EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:

In situ Grazing-Incident Diffraction on Nickel Nanoparticle Catalysts during Electrochemical Hydrogen Oxidation Reaction in Alkaline Electrolyte

Experiment number:
CH-6564

Beamline:
ID31

Date of experiment:
from: 28/03/2023 to: 01/04/2023

Date of report:
28/06/2023

Shifts:
12

Local contact(s):
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Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

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* Michal RONOVSKY (ESRF)

Report:

In this project we have applied *in operando* wide angle X-ray scattering (WAXS) to study structural transformations which affect the activity of nickel nanoparticle catalysts for the hydrogen oxidation reaction (HOR). In fuel cell research community, proton exchange membrane fuel cell (PEMFC) and anion exchange membrane fuel cell (AEMFC) are two clean-energy technologies that have gained significant research interest and focus in the past decades. As a cost-effective alternative to the currently commercialized PEMFC, the promising AEMFC offers several potential advantages over PEMFC. Among them, the wide availability of less costly Pt-free or precious group metal (PGM)-free catalysts in alkaline medium is particularly attractive. To date, PGM-free catalysts for the ORR at the cathode have achieved performances comparable to their PGM counterparts, and highly conductive and stable hydroxide exchange membranes have been newly developed. Now, the main barrier to the progress of AEMFC is the lack of active PGM-free catalysts for the HOR at the anode. Among various earth-abundant metals, nickel-based catalyst materials have been proved to be active for alkaline HOR. However, their performances still lack practical competitiveness. One of the main issues associated with Ni-based HOR catalysts was the tendency to oxidize and lose HOR activity under higher polarization potentials. The proposed mitigation strategies included making intermetallics or alloys with higher resistivity to oxidation, and using nitrogen-doped carbon as conductive support. It was reported that the electronic interaction between the Ni nanoparticles and the N-doped carbon support leads to balanced hydrogen and hydroxide binding energies.

To study this process, we have measured *in operando* WAXS of three different Ni-based catalysts pyrolyzed at three different temperatures, in the following abbreviated as Ni-H2-400, Ni-H2-425 and Ni-H2-450. Several samples were prepared by drop casting an ink on glassy carbon (GC) cylinders with a nickel loading of ~20–30 μg_{Ni} cm^{-2}. WAXS was measured using our customized three-electrode electrochemical X-ray cell made of PEEK and based on thin-layer concept. The cell was designed for grazing incident geometry and accommodated a glassy carbon cylinder electrode (Ø ~ 5 mm) and filled with 0.1 M KOH electrolyte. PEEK foil was used as X-ray window. X-ray attenuation due to the electrolyte film was reduced significantly thanks to the high-energy X-ray radiation. First for each sample, the activation was achieved by cycling 10 times between −0.02 V_{RHE} and 0.05 V_{RHE} at 20 mVs^{-1} scan rate in N2-saturated electrolyte to remove surface oxygen species on nickel. Then, the electrolyte was saturated with H2. A staircase potentiostatic protocol which consisted of successive potential steps of fixed step size (40 mV) and duration (10 min) was performed and WAXS measured every ~10 min. The potential was first decreased in steps of 40 mV from the initial state, 0 V_{RHE} to −0.08 V_{RHE}, then increased to HOR conditions at the maximum potential of 0.56 V_{RHE}, then decreased back to the initial state, 0 V_{RHE}.

- Staircase potentiostatic protocol I: potential range: −0.08–0.56 V_{RHE}, 33 steps in total, step size: 40 mV, duration of each step: 10 min.

Protocol type I has a potential range that extends well inside the Ni oxidation region and reduction region. To observe dynamical structural changes induced by Ni oxidation and reduction, WAXS measurements were performed at the end of each potential steps.

The plot of potential vs time is illustarted in Figure 1. A KCl-saturated Ag/AgCl electrode (0.943 V_{RHE}) was used as the reference electrode. Before use, it was first calibrated by LSV scans with polycrystalline Pt RDE as the working electrode in H2-saturated electrolyte. The potential in Figure 1 are reference to the Ag/AgCl electrode.

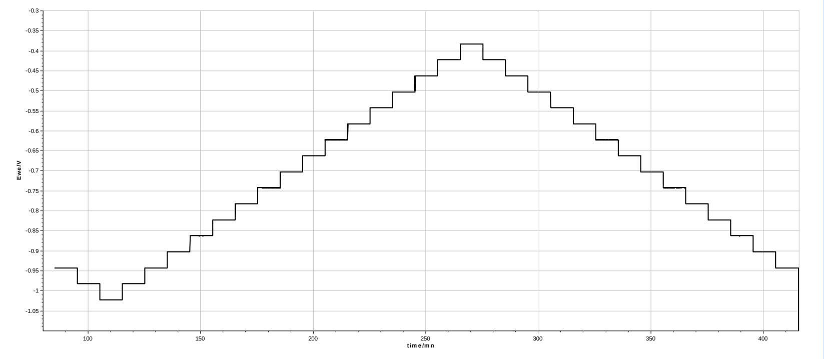

Figure 1: The plot of potential vs time of staircase potentiostatic protocol type I.

We performed the above mentioned protocol (type I) for all three catalysts. To make sure that this *in operando* WAXS technique also works well for Ni-based materials, we also designed another "safe" protocol (type II). Given the limited beamtime, we only performed type II protocol for one selected catalyst (Ni-H2-450).

- Staircase potentiostatic protocol II: potential range: −0.20–1.40 V_{RHE}, 17 steps in total, step size: 200 mV, duration of each step: 10 min.

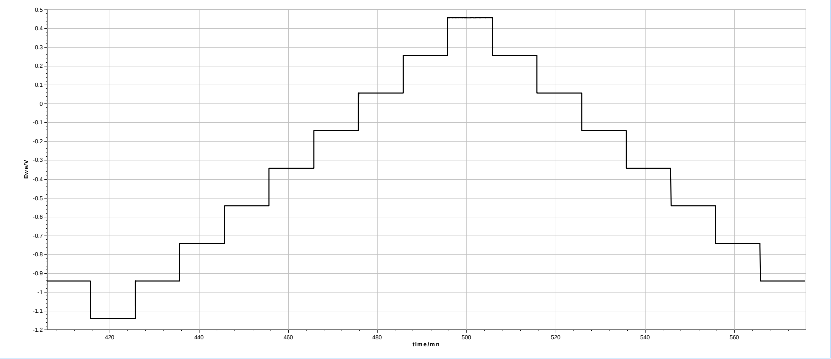

Figure 2: The plot of potential vs time of staircase potentiostatic protocol type II.

The data analysis is in progress and will further reveal differences, for example in change of the structural coherence length of metallic Ni, occurring with different potential steps. The analysis of the diffraction patterns measured during the staircase potentiostatic protocol will also help to understand the structural evolution of Ni under electrochemical potential control and during HOR in alkaline electrolyte in detail. In conclusion, we were able to measure in situ WAXS on highly active Ni-based HOR catalysts. A deeper analysis of the data with Rietveld refinement is expected to provide additional information to clarify the poisoning mechanism and understand the causes of activity loss for Ni-based HOR catalysts.