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ESRF

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:** In-situ WAXS investigations of NiFe-LDH during electrochemical seawater oxidation	**Experiment number**: CH 5167
Beamline: ID 31	**Date of experiment**: from: 25.October.2017 to: 29.October.2017	**Date of report**: *Received at ESRF:*
Shifts: 12	**Local contact(s)**: Agnieszka Poulain	

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In this beamtime, we applied wide angle X-ray diffraction (WAXS) to study the influence of the electrolyte, in particular the presence of Na^+ and Cl^-, which simulate seawater condition, to the NiFe LDH reversible structure transformation under operating conditions and correlate the observed changes to degradation mechanisms and to the electrochemical behaviour. We expected an improved signal on supported material. For this we prepared on Vulcan XC72R supported and unsupported NiFe-LDH materials. The as prepared NiFe-LDH has a layered structure with water and carbonate anions in the interlayer region. High OER potentials lead to a phase transformation to a γ-Ni(Fe)OOH phase, which is characterized by a smaller interlayer distance, absence of intercalated anions and possible incorporation of cations. The intercalated carbonate anions are expected to be expelled during the transition and the presence of Na^+ and Cl^- might interfere in this process. For example, Cl^- can be inserted in the interlayer during potential cycling, which will cause a slight expansion of the interlayer distance that would be detected by WAXS. Differences in the cyclic voltammetry in alkaline seawater were reported that could indicate this process[1].

In Figure 1, we show the WAXS pattern for supported and unsupported material after background subtraction. The (003) Peak (Figure 1a),which correlates to the interlayer distance of the NiFe–LDH, shows the expected shift to smaller distances from resting state to OER potentials for both catalyst materials. However, the shift for the unsupported material is slightly smaller. In Figure 1b, the change of the signal is more pronounced for the supported material. The new reflection at ~ 1.4 Å is believed to be the shifted peak of the (110) peak, which is indicated with (110*). The decrease of the (110) and (113) peak and the increase of the new (110*) peak is more present for the supported material. Consequently, the unsupported material seems to be more inert than the supported catalyst material. Thus, the unsupported material is on the one hand less influenced by the applied potential and on the other hand shows a bigger interlayer distance for the active phase closer to the resting state (see also Figure 2b). This confirmed our assumption that a better signal can be achieved with the supported catalyst material. Hence, we decided to perform the remaining measurements with supported catalyst material.

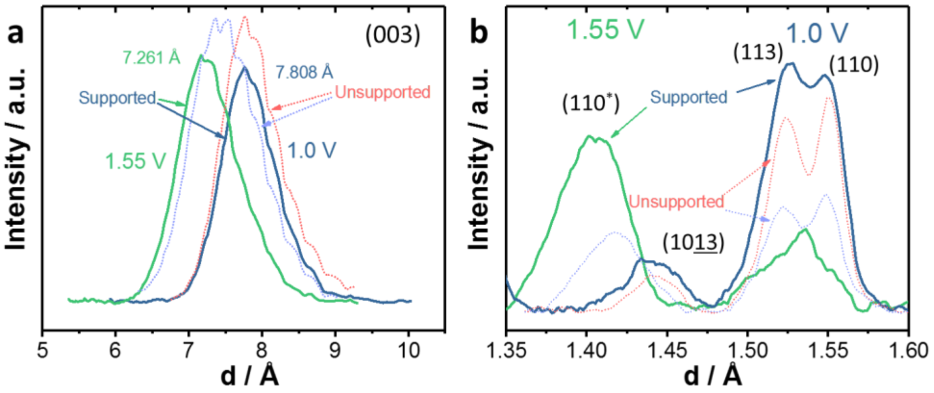

***Figure 1** In operando WAXS data of unsupported and on Vulcan XC72R supported NiFe-LDH at resting state and under OER potentials showing **(a)** the (110), (113) and (1013) peaks and **(b)** the (003) peak*

In Figure 2a, we show the (003) Peak under OER potentials for the supported NiFe-LDH measured in the remaining electrolyte compositions of 0.1 M KOH, 0.5 M KOH and 1.0 M KOH with and without 0.5 M NaCl. The evaluation of this data is shown in figure 2b, where the interlayer distance is plotted against the KOH concentration.

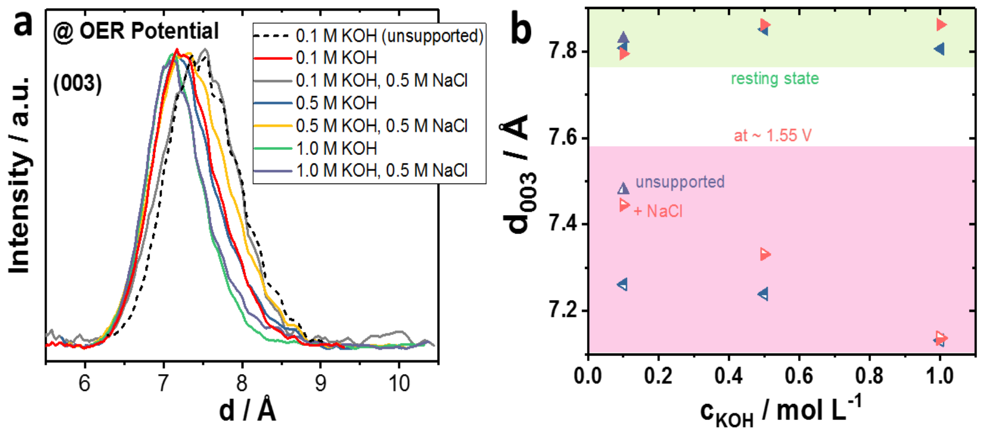

***Figure 2** In operando WAXS showing **(a)** the (003) peak of NiFe LDH at ~1.55 V vs RHE in different concentrations of KOH with and without 0.5 M NaCl **(b)** The determined interlayer distance for the supported and unsupported NiFe-LDH in different alkaline electrolytes with and without 0.5 M NaCl*

In the resting state no significant difference is detected. Contrary, at OER potentials a relation of KOH concentration and interlayer distance of the active phase is determined for NaCl containing as well as for NaCl free electrolyte. However, in the NaCl containing electrolyte the difference is much more pronounced. In fact, at low KOH concentration (0.1 M KOH) the distance of NiFe-LDH in the NaCl containing electrolyte is almost similar to the “inert” unsupported distance. With increasing KOH concentration the interlayer distances in NaCl free and NaCl containing electrolyte converge, while the overall distance decreases. We explain this with the intercalation of excess Cl- at low OH- concentrations and consequent minimization of OH- ions within the catalyst layer. With increasing OH- concentration the presence of Cl- ions can be compensated. While in an electrolyte of 0.5 M KOH and 0.5 M NaCl the presence of Cl- still results in an increased interlayer distance, at 1 M KOH the difference between NaCl free and NaCl containing electrolyte almost disappeared. As a conclusion, a double concentration of OH- Ions is able to compensates the Cl- effect to the NiFe-LDH phase at OER potentials entirely. In particular, Cl- Ions only effect the phase structure of the active phase under OER potentials under a specific concentration.

In conclusion, in-operando WAXS revealed to be a powerful technique to monitor structural transformations and differences at different pH and the presence of other ions leading to the OER active phase of NiFe-LDH electrocatalysts. Our hypothesis expressed in the proposal application could be fully proofed. This results will give new insights about the NiFe-LDH catalyst system and provide more insight in the mechanism behind structural transformation of NiFe-LDH and in particular to the role of participating anions and cations in the electrolyte. The anion role is a very important parameter to be considered for the oxygen evolution seawater catalyst development.

1. Dionigi, F., et al., *Design Criteria, Operating Conditions, and Nickel–Iron Hydroxide Catalyst Materials for Selective Seawater Electrolysis.* ChemSusChem, 2016. **9**(9): p. 962-972.