



	Experiment title: Operando studies on transition metal oxides/hydroxides during OER	Experiment number: CH6559
Beamline: ID31	Date of experiment: from: 05.07.2023 to: 09.07.2023	Date of report: 18.09.2023
Shifts: 12	Local contact(s): Andrea Sartori	<i>Received at ESRF:</i>
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Report:

1. Abstract

Transition metal oxide/hydroxide catalysts, based on Fe, Co, and Ni, are active electrocatalysts for the oxygen evolution reaction (OER) in alkaline media. However, the structure/property relations are far from understood. With the performed experiment we aim to elucidate the structural changes of NiFe(oxy)hydroxides when used as electrocatalysts for the OER. We use wide-angle x-ray scattering (WAXS) in combination with x-ray total scattering and Pair Distribution Function (PDF) analysis to obtain in-depth insight into structural changes and rearrangements taking place under applied potential.

2. Experimental Details

In the experiment at ID31, we used our home-developed *operando* electrochemical flow-cell set-up optimized for X-ray scattering total scattering. The catalyst layers of the Ni-LDH catalysts were prepared by vacuum filtration onto a gas diffusion layer in our home lab. They were used as working electrodes in the electrochemical cell, with a platinum counter electrode and an Ag/AgCl reference electrode. The 0.5M KOH electrolyte was flown through the cell during the experiment. A series of potential steps were applied, gradually stepping from the open circuit potential (OCP) to oxidizing potentials where significant currents oxygen evolution currents were measured. The potential was then gradually stepped back to OCP, to observe if the changes under applied potential were reversible or not. At each potential, total WAXS and scattering data were collected at different depths of the catalyst layer. Careful background subtraction is necessary to treat the total scattering data. This was performed based on the height scans through the catalyst later, where scattering data of both the carbon background and electrolyte in the cell was collected. In that way, it was possible to subtract both the contributions from the cell and electrolyte as well as from the carbon-based gas-diffusion layer. As the carbon changes as a function of applied potential, background data were recorded and subtracted for each potential step.

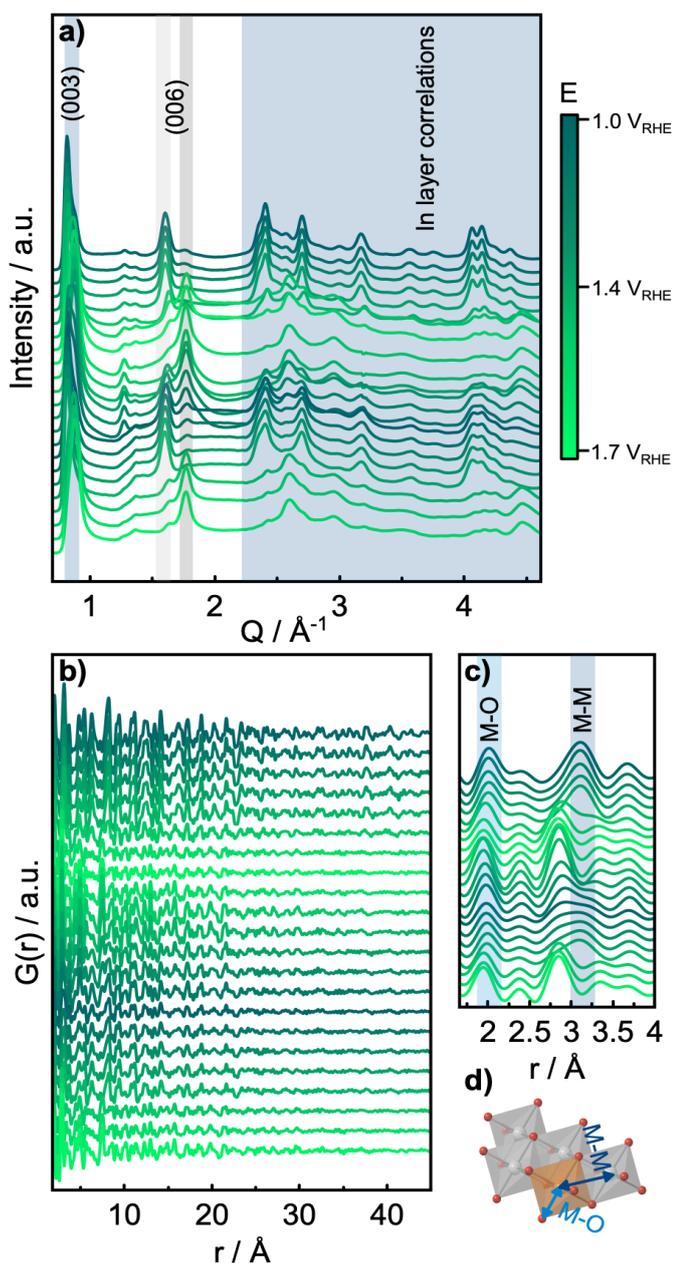


Figure 1 a) X-ray diffraction (WAXS data) and b) PDFs of the NiFe-LDH catalyst as a function of applied potential with c) zoom in the low R-region showing the local coordination of M-O and M-M according to the LDH structural model as shown in d).

3. Results

In Figure 1 we show an initial analysis of the collected scattering data. The WAXS data are shown in q-space in Figure 1 a. A clear shift in the LDF layer spacing can be followed when moving to oxidative potentials. The shift in interlayer distance appears to be reversible. Minor changes in the layer correlations are also evident. These are easier to follow in the total scattering data (Fig 1b and c). We have analyzed the total scattering data and the PDFs that could be obtained after careful background subtraction. The PDF overview as a function of potential in Fig 1b shows fewer peaks at the high oxidative potentials where OER occurs. This indicates a less ordered oxide structure of the OER active oxide. Such structural flexibility and possible amorphization have been suggested for several OER active oxides. Here careful analysis of the collected PDF data will help to gain a deeper understanding of the structural features that are required for good electrocatalytic performance. When zooming in to the low R-region of the PDFs for a deeper analysis of the local coordination in the Ni-LDH (Fig 1c) collected in *operando* we observe two effects: the M-O distance shrinks, indicating oxidation of the active transition metal. Furthermore, the M-M distance of the nearest neighboring metal site shows changes in the octahedral coordination of Ni and Fe in the LDH layers (see also structural model in Figure 1d).

4. Conclusions and future work

The beamtime has been a success in demonstrating the possibility of collecting total scattering data during OER electrocatalysis in alkaline media. The data can be analyzed if a very careful background subtraction is performed. Careful measurement of high-quality background data is, therefore, required. With this, it was possible to obtain *operando* PDFs that show the structural changes of the Ni LDF catalysts. We are now in the process of analyzing the data in detail, including real-space Rietveld refinement of the PDFs and combining the PDF analysis with the results obtained from the Q-space

WAXS data where changes in the LDH interlayer spacing can be followed precisely. The results from this beamtime have shown that both the interlayer spacing changes as a function of potential, as well as the M-O and M-M coordination inside the layers. These results were only possible to obtain with combined WAXS with total scattering and PDF analysis.

5. Publications resulting from the work

We expect to publish the results once the detailed data analysis of both WAXS and PDF data is finished.