

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>

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.

**Experiment title:**

Active phase of Ni, Co, Mn, Fe binary catalysts with layered double hydroxide structure during electrochemical oxygen evolution reaction using in situ XRD and SAXS

Experiment**number:**

CH-4624

Beamline: ID31	Date of experiment: from: 04 May 2016 to: 08 May 2016	Date of report: 12.09.16
Shifts: 12	Local contact(s): Jakub Drnec, Maria Blanco	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):***Fabio Dionigi, TU Berlin*****Arno Bergmann, TU berlin*****Henrike Schmies, TU Berlin*****Elisabeth Hornberger, TU Berlin****Peter Strasser, TU Berlin****Report:**

In this project, we have applied *in operando* wide angle X-ray scattering (WAXS) to study structural transformations and determine the active phase of layered double hydroxide (LDH) electrocatalysts during oxygen evolution reaction (OER) in alkaline electrolyte. NiFe LDH [1,2] and CoFe LDH [3] have been reported to exhibit high catalytic activity for OER in alkaline media, with NiFe LDH in particular showing the best performances, comparable with noble metal based catalysts such as IrO₂ in alkaline electrolyte. However, the nature of the catalytic active site is under debate. Structural transformations are induced by increasing the potential more anodic than typical transition metals oxidation peak potential, after which OER starts, resulting in an OER active phase that is different than the as synthesized one. Due to reversibility or partial reversibility of these transformations, *in operando* characterization techniques are necessary to study the OER active phase. For this reason we synthesized NiFe LDH and CoFe LDH nanoplates and investigated them with *in operando* WAXS and Small angle X-ray scattering (SAXS). For electrochemical testing, an ink was prepared with unsupported catalyst particles and drop casted on glassy carbon (GC) electrodes. A grazing incident diffraction (GID) cell was necessary due to strong preferential diffraction caused by the stacking of the LDH nanoplates, which excluded the use of transmission setup with the X-ray beam parallel to the stacking direction. Therefore, the experiments were performed with the GID cell, based on thin film concept. A peek foil was used as X-ray window. X-ray attenuation due to the thick electrolyte film was reduced significantly thanks to the high-energy X-ray radiation. In the case of NiFe LDH, three loadings were tested: 100 $\mu\text{g cm}^{-2}$ (standard loading that we use also for RDE measurements), 33 $\mu\text{g cm}^{-2}$ (1/3rd of the standard loading), 20 $\mu\text{g cm}^{-2}$ (1/5th of the standard loading). The electrochemical measurements showed consistent behaviour with what was observed in our laboratory. Therefore WAXS was measured after each cycle during the activation cyclic voltammetry protocol developed in our laboratory and in a following constant potential protocol with potential steps of $\sim 10\text{-}15$ min, spanning the range from the catalytic silent state (restings state) and the OER active state. The measurements revealed the appearance of a secondary phase for potentials above the Ni oxidation potential and under OER conditions. This is particularly evident

in the 003 diffraction peak, which is associated to the LDH interlayer distance (Figure 1a). This phase is observed to disappear when the potential is further decreased below the Ni reduction potential (Figure 1b). This confirms the reversibility of the phase transformation and the necessity to use *in operando* techniques to characterize this phase. The loading study also shows that this phase is difficult to observe with thick samples, where most likely occurs only on a fraction of material which is well connected with the substrate and electrolyte-accessible. [1] SAXS was also performed at constant potentials to evaluate possible dissolution of unwanted Fe based impurity phases, observed with transmission electron microscopes. However, the SAXS measurements did not show any significant difference in the time scale of the experiment.

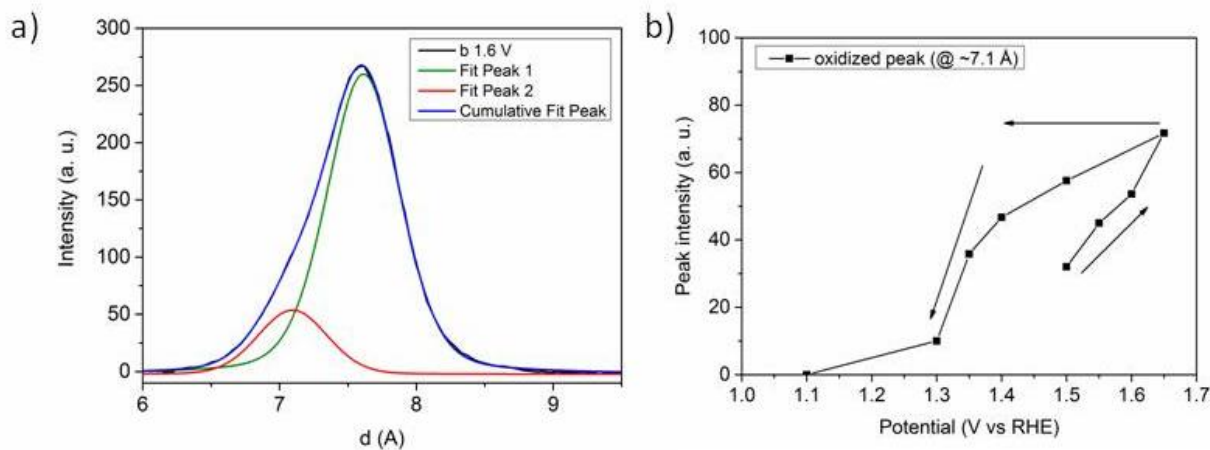


Figure 1: In operando WAXS showing the 003 peak of NiFe LDH at 1.6 V vs RHE in 0.1 M KOH (a). The Peak can be fitted with two peaks. The low d peak is assigned to the OER active phase and its intensity is plotted as a function of potential (b).

Similar behaviour was observed with CoFe LDH. A phase with contracted interlayer distance appears after increasing the potential above the Co oxidation potential and during OER (Figure 2). Decreasing the potential below the Co reduction potential also induced an expansion of the interlayer distance. In this case, however, the behavior is more complicated than in the case of NiFe LDH, due to multiple redox peaks in Co based materials.

In conclusions, *in operando* WAXS revealed to be a powerful technique to monitor structural transformations leading to the OER active phases of LDH electrocatalysts. Both for NiFe LDH and CoFe LDH the active phase consists in a similar LDH structure with contracted interlayer.

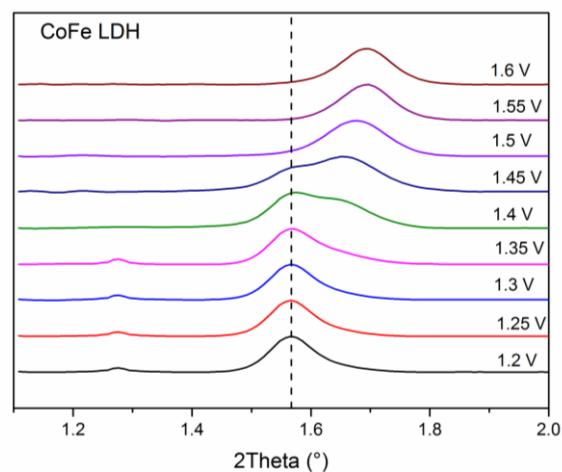


Figure 2: In operando WAXS showing the 003 peak of CoFe LDH at different potentials in 0.1 M KOH. The shift to higher 2Theta angles is consistent with a contraction of the interlayer.

[1] F. Dionigi and P. Strasser, "NiFe-Based (Oxy)hydroxide Catalysts for Oxygen Evolution Reaction in Non-Acidic Electrolytes", *Adv. Energy Mater.*, doi:10.1002/aenm.201600621 (2016).

[2] M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei and H. Dai, *J. Am. Chem. Soc.*, 135, 8452 (2013).

[3] M. S. Burke, M. G. Kast, L. Trotochaud, A. M. Smith, S. W. Boettcher, *J. Am. Chem. Soc.*, 137, 3638 (2015).

