EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Tracking structural changes of Ni/Fe_3O_4 model electrodes during the Oxygen Evolution Reaction (OER) using High Energy Surface Diffraction	**Experiment number**: CH-6084
Beamline: ID31	**Date of experiment**: from: 22.02.2022 to: 28.02.2022	**Date of report**: 13.04.2022
Shifts: 18	**Local contact(s)**: Jakub Drnec	*Received at ESRF:*

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Report:

The aim of this experiment was to use High Energy Surface X-ray Diffraction (HESXRD) to follow the structural changes of well-defined Ni- and Fe-based thin film model electrodes during OER conditions. In the preparation for this beamtime we found that the growth of epitaxial NiO(100) thin films on Pt(001) single crystals turned out to yield the most well defined films. Accordingly, the main sample studied in this beamtime featured a NiO(001)/Pt(001) sample grown by means of controlled Physical Vapour Deposition of Ni under O_2 atmosphere.

To elucidate the sample structure before and during selected OER potentials up into the catalytically active regime of O_2 production, rotational scans of the sample around its surface normal were performed while 2D images were aqcquired with the 2D detector. This allowed to probe the full 3D reciprocal space data at selected potentials.

Fig. 1 shows the diffraction pattern measured on the as-prepared NiO(001)/Pt(001) sample in air prior to the electrochemical reaction during such a rotational scan and projected onto a 2D image. The red circles indicate the strong Bragg peak signals stemming from (001)-oriented NiO. The by far weaker diffraction signals from the (111)-oriented NiO are indicated by orange circles. The high intensity of the NiO(001) peaks compared to the ones from NiO(111) as well as the observance of Laue oscillations in out-of-plane direction (see inset on the bottom right of Fig. 1) confirm the high qualitiy of the epitaxial NiO(001) film.

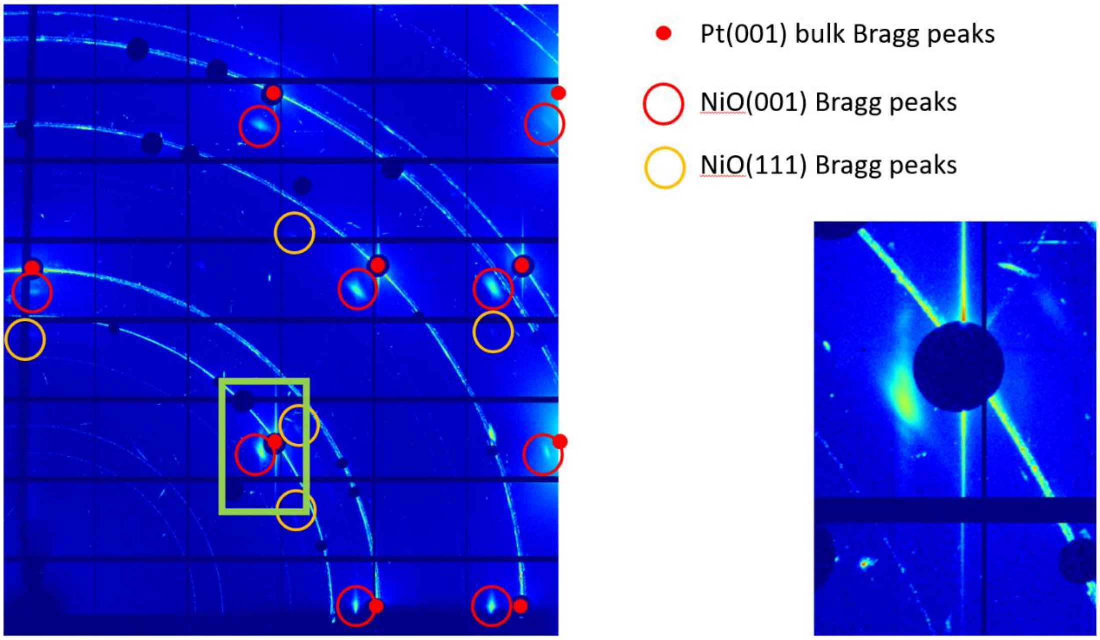

Fig. 1: *Sum over 2D images acquired during a rotational scan in which the highest intensity per pixel probed during the rotation is shown. Red circles indicate positions of the substrate Pt Bragg peaks which we blocked with tungsten pieces to not damage the detector. Red open circles indicate the diffraction positions of (001)-oriented NiO, orange open circles the positions of (111)-oriented NiO. The image on the bottom right shows a zoom-in to the NiO(202) Bragg peak.*

During OER conditions the same set of rotational scans were repeated at selected potentials to map structural changes in the NiO(001) film as well as the potential appearance of transient phases (including NiOOH and $Ni(OH)_2$ phases).
To allow for a time-resolved correlation between structural changes in the NiO thin films and the potential, 2D maps were repeatedly measured at selected rotational angles while the potential was sweeped up and down (typically with a rate of 5 mV/s). As far as we can tell from the data already now, the NiO(001) thin film appeared to be surprisingly stable under reaction conditions.
In a second set of measurements, the effect of the electrodeposition of Fe onto the NiO film was investigated, and the data indicated a clear increase in the catalytic activity of the sample.

As time allowed we also studied additional samples for the OER reaction including HOPG-supported Co_3O_4 nanoparticles as well as a Ni(111) single crystal for which transient $Ni(OH)_2$ and NiOOH structures were observed. Moreover, Cu-Zn cubes were investigated during the CO_2 electroreduction reaction by means of powder diffraction and Ir nanoparticles on $SrTiO_3$ in air.

No major technical difficulties were encountered during the experiment and also the synchrotron beam was very stable.

In summary, the beamtime allowed us to obtain important information in the structure and the structural changes of a NiO(001) thin film model electrocatalyst as a function of the applied potential. The measurements will accordingly yield important insight into the structure-function relationship for the OER, an electrochemical reaction of utmost importance for a sustainable society.
We believe that parts of the data are sufficient for publication and we expect the ESRF staff to be included as co-authors.