



Experiment title: In-situ surface X-ray diffraction of electrodeposited Co oxide ultra thin films under water splitting reaction

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MA-3074

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Introduction

Water splitting is one of the most promising routes for renewable energy conversion and storage. Iron group metal oxides 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). In this work we performed operando studies of electrodeposited $\text{Co}_3\text{O}_4/\text{Au}(001)$ thin films during oxygen evolution using surface X-ray diffraction (SXRD) and optical reflectivity. 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 new in situ cell shown in **Fig. 1**. The cell was made from PEEK which also served as an X-ray window. Special care was taken to ensure stable electrochemical operation and XRD measurements even during large gas evolution. The cell was designed 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 deposition and adsorption processes. Electrolyte can be pumped into and out of the cell by a system of 4 syringes (blue arrows in **Fig. 1** indicate direction of flow). This allows us to rapidly (up to 100 $\mu\text{l/s}$) exchange electrolyte and to adjust the electrolyte level inside the cell. The cell has 5 additional inlets at the top. These were used for the reference electrode (RE) and an inlet and an outlet for Ar gas. The last 2 inlets were used for a glassy carbon electrode and a Pt electrode which served as water level detectors. They could also be connected as an additional counter electrode (CE) allowing large currents ($\sim 20 \text{ mA/cm}^2$) during OER. A camera was mounted inside the cell 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 Co_3O_4 films on Au(001) and Au(111) during OER. We used two different approaches to deposit the oxide. The first approach was to deposit epitaxial Co layers on Au(111) and Au(001) using the method developed in our previous experiments [1] (see report MA-2254, MA-2858). The Co film was deposited from 0.1 M NaClO_4 + 1.3 mM HCl + 1 mM CoCl_2 . After removing Co ions from the solution, the electrolyte was exchanged to 0.1 M NaOH. By stepping the potential to 0.4 V_{Ag/AgCl} we formed an anodic oxide. By measuring the Co CTRs before and after the potential step we could determine the amount of oxide that was formed. Bragg peaks of the oxide were not observed

indicating that the oxide grows in a disordered fashion. A full structural characterisation of the oxide was therefore not possible. In the second approach, we directly deposited Co_3O_4 on Au(001) and Au(111) in 2 M NaOH + 1 mM $\text{Co}(\text{NO}_3)_2$ + 1.2 mM tartrate acid using a reflux cell at 100°C [2]. A film with an equivalent thickness of 17 nm of Co_3O_4 was deposited at a potential of $-0.5 \text{ V}_{\text{MSE}}$. The deposition is performed in a separate cell and then the sample is transferred into the XRD cell.

The structure of the oxide was characterised by CTRs (see **Fig. 2** as an example). We found that a (111)-oriented Co_3O_4 is deposited in epitaxy with the substrate with the Co_3O_4 [02-2] direction parallel to the [220] direction of the Au(001) substrate. This finding is distinct from what was observed for thick layers [2] and is more consistent with the plane interatomic distances. Furthermore, we found evidence for a modified oxide structure which was compressed along the surface normal direction. After initial characterisation of the oxide film, the cell was filled with 0.1 M NaOH to investigate the OER. **Fig. 3** shows simultaneous XRD (recorded with a sampling rate of 1 Hz), optical reflectivity measurements and electrochemical current during a sample potential sweep into the OER regime. The position of the peak on the detector frame was calculated and fitted in order to obtain the potential dependent strain in the in-plane and out-of-plane direction which show a similar trend. The lattice is compressed towards more positive potentials and relaxes at lower potentials. The electrochemical current shows a peak at $0.5 \text{ V}_{\text{Ag/AgCl}}$ which corresponds to the oxidation of Co(III) to Co(IV) [2]. This process is accompanied by a clear change in the optical reflectivity and an increase in the potential dependent compression of the Co_3O_4 lattice. OER starts at potentials more positive than this peak. In this potential range the value of the strain saturates. Similar results were obtained for Co_3O_4 deposited on Au(111).

Conclusion

We successfully measured simultaneously electrochemical data, SXRD, and optical reflectivity during the water splitting reaction on Co oxide model electrocatalysts using our new in situ XRD cell. Thin epitaxial $\text{Co}_3\text{O}_4(111)$ films were deposited on Au(001) and Au(111) in a reflux cell and transferred to the XRD cell. Preliminary data analysis showed potential dependent changes in the strain of a thin film. A detailed data analysis is in progress.

References

- [1] F. Reikowski et al, *Electrochim. Acta* **197**, 273 (2016)
- [2] J.A. Koza et al, *Chem. Mater.* **24**, 3567 (2012)

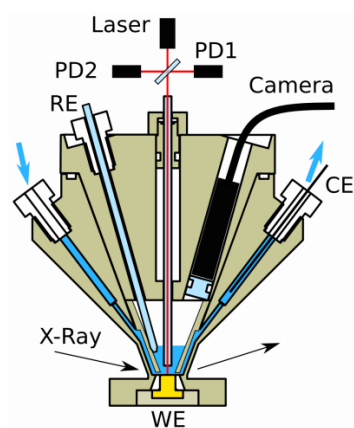


Fig. 1: SXRD cell for in situ measurements during gas evolution. The working electrode (WE) is a hat shaped Au single crystal. The counter electrode (CE) is placed in the electrolyte outlet, the reference electrode (RE) is brought close to the WE. A laser and two photo diodes (PD1/2) are used to measure the optical reflectivity.

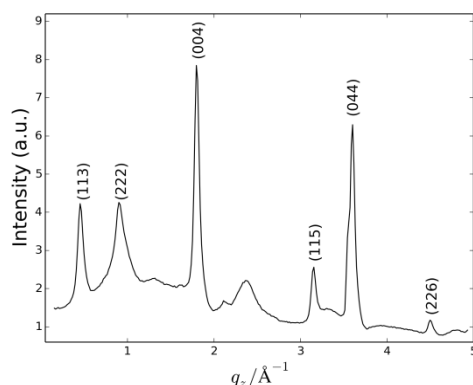


Fig. 2: CTR of Co_3O_4 deposited on Au(001). The observed Bragg peaks correspond to those expected from Co_3O_4 bulk diffraction. The oxide was observed to grow with a (111) orientation, the Co_3O_4 [02-2] direction was parallel to the [220] direction of the Au(001) substrate. Other unlabelled peaks correspond to powder rings of PEEK used for the cell walls. The broad peak at $q_z = 2.4 \text{ \AA}^{-1}$ corresponds to a modified oxide structure.

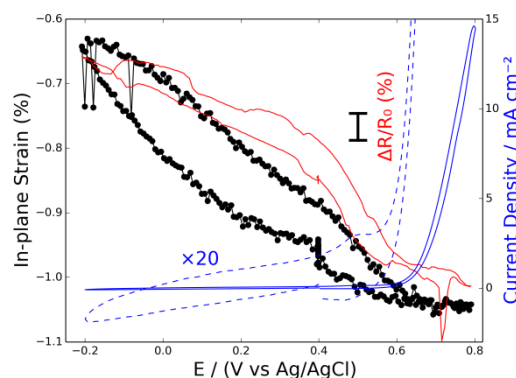


Fig. 3: Simultaneous XRD and optical reflectivity measurement during a potential sweep into the OER regime. The in-plane strain (black curve) was determined from the position of the $\text{Co}_3\text{O}_4(044)$ peak shown in Fig. 2. The electrochemical current (blue curve, blue dashed curve magnified by 20), shows a peak at 0.5 V which corresponds to the oxidation of Co(III) to Co(IV). OER commences at more positive potentials. Large changes in the in-plane strain and the optical reflectivity can be seen at potentials negative of the OER.