



	Experiment title: Role of surface facets of novel ferrihydrites in electrocatalytic water splitting	Experiment number: MA-3650
Beamline:	Date of experiment: from: 17 th october 2017 to: 21 st october 2017	Date of report:
Shifts: 12	Local contact(s): Jakub Drnec	<i>Received at ESRF:</i>
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Report:

The initially proposed experiments were carried out using the CdTe detector and an electrochemical cell provided by the electrochemistry lab of ID-31 at the ESRF.

In preparation of the experiments, several iron-only layered double hydroxides have been used repeatedly and successful for the electrocatalytic water oxidation with rotating disk electrodes. Though the samples mainly belong to the family of fougèrites, variations of the reaction conditions during the synthesis yielded samples with greatly varying surface ratios of lateral and longitudinal surface areas. The aim of the experiment was to identify the active sites during the electrochemical water oxidation. By using the electrochemical cell provided by ID-31 and being made out of PEEK, we aimed to observe the structural changes of the surfaces of the layered double hydroxides by grazing incidence diffraction.

The cell was equipped with a potentiostat to record the current/voltage responses during the catalysis. Due to the amorphous nature of the material, the detected signal on the Pilatus detector was very weak, but present. Unfortunately, the electrochemical cell did not respond as expected when cyclic and linear sweep voltammetry impulses were applied to the material. Indeed, the recorded current was several magnitudes lower than expected. While the material yielded 10 mA/cm² in standard rotating disk electrodes at 1.63 volt vs the reversible hydrogen electrode, we did not record any current at all with an applied voltage of 2 volts vs the reversible hydrogen electrode. This was assumed to be a problem with the catalyst at first. Several different electrolyte concentrations were used in the cell and the voltage range was extended greatly. All electrolyte solutions were exchanged multiple times and the beamline staff supported us a lot to perfectly mount and align the cell. However, the cell did not yield any sufficient current. Even at voltages where the glassy carbon catalyst support would catalyse the electrocatalytic water oxidation, the potentiostat did not show reasonable current densities. All electrochemical equipment was checked for malfunctions, but the issues with the cell could not be solved.

Besides the in-operando experiments, we also brought multiple powders of ion-only layered double hydroxides, namely from the family of mössbauerites, with us. These powders had been used for the electrocatalytic oxygen evolution reaction in standard rotating disk electrodes successfully in the lab and the different samples had undergone different catalytic histories. Figure 1 shows the electrochemical performance of the material as recorded in our lab.

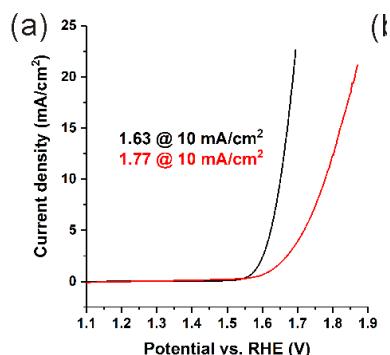


Figure 1. Electrochemical performance of different Mössbauerite samples during the electrochemical water oxidation.

A 4h long-term stability test proved, that the material is sufficiently stable during operation, yet showing slight changes in catalytic activity. Based on the recorded scattering data on the powder mössbauerites at ID-31, we could reveal slight structural changes between the diffractogram of the used (M-50 4h) and as-synthesized (M-50 0h) mössbauerites (Figure 2). The post mortem diffractogramm of the isolated material shows little changes.

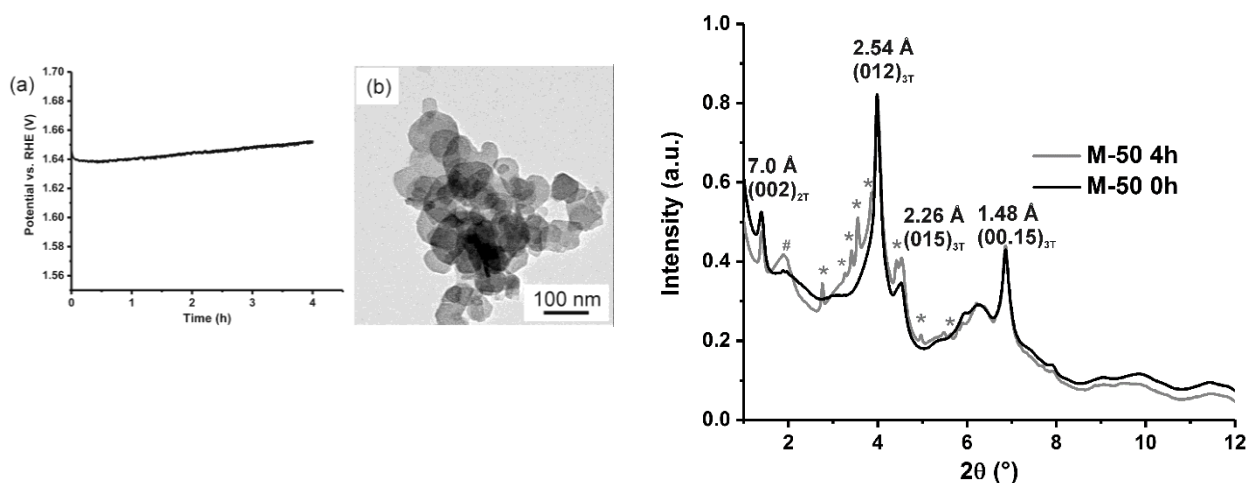


Figure 2. Stability test and *post-mortem* characterization of **M-50**. (a) Chronoamperometric measurement of **M-50** in 1M KOH at 10 mA/cm². (b) TEM image of **M-50** after 4h long term measurement (**M-50 4h**) displaying thin platelets. The pre- and post-mortem diffractogramm of the catalyst show little change during operation

Since iron oxihydroxides are slightly soluble in basic solution, the catalyst seems to dissolve and reprecipitate as amorphous akaganeite. These structural results nicely explain the catalytic behaviour, and we just recently included these diffraction results in a manuscript, currently in review at Angewandte.