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## Introduction

Water splitting is one of the most promising routes for renewable energy conversion and storage. Iron group metal oxides such as Co and FeCo oxides are promising candidates for noble metal free catalysts for transforming renewable energy by decomposition of water into oxygen via the oxygen evolution reaction (OER). Within a systematic study of these electrocatalysts, we performed *operando* surface X-ray diffraction (SXRD) measurements in the OER potential range of thin films of FeCo oxide, prepared electrochemically on Au(111) single crystals at high temperature in alkaline media. The aim of the study is to determine the oxide surface structure under reaction conditions.

## Experimental details

All experiments were carried out at 22.5 keV in our in situ flow cell designed for X-ray diffraction under strong gas evolution. The cell is made from PEEK which also served as an X-ray window. The cell allows to simultaneously measure the X-ray scattering, the electrochemical current and the optical reflectivity of the sample. The latter is very sensitive to small changes on the sample surface allowing real time monitoring of thin film modifications. Electrolyte can be pumped into and out of the cell by a system of 4 syringes allowing rapid electrolyte exchange (within one minute). The cell has also an auxiliary counter electrode (for high current measurements up to 100 mA/cm<sup>2</sup>) and a camera to monitor the formation of gas bubbles on the sample surface.

## Results

The aim of the experiment was to investigate during OER the structure of ultra thin FeCoO<sub>x</sub> on Au(111) precovered by a CoOOH thin film. The presence of CoOOH film improves significantly the flatness and the surface coverage of the FeCoO<sub>x</sub> films. We used the following preparation procedure: deposition of CoOOH at -0.50 V<sub>MSE</sub> in 5M NaOH + 1.2mM Tartrate + 1mM Co(NO<sub>3</sub>)<sub>2</sub> electrolyte [1] followed by the deposition of FeCoO<sub>x</sub> at -0.50 V<sub>MSE</sub> in 1M NaOH + 1.2\*(1+x) mM Triethylamine + 1mM CoCl<sub>2</sub> + x mM FeCl<sub>3</sub> electrolyte with x in the range of 0.5-2. Deposition of both films took place at reflux temperature under Ar atmosphere. At the end of the deposition procedure, the sample was transferred in air to the X-ray cell. Films were typically 20 nm thick (CoOOH ~10 nm thick). Deposition took place in the electrochemistry laboratory of ID03.

The structures of the oxides were first characterised by performing CTRs in Ar atmosphere at the main oxide positions. Figure 1a presents a (10L) scan of FeCoO<sub>x</sub>/CoOOH/Au(111). We can identify Bragg peaks of both films and deduce that both films are epitaxial with the following orientations: (001) for CoOOH and (111) for FeCoO<sub>x</sub>. This L scan clearly shows that we have two separated phases with negligible intermixing.

After filling the cell with alkaline electrolyte, we studied the film strain and thickness as a function of the potential from the double layer up to the OER range. For this purpose, we recorded one of the  $\text{FeCoO}_x$  oxide Bragg peaks with a 2D detector during a potential sweep. The film in-plane and out-of-plane strain and thickness as a function of potential are obtained by fitting the Bragg peak position and width. The results are presented in **Fig 1b-c**. When the potential is swept positively, we observe a reversible decrease in the in-plane and out-of-plane strains. However, these changes are of the order of 0.02% more than one order of magnitude smaller than those obtained for  $\text{Co}_3\text{O}_4$  (0.3 to 0.8% [1]). This difference is clearly due to the presence of Fe in the oxide lattice and needs further investigations. On the other hand, we observe reversible out-of-plane and in-plane size changes with potential of the order of 0.5 nm. Similar changes have been observed on  $\text{Co}_3\text{O}_4$  and are attributed to the formation of a skin layer with different crystallinity. Here, the presence of Fe does not alter the skin layer formation.

## Conclusion

We succeeded in preparing  $\text{FeCoO}_x(111)$  epitaxial films on  $\text{Au}(111)$  precovered by a  $\text{CoOOH}(001)$  film with negligible intermixing between the two films. In addition, we successfully measured simultaneously electrochemical data and SXRD prior to and during the OER. Preliminary data analysis showed that the presence of Fe in the film reduces the potential dependent changes in the strain but does not affect the thickness changes as a function of potential.

## References

[1] F. Reikowski et al, ACS Catal. **9** (2019) 3811

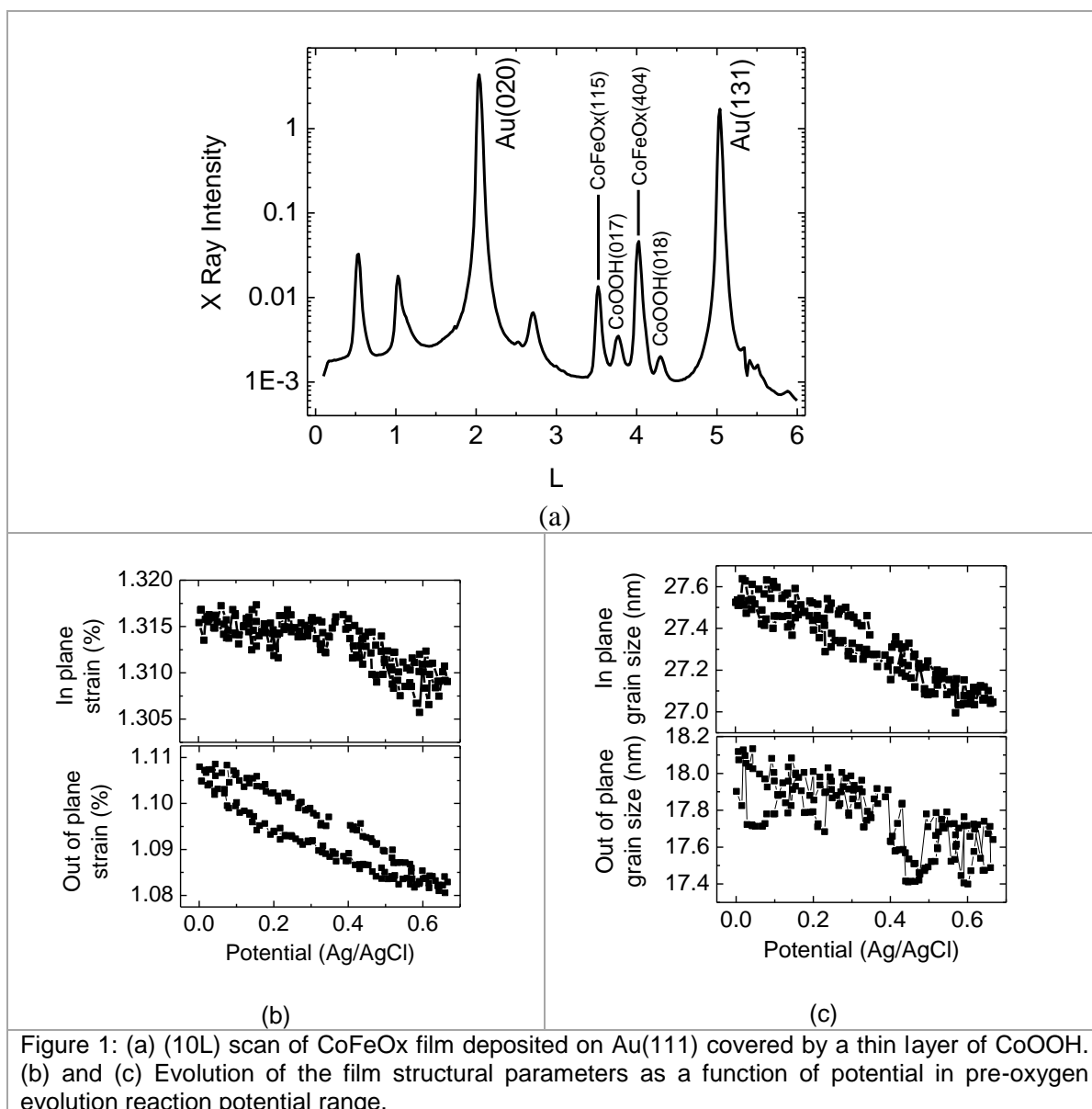


Figure 1: (a) (10L) scan of  $\text{CoFeO}_x$  film deposited on  $\text{Au}(111)$  covered by a thin layer of  $\text{CoOOH}$ . (b) and (c) Evolution of the film structural parameters as a function of potential in pre-oxygen evolution reaction potential range.