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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

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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:** Full 3D characterization of the proton exchange membrane fuel cell in operando conditions	**Experiment number**:MA-3416
Beamline:	**Date of experiment**: from:12/07/2017 to: 17/07/2017	**Date of report**: 20/07/2018
Shifts:	**Local contact(s)**: Maria Valeria Blanco	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Experimental details:

As said in the proposal, we used a 5cm^2 PEMFC PEEK cell, specially built to perform in operando X-ray diffraciton studies. The cell was operated at 75°C and gas flow rates were set in order to have a fixed stoichiometry ratio 1.2 for hydrogen and 2 for air. The absloute gas pressure was set to 1.2 bar and the relative humidity was set to 40% at the cathode and 100% at the anode. Prior to the beginning of the measurements the membrane was completely dehydrated by flowing Ar at both, cathodic and anodic gas inlets for several hours.

We performed XRD-CT measurementsduring the operation od PEMFC, obtaining spatial and time-resolved information regarding the distribition and structural evolution of the catalyst layer, as well as water distrubution in the membrane.

Results:

XRD-CT datasets have been integrated (without using any filters). The initial preprocessing step included centering of the sinograms and background subtraction. All datasets have been reconstructed. These datasets were then aligned as the starting position was not the same in all XRD-CT scans (due to the zig-zag data collection strategy).

In total, four different z positions (i.e. P1 = 9.92, P2 = 10.2, P3 = 10.25, P4 = 10.3) along the PEMFC were probed under different operating conditions. A summary of the *operando* XRD-CT experiment with the PEMFC is presented in Table 1. The first z position (P1) corresponds to the PEMFC flow channels. The sample was then moved in z by 300 µm in order to probe the catalyst layer (P2). XRD-CT scans were also collected at two more z positions (i.e. P3 and P4). Positions P2, P3 and P4 were 50 µm apart from each other. As shown in Table 1, XRD-CT scans at these four positions were collected under different operating conditions (i.e. no operation, 1 V and 0.6 V).

Table 1: Summary of the XRD-CT datasets

Name	XRD-CT No.	Z Position	Voltage (V)
tomo_1_Biologic	1	P1	-
tomo_2_Biologic	2	P2	-
tomo_3c_Biologic	3	P3	-
tomo_3c_hr_Biologic	4	P3	-
tomo_4_Biologic	5	P4	-
tomo_5_hr_Biologic	6	P1	-
tomo_6_Biologic	7	P2	1
tomo_7_Biologic	8	P3	1
tomo_8_Biologic	9	P4	1
tomo_9 _Biologic	10	P1	1
tomo_11_Biologic	11	P2	0.6
tomo_12_Biologic*	12	P3	0.6
tomo_13_Biologic	13	P4	0.6
tomo_15_Biologic	14	P1	0.6

The first XRD-CT scan was performed at a z position probing the PEMFC flow channels (P1). As shown in Figure 1, there are four main components present. Each image in Figure 1 has been normalized with respect to the maximum intensity. Also shown, at the right side of Figure 1, is the combined image which serves to illustrate that we can obtain a high quality XRD-CT image of the PEMFC.

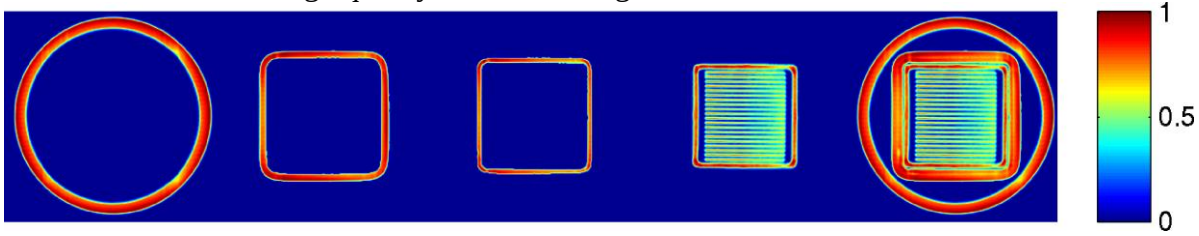

Figure 1: The four main components present in the XRD-CT dataset 'tomo_1_Biologic'. Right side: combined image

The diffraction patterns generated by these four components are presented in Figure 2 (left). These are the summed diffraction patterns from the voxels corresponding to the four regions presented in Figure 1. Each of these diffraction patterns was also normalised with respect to the maximum intensity.
The diffraction pattern from the outer component corresponds to a PEEK diffraction pattern. The diffraction pattern from component 2 (second from the left in Figure 1) is a lot more complex. On the other hand, the diffraction pattern from component 3 (third from the left in Figure 1) seems to generate a diffraction pattern identical to the first one (i.e. PEEK). Finally, the material consisting the flow channels generates a characteristic strong diffraction peak at ca. Q = 1.88 $Å^{-1}$.

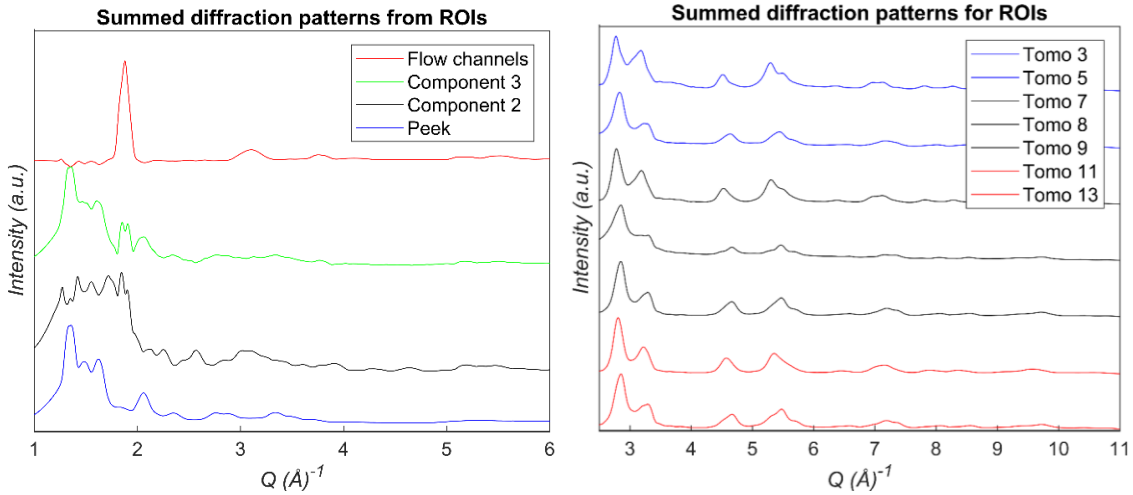

Figure 2: Left) Summed diffraction patterns from the four regions presented in Figure 1. Right) Summed diffraction patterns from a region of interest. Blue: XRD-CT scan no. 3 and 5 (OCV), Black: XRD-CT scan no. 7-9 (1 V), Red: XRD-CT no. 11 and 13 (0.6 V).

The main advantage of XRD-CT lies on the fact that the diffraction/scattering signal from each voxel in the reconstructed data volume corresponds to signal generated by this sample volume. For example, in the case of the PEMFC, we are able to apply a mask in a region of interest where the catalyst is present (middle of the sample) and extract the summed diffraction pattern from only this area. These diffraction patterns are presented in Figure 2 (right) where the only phase present is metallic Pt.

Closer inspection of these diffraction patterns reveals that there is a difference in the position of the Pt diffraction peaks in the various datasets. This shift of the diffraction peaks implies a significant difference in the size of the Pt unit cell. However, as it is clearly shown in Figure 8, this shift of the peaks seems to primarily depend on the z position and not on the operating conditions (which is rather intriguing).

The global XRD-CT images from the low resolution XRD-CT scans are presented in Figure.

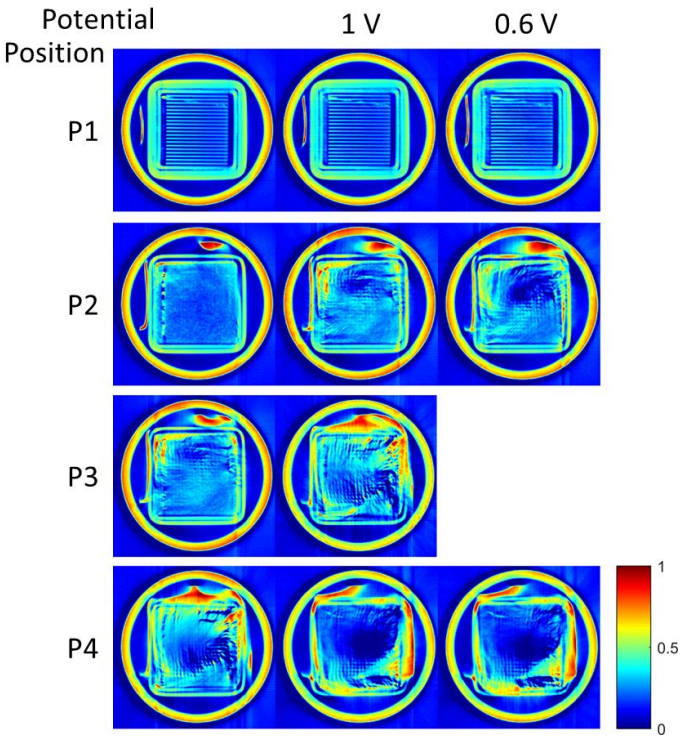

Figure 3: Global XRD-CT images from the low resolution XRD-CT scans. First row: XRD-CT scan no. 1, 10 and 14. Second row: XRD-CT scan no. 2, 7 and 11. Third row: XRD-CT scan no. 3 and 8. Fourth row: XRD-CT scan no. 5, 9 and 13.

The results obtained in this experiment were reported in a conference:

1) In-Situ Electrochemical X-Ray Diffraction of Pt Oxidation and Reduction in Hydrogen Fuel Cells. 233rd ECS Meeting (May 13-17, 2018) (Fuel Cells, Electrolyzers, and Energy Conversion).

2) Full Characterization of an Operating Fuel Cell Using High Energy X-Rays. 233rd ECS Meeting (May 13-17, 2018) (Fuel Cells, Electrolyzers, and Energy Conversion).

A publication is in preparation which will include results of this experiments.