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:** **Mapping PEMFC Catalyst Surface Distortion Operando with XRD-CT Algebraic Reconstruction**	**Experiment number**: CH-5697
Beamline: ID31	**Date of experiment**: from: 28 October 2020 to: 06 November 2020	**Date of report**: 21/02/2022
Shifts: 18	**Local contact(s)**: Jakub Drnec, Marta Mirolo	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Raphaël Chattot*

Frédéric Maillard*

Jakub Drnec*

Isaac Martens*

Report:

We would like to first apologize for the consequent delay regarding the submission of this experimental report. The experiment was in itself quite challenging, and consequent time in data analysis was needed to conclude on the outcome of the experiment.

Different membrane-electrode assemblies (MEAs), each containing one of the catalyst of interest synthetised by LEPMI, were manufactured by SYMBIO (Figure 1):

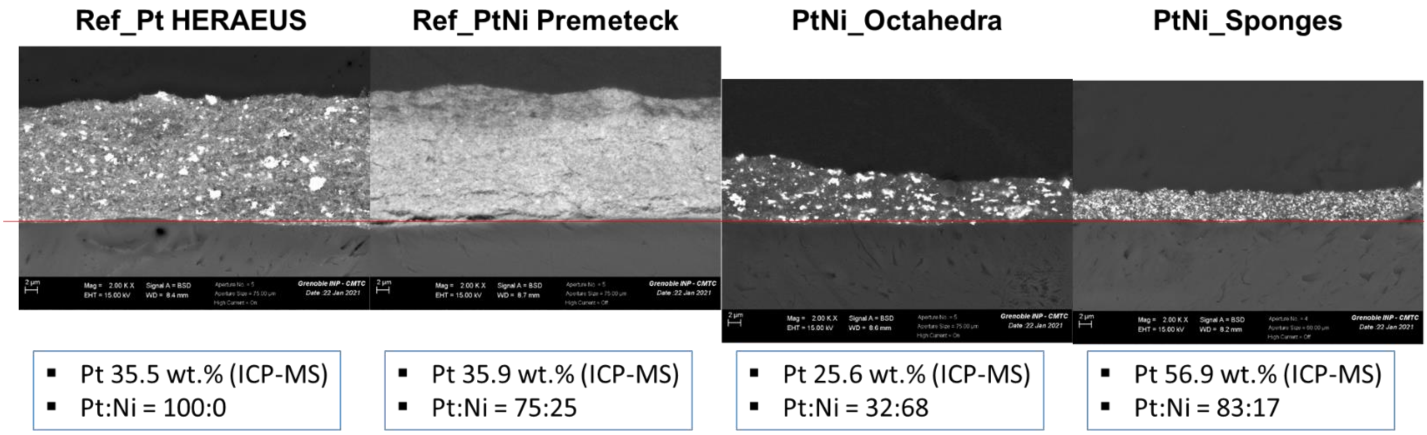

Figure 1: Scaning electron microscope (SEM) images of the different MEA cathodes investigated during this experiment, with associated chemical composition obtained from ICP-MS.

Each one of the sample were investigated according to the following protocol (Figure 2). The structure of the cathode materials were investigated with XRD at each one of the mentionned step.

Operando

Beginning of Life:
- Cell conditioning
- Polarization curve
- Cyclic voltammetry

Accelerated Stress Test
- 10,000 square-wave potential cycles
  3 s @ 0.60 V – 3 s @ 1.00 V

End of Life:
- Cyclic voltammetry
- Polarization curve

In situ

Beginning of Life:
- XRD-CT

End of Life:
- XRD-CT

Ex situ

Beginning of Life:
- Powder XRD
- Piece of fresh MEA

End of Life:
- Powder XRD

Figure 2: Experimental protocol followed for the evaluation of the catalysts structure along different key steps of its life.

The purpose of the experiment was to measure accurately the microstrain content within each sample materials and its evolution during fuel cell operation. As detailed in a previous recent strudy from our consortium (10.1021/acsenergylett.1c00718), the challenge when measuring 'real' MEA operando, is the parallax-induced broadening of the XRD peaks due to the large dimensions of the sample. Especially, parallax and microstrain boradening have a very similar evolution with scatering angle (~tan(theta)), which make their disantangling very difficult, if not impossible. For example, as shown in Figure 3, using the 'classical' data refinement approaches such as the Rietveld method, the microstrain values measured operando (black line, with parallax) largelly exceed the values measured ex-situ (red stars markers, without parallax)

In the present experiment, by combining the different measurements listed in Figure 2, we validated an approach able to estimate the microstrain values operando, free from the parralax contribution (green curve in Figure 3):

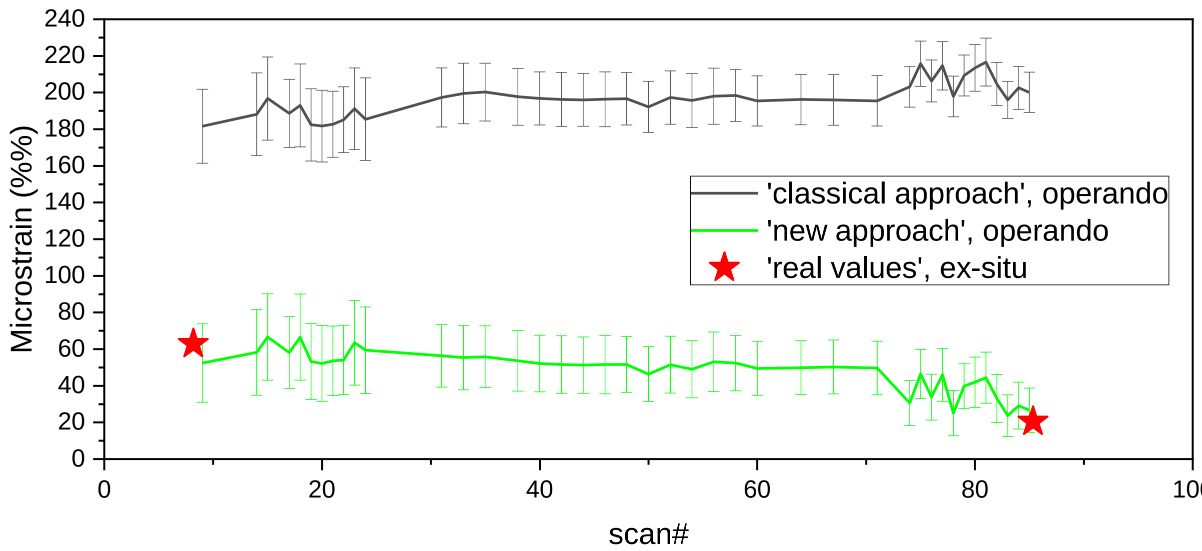

Figure 3: validation of the 'new' vs. 'classical' estimation of the microstrain values operando, in light of the microstrain values measured ex-situ at the beginning and end of life of the reference Pt/C material.

Manuscript(s) about the elaboration of the 'new' method and on the results regarding the 'real'microstrain evolution of defects-engineered materials is (are) under preparation (method possibly valorized independently from the results). The obtained results on 'the true fate of surface distortion in operating fuel cell' are unique in the field and will provide answer to the fundamental question introduced in a previous contribution (10.1038/s41563-018-0133-2) regarding the viability of 'defect-engineered' nanocatalysts for fuel cell applications.

Parts from the data collected during this experiment have been published in the following contributions:

Structural changes measured during the conditioning of the Sponges PtNi/C and PtNi Octahedra:

(1) Chattot, R.; Roiron, C.; Kumar, K.; Martin, V.; Campos Roldan, C. A.; Mirolo, M.; Martens, I.; Castanheira, L.; Viola, A.; Bacabe, R.; Cavaliere, S.; Blanchard, P.; Dubau, L.; Maillard, F.; Drnec, J. Break-In Bad: On the Conditioning of Fuel Cell Nanoalloy Catalysts. *ACS Catal.* **2022**, *12* (24), 15675–15685. https://doi.org/10.1021/acscatal.2c04495.

Structural changes measured during the accelerrated stress test of the Ref Pt/C HERAEUS:

(2) Chattot, R.; Mirolo, M.; Martens, I.; Kumar, K.; Martin, V.; Gasmi, A.; Dubau, L.; Maillard, F.; Castanheira, L.; Drnec, J. Beware of Cyclic Voltammetry! Measurement Artefact in Accelerated Stress Test of Fuel Cell Cathode Revealed by Operando X-Ray Diffraction. *J. Power Sources* **2023**, *555* (xxx), 232345. https://doi.org/10.1016/j.jpowsour.2022.232345.