fuel cells	**Experiment number**: MA-2936
Beamline: BM08	**Date of experiment**: from: 29/06/2016 to: 05/07/2016	**Date of report**: 31/07/2016
Shifts: 18	**Local contact(s)**: Francesco d'Acapito	*Received at ESRF:*

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Report

Introduction

In two previous experiments we have set up and tested a new electrochemical cell for the in situ operando investigation of electro catalysts with Fixed Energy X-Ray Absorption Voltammetry (FEXRAV). This has unravelled fundamental aspects of Palladium electrochemical oxidation in a electrochemical half-cell set up. Such conditions are not completely representative of the fuel cell environment, where many factors, that cannot be included in fundamental electrochemical measurements, can concur to catalyst deactivation. To do so we have realized a new fuel cell set up for in situ operando X-ray Absorption Spectroscopy. Additional aim was the demonstration the effectiveness of fixed energy X-ray absorption as a technique to probe fuel cell catalysts in "real world" devices. Specifically designed fuel cells, adapted and tested at the BM08 beamline, will allow simultaneous Fluorescence and Transmission measurements.

Samples

Four kind of samples were analysed during this experiment. They are listed below. The Table also lists the differences in the experimental setup necessary to obtain the spectral information required.

sample	preparation	XAS mode	measurement	Details
Pd/C nps	pellets	Fluorescence	Ex situ	-
Pd/C thin films	As they are / Electrochemically aged	Fluorescence	Ex situ	-
Pd/C Half cell	Ink of nps +KOH (+EtOH)	Fluorescence /Transmission	In situ, operando	Electrochemical cell operated by a remotely controlled potentiostat; FEXRAV and chronoamperometric measurements performed
Pd/C Fuel cell	Ink of nps +KOH +EtOH	Fluorescence /Transmission	In situ, operando	Electrochemical cell operated by a remotely controlled potentiostat; FEXRAV, potentiostaic and galvanostatic measurements performed

Experimental details

The difference in the set up necessary to establish optimal X-ray Absorption Spectroscopy conditions for the different samples has required a relevant amount of time and many efforts dedicated to the sample and beamline preparation. In particular, conventional preparation of nanoparticles (nps) pellets and thin films was operated in the preparation laboratory at BM08, whereas electrochemical cell was assembled in the half cell and fuel cell mode in the Electrochemical Laboratory at ESRF. In the same laboratory, all the preliminary electrochemical tests were performed, as well as the ageing of the catalyzer thin films.

The experimental set up on the beamline has required a specific optimisation through a trial-and-error procedure. The basic approach included the implementation of the remote control of the potentiostat in the command set of SPEC. After numerous attempts, we found an optimal configuration having the XAS motors and counters and the potentiostat motors and counters controlled by two different SPEC sessions. Accordingly, FEXRAV is performed by starting a voltammetry on the potentiostat session, while X-ray Fluorescence counts are registered on the primary SPEC session (trhough a timescan acquisition). The two files are then calibrated in time by the use of the epoch counter.

Concerning the difference between the investigations in the half cell or fuel cell modalities, they were realised using the same electrochemical cell, already used in previous experiments, and opportunely changing the working and counter electrodes. The catalyzer was used as a form of ink supported by carbon cloth foils.

Preliminary results

- *Evaluation of the peak to noise ratio for FEXRAV spectra of Pd (half cell set up).*

A first part of the operando beam time was dedicated to establish from an experimental point of view the uncertainty of the oxidation state determination through FEXRAV for Pd electrochemical experiments. The results can be summarised as follows: 15% under the adopted conditions.

- *Determination of the FEXRAV spectra for a controlled amount of catalyst (half cell set up).*

This specific activity was devoted to ascertain under which experimental conditions the requirements of accuracy and reproducibility of the FEXRAV measurements meet the optimal electrochemical set up (in terms of catalyser amount) to achieve a significant voltammetric scan. As an example, the FEXRAV of 20 μg of Pd is shown in the **Figure 1a**. Combined with the previous point, this activity enables FEXRAV as a quantitative tool for the investigation of the redox changes during Pd heterogeneous catalysis.

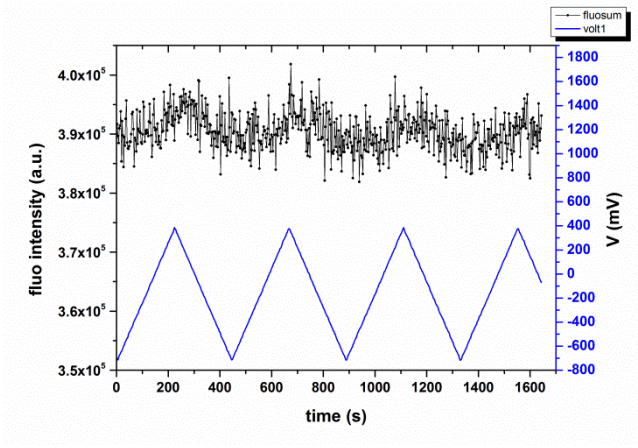
- *First experimental operando FEXRAV characterisation of a fuel cell (fuel cell set up)*

The main achievement of the present experiment is the first FEXRAV monitoring of a operating fuel cell under the potentiodynamic control. To do this, a specific set up of the fuel cell was designed, allowing to maintain good performances of the cell itself, while minimising any kind of disturb to the acquisition of the X-ray Fluorescence signal. To do so, our cell didn't make use of the metallic current collector that are in use in conventional fuel cell devices. Our experimental design allowed a very small size of the active electrode area (ca. 0.5 cm^2). According to this, we have been able to operate the cell with low total current while keeping high current density. This limits the ohmic drop due to the large (as compared to metals) resistance of the carbon paper support of the catalysts. This has also allowed the use of the potentistat hardware implemented at ESRF that, for the moment, doesn't allow operation at current exceeding 100 mA. In the **Figure 1b**, the FEXRAV of a cell let operate through 12 voltammetric cycles is proposed. Interestingly, the process seems to shifts from the initial conditions towards a stationary operating mode, and from this state the process recovers its initial conditions after having interrupted the voltammetric cycles.

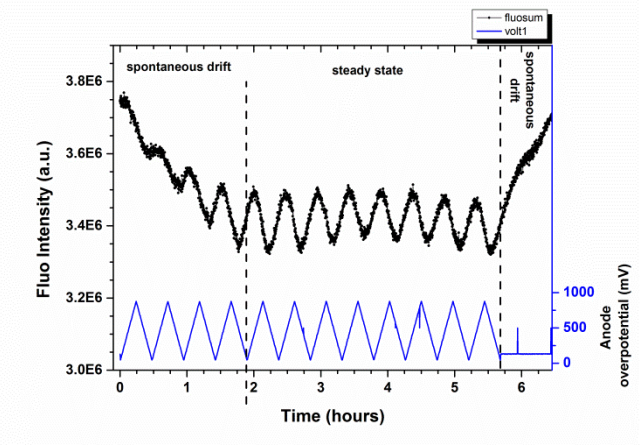
- *Preliminary EXAFS characterisation of thin films (ex situ set up)*

This task was aimed at ascertaining if the interesting results obtained on nps inks could be reproduced also on thin films of catalyzer. For this reason, two different kind of targets were prepared: Pd sputtered over soda lime glass and Pd sputtered over Ta-coated soda lime glass. In both cases, different thicknesses of the Pd thin film were achieved, down to 2.5 nm. Some of the investigated targets were also electrochemically aged in the EC lab, to observe the detectability of the XANES features through ex situ redox cycling (**Fig. 1c**).

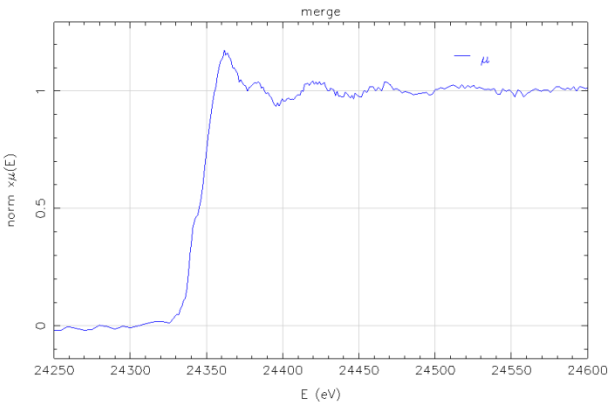
Figure 1


fluosum
volt1
fluo intensity (a.u.)
V (mV)
time (s)

a


fluosum
volt1
spontaneous drift
steady state
spontaneous drift
Fluo Intensity (a.u.)
Anode overpotential (mV)
Time (hours)

b


merge
μ
norm xμ(E)
E (eV)

c