



## 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

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> 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:** Understanding the Platinum-Rare Earth Nanoalloys Fine Surface Structure Dynamics during Operating Electrochemical Environment

**Experiment number:**  
CH-6562

<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 09/03/2023 at 8h00 to: 13/03/2023 at 8h00	<b>Date of report:</b>
<b>Shifts:</b> 12	<b>Local contact(s):</b> DRNEC Jakub, and VINCI Valentin	<i>Received at ESRF:</i>

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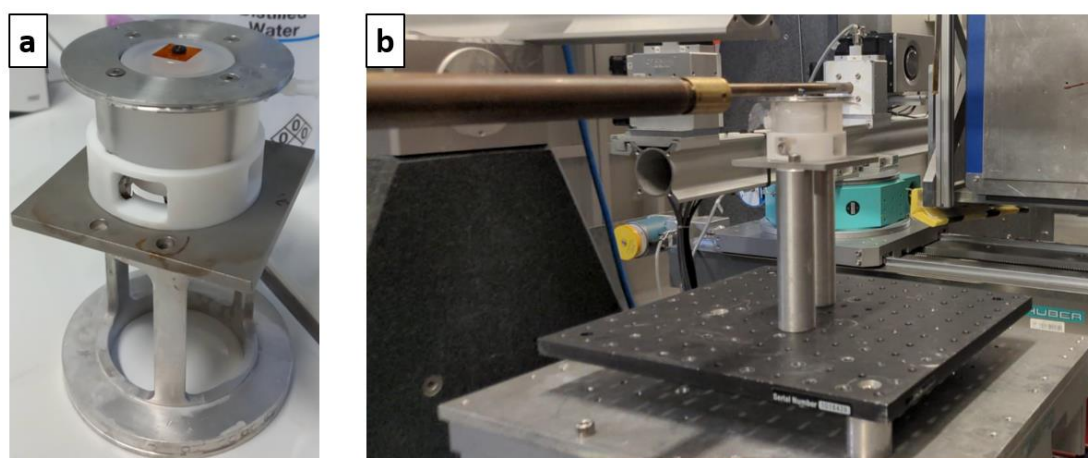
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## Report:

Before starting the beamtime using for the **CH-6562** experiment, the corresponding glassware and the X-ray-transparent electrochemical flow cell (EFC) components were cleaned with a  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$  mixture and thoroughly washed in Milli-Q water (Millipore,  $18.2 \text{ M}\Omega \text{ cm}$ ,  $\text{TOC} < 3 \text{ ppb}$ ). Thereafter, the EFC was assembled and mounted, see **Figure 1**.

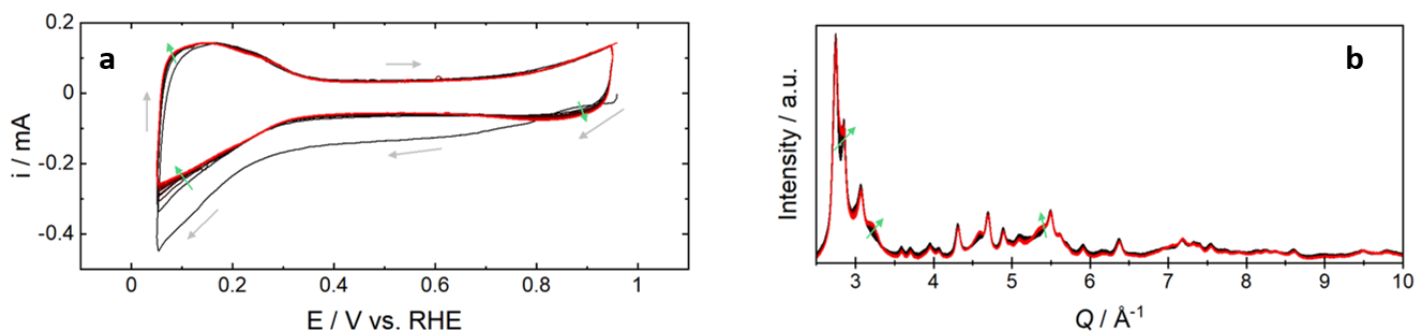


**Figure 1.** (a) X-ray-transparent electrochemical flow cell used for the *operando* WAXS measurements, and (b) its assembly and mounted.

The electrocatalytic ink was prepared by ultrasounding *ca.* 3.6 mg of the electrocatalyst powder (the metal content was determined previously by ICP-MS) in 3.990 mL of Milli-Q water, 1 mL of isopropanol and 10  $\mu\text{L}$  of Nafion® 5% v/v. Thereafter, 20  $\mu\text{L}$  of the resulting suspension were carefully deposited onto a glassy carbon

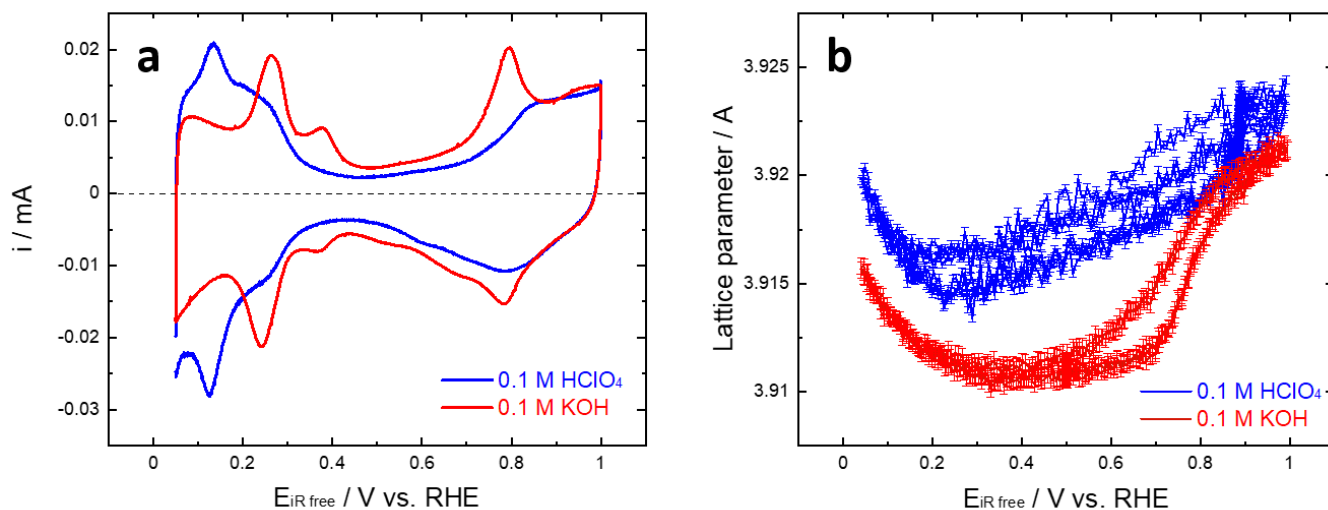
rod ( $0.196 \text{ cm}^2$ ) and dried at room conditions by rotating the electrode, obtaining a Pt loading of  $ca. 20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}_{\text{geo}}$ . Fresh electrolyte (0.1 M  $\text{HClO}_4$ , Suprapur®, Merck) was prepared prior to each sample measurement and flowed constantly through the EFC at  $20 \text{ mL min}^{-1}$  using a peristaltic pump. The counter-electrode was a graphite rod and the reference electrode a commercial leak-free miniature  $\text{Ag}/\text{AgCl}$  electrode (ET072, eDAQ). The reference electrode was calibrated using a Pt electrode submerged in  $\text{H}_2$ -saturated 0.1 M  $\text{HClO}_4$ . All potentials in this report are referred to the reversible hydrogen electrode (RHE) scale. The EFC was controlled with a Biologic potentiostat SP300. After the mounting of the sample in the EFC and the electrolyte flowing, the working electrode potential was kept at the open circuit potential (OCP) prior to any measurement. Simultaneously, the X-ray beam was carefully aligned, reaching a high signal to noise ratio.

Once the X-ray beam has been aligned, the electrochemical test protocol started with electrode preconditioning (or electrochemical activation) procedure, consisting of potential cycling between 0.05 and 0.95  $\text{V}_{\text{RHE}}$  at  $100 \text{ mV s}^{-1}$  for 20 cycles. WAXS patterns were simultaneously collected with 1 s temporal resolution. **Figure 2** shows an example of the recorded cyclic voltammograms (a) and the simultaneously recorded WAXS patterns (b) during the electrochemical activation procedure.



**Figure 2.** (a) Cyclic voltammograms and (b) WAXS patterns recorded during the electrochemical activation protocol. The electrochemical measurements were carried out in  $\text{N}_2$ -saturated 0.1 M  $\text{HClO}_4$  at  $100 \text{ mV s}^{-1}$ . The gray arrows indicates the potential scan direction. In both profiles, the green arrows indicates changes induced by the potential control.

Following the electrochemical activation protocol, three potentiodynamic cycles, under the same potential range at  $20 \text{ mV s}^{-1}$ , were recorded, and simultaneously, the WAXS patterns were acquired, but with higher temporal resolution (250 ms exposure time). The refinement of the structural data extracted from this experiment allow us to follow the evolution of the lattice parameter and, therefore, the induced strain as function of the potential, namely, the nanocrystal strain variations associated with electrochemical adsorption processes on the electrode. It is worth to mention that, due to the effect of the chemical nature of the electrolyte on the adsorption processes at the electrode/electrolyte interphase, we have done the comparison between the strain dynamics in acidic (0.1 M  $\text{HClO}_4$ ) vs. alkaline (0.1 M  $\text{KOH}$ ) medium, an example of which is shown in **Figure 3**.



**Figure 3.** (a) Cyclic voltammograms of Pt/C in  $\text{N}_2$ -saturated 0.1 M  $\text{HClO}_4$  and 0.1 M  $\text{KOH}$ . Measurements were carried out at  $20 \text{ mV s}^{-1}$ . (b) Refined lattice parameter, extracted from the WAXS patterns, as function of the electrode potential recorded in 0.1 M  $\text{HClO}_4$  and 0.1 M  $\text{KOH}$ .

The preliminary results shown in **Figure 3** clearly testify for the effect of the pH on the potential-depended strain dynamics. This captured electrolyte effect on the strain dynamics might be the subject of a coming publication.

The stability of the electrocatalysts under study was explored using an accelerated stress test (AST) protocol in 0.1 M HClO<sub>4</sub>. The AST consisted of 5,000 potential steps cycles (3s at 0.6 V<sub>RHE</sub> + 3s at 0.95 V<sub>RHE</sub>) under O<sub>2</sub>-saturated electrolyte, and the WAXS patterns were measured at cycle number 0, 100, 200, 400, 800, 1000, 2000, 3000, 4000, 5000. At the end of the AST, three potentiodynamic cycles between 0.05 and 0.95 V<sub>RHE</sub> at 20 mV s<sup>-1</sup> were recorded in O<sub>2</sub>-saturated electrolyte in order to calculate the electrochemical strain dynamics at the end of the AST.

The protocol in 0.1 M HClO<sub>4</sub> described above was applied to a series of Pt-RE/C nanoalloys (RE= Y, Sm or Gd), as well as the Pt/C benchmark. Besides, the measurements of the strain dynamics in 0.1 M KOH was applied to a series of Pt-RE/C nanoalloys (RE= La, Ce or Nd), as well as the Pt/C benchmark. All the acquired images during the beamtime were reduced to diffraction patterns using the pyFAI software package, and the resulting patterns are being analysed using FullProf software and Rietveld refinement. The refinement and analysis of the obtained results are in progress so far, and we expect they might strongly support complementary characterization for two coming publications.

The information extracted during the **CH-6562** experiment, coming along with supplementary characterization, will shade light on consistent structure-activity-stability relationships for the Pt-RE family of alloys, which remain poor understood at the nanoscale and is essential to accomplish their potential applicability in proton exchange membrane fuel cells.