



Experiment title: Determining the surface structure / catalytic property relationship of Co oxides grown at high temperature for water splitting

Experiment number:
MA-3886

Beamline:
ID03

Date of experiment:
From: 31 May 2017 to: 5 June 2017

Date of report:
22 Jun 2018

Shifts:
15

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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 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) and optical reflectivity measurements of thin films of two Co oxide phases, prepared electrochemically on Au(111) at high temperature in alkaline media, during oxygen evolution. 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 was 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/cm²) and a camera to monitor the formation of gas bubbles on the sample surface.

Results

The aim of the experiment was to investigate the structure of ultra thin Co₃O₄ and CoOOH films on Au(111) during OER. We used the following preparation procedure: deposition of cobalt oxide at reflux in xM NaOH + 1.2mM Tartrate + 1mM Co(NO₃)₂ electrolyte by stepping the potential to -0.50 V_{MSE}, where x = 2 for depositing Co₃O₄ and x=5 for depositing CoOOH. Deposition took place in a reflux cell under Ar atmosphere. At the end of the deposition procedure, the sample was transferred in air to the X-ray cell. Films were typically 14-18 nm thick.

The structures of the oxides were first characterised by performing CTRs in Ar atmosphere at the main oxide positions. When depositing in the 2 M NaOH electrolyte, we found a (111)-oriented Co₃O₄ in epitaxy with the substrate and no signature of other Co oxide, hydroxide or oxy-hydroxide phases. In contrast, when the 5 M NaOH electrolyte was employed, the deposit corresponded to (001)-oriented CoOOH in epitaxy with the substrate with no presence of other Co oxide or hydroxide phases.

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 Co oxide

Bragg peaks with a 2D detector during a potential sweep. Optical reflectivity measurements and electrochemical current were performed simultaneously. The film out-of-plane strain and thickness peak are obtained by fitting the Bragg peak position and width along L . The results are presented in **Fig 1** for Co_3O_4 and **Fig. 2** for CoOOH . For Co_3O_4 , the lattice is slightly compressed ($\sim 1\%$) and the thickness significantly decreases ($\sim 1\text{nm}$) when the potential is swept positively. These reversible structural changes are correlated with clear reversible changes of the optical reflectivity (not shown). All these modifications are mainly taking place before the onset of the OER ($\sim 0.6\text{V}$). For CoOOH layers, the observed changes in the out-of-plane strain is 2 orders of magnitude small and out-of-plane thickness is 10 times smaller. We also studied the influence of the pH on the Co_3O_4 film structure during these potential sweeps (**Fig 1**). In addition to the shift of the curve due to the shift of the OER onset, we observe interesting changes in the potential dependent behaviour. These changes are under detailed analysis. We also studied the influence of the main cation in the electrolyte and no measurable differences were observed.

Conclusion

We succeeded in preparing $\text{Co}_3\text{O}_4(111)/\text{Au}(111)$ and $\text{CoOOH}(001)/\text{Au}(111)$ films on $\text{Au}(111)$ in our ex-situ reflux cell. In addition, we successfully measured simultaneously electrochemical data, SXRD and optical reflectivity prior to and during the OER. Preliminary data analysis showed potential dependent changes in the strain and the thickness of Co_3O_4 films as a function of potential in contrast to CoOOH films.

References

- [1] F. Reikowski et al, *Electrochim. Acta* **197**, 273 (2016)
 [2] R. V. Gudavarthy et al, *Chem. Mater.* **23**, 2017 (2011)

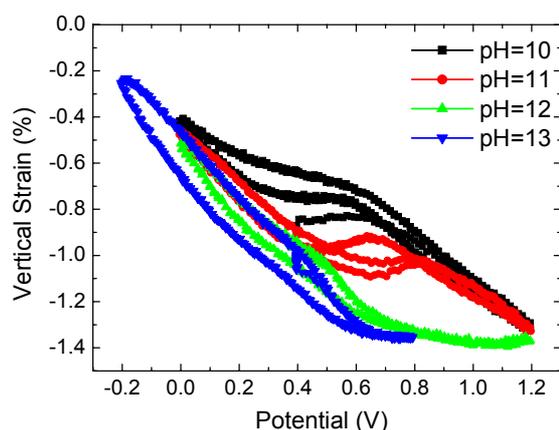


Figure 1a: out-of-plane strain of the Co_3O_4 film as a function of potential at different electrolyte pH.

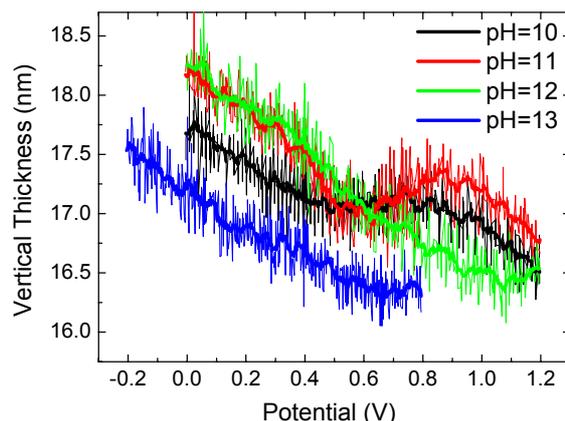


Figure 1b: out-of-plane thickness of the Co_3O_4 film as a function of potential at different electrolyte pH.

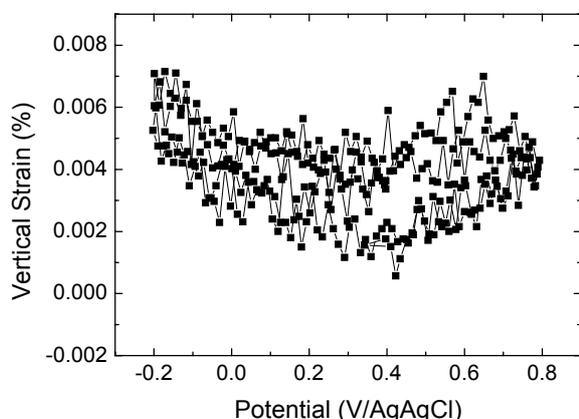


Figure 2a: out-of-plane strain of the CoOOH film as a function of potential. Notice the much smaller changes as compared to Co_3O_4 .

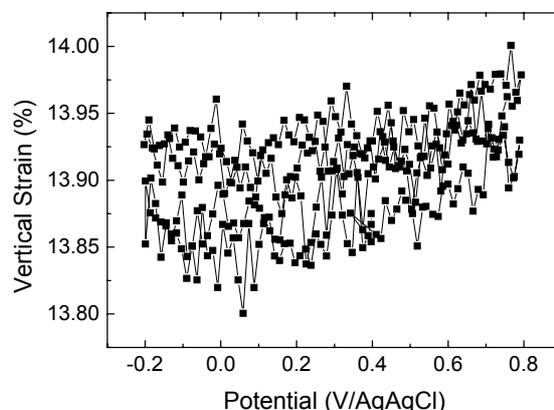


Figure 2b: out-of-plane thickness of the CoOOH film as a function of potential. Notice the much smaller changes as compared to Co_3O_4 .