

**Experiment title:**

Following the structural adaptation of CoFe-based electrocatalysts for alkaline water splitting using operando high energy X-ray diffraction

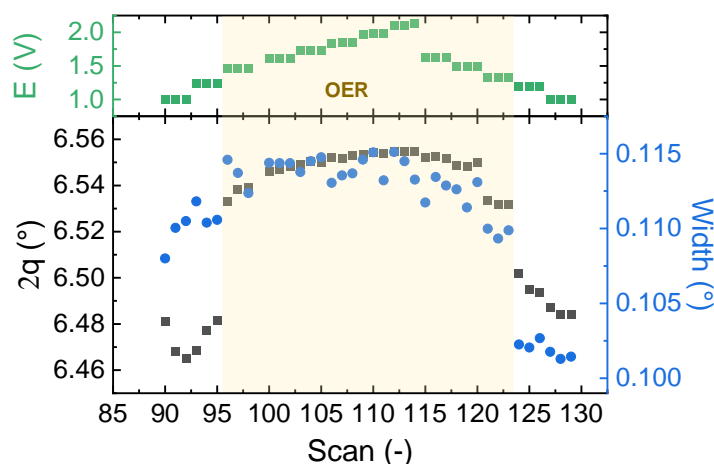
**Experiment number:**

CH6561

<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 20.6.2023 to: 26.6.2023	<b>Date of report:</b> September, 1 <sup>st</sup> 2023  <i>Received at ESRF:</i>
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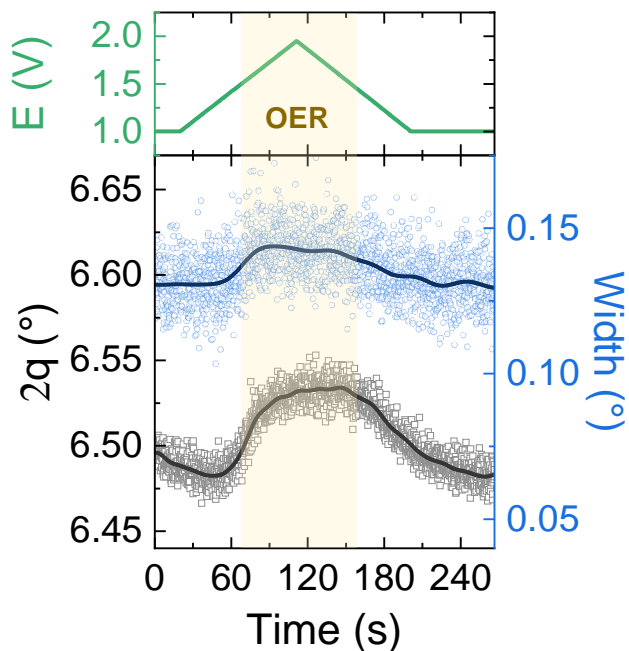
The goal of this experiment at ID31 was to unravel the structural adaptation of CoFe-based electrocatalysts during alkaline oxygen evolution reaction (OER). It is known that  $\text{Co}_3\text{O}_4$  electrocatalysts restructure in the near-surface region owing the oxidizing reaction conditions driven by the change  $\text{Co}^{2+}$  coordination from tetrahedral to octahedral. Recent studies on epitaxial thin film catalysts proposed a correlation between the extent of restructuring – the formation of a reaction zone – and the catalytic activity. It was our goal to screen the restructuring of a variety of Co-based powder electrocatalysts to be able to check the validity of the findings.



**Figure 1** Fitting results – peak position (bottom panel, black squares) and peak width (bottom panel, blue circles) of the (511) reflection of the  $\text{CoV}_{1.5}\text{Fe}_{0.5}\text{O}_4$  sample under stationary electrochemical and electrocatalytic conditions with varying electrode potential (upper panel, green squares)

In the experiment, we successfully investigated a series of  $\text{CoV}_x\text{Fe}_{2-x}\text{O}_4$  particles under various electrocatalytic conditions. We successfully identified the onset potential of the restructuring and are currently undergoing in depth data analysis. Preliminary insights on single Bragg peak fittings of a  $\text{CoV}_{1.5}\text{Fe}_{0.5}\text{O}_4$  sample is shown in Figure 1 and Figure 2.

Figure 1 shows the changes in Bragg peak position and thus, lattice parameter as well as the width of the Bragg peak during potential step experiments while holding the potential for 15 min to allow equilibration of the restructuring. It can be clearly seen that the increase in potential leads to a shift of the



**Figure 2** Fitting results – peak position (bottom panel, black squares) and peak width (bottom panel, blue circles) – of the (511) reflection of the  $\text{CoV}_{1.5}\text{Fe}_{0.5}\text{O}_4$  sample during cyclic voltammetry in 0.1M KOH with varying electrode potential (upper panel, green). The lines represent Fourier-filtered profiles of the peak position and peak width.

Bragg peak to a higher position and thus, to a contraction of the lattice. This contraction is accompanied by a broadening of the Bragg peak reflecting the shorter coherence length. Both processes are clearly linked to the onset of OER and are reversible.

To identify the possibilities to study the kinetics of the restructuring, we recorded diffraction pattern also under dynamic potential sweep experiments. Figure 2 shows the Bragg peak position as well as the peak width recorded with a counting time of 127 ms. The active state formation as shown under static conditions can be followed and thus, the onset potentials and its linked to the redox electrochemistry more precisely determined.

More detailed and robust data analysis using Rietveld refinement is currently ongoing.