



	Experiment title: Ni-Fe oxide model catalysts for water oxidation	Experiment number: MA-3589
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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 and NiFe 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 (SXR) and optical reflectivity measurements of Fe and NiFe oxide thin films, prepared electrochemically on Au(111), 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 Fe and NiFe oxide films on Au(111) during OER. We used two different preparation procedures: (i) deposition in the X-ray cell of the metal film (Fe or NiFe) followed by electrochemical oxidation in alkaline electrolyte in the X ray cell; (ii) direct deposition of the oxide at high temperature in a reflux cell, followed by the transfer of the sample in air to the X ray cell. In the first procedure, the deposition of the metal layers on Au(111) was done in a similar manner as for depositing Co epitaxial layers [1] (see also reports of MA-2254, MA-2858). The Fe (respectively NiFe) film was deposited from 0.1 M NaClO₄ + 1.3 mM HCl + 1 mM FeCl₂ (respectively 0.5 mM FeCl₂ + 0.5 mM NiCl₂) After removing Fe (and Ni) ions from the solution, the electrolyte was exchanged to 0.1 M NaOH. By stepping the potential to 0.6 V_{Ag/AgCl} (Fe) or 0.5 V_{Ag/AgCl} (NiFe) we form the anodic oxide. SXR confirm that metallic films are crystalline and in epitaxy with Au but Bragg peaks of the oxides, hydroxydes and oxyhydroxydes were not observed in spite of an extensive search in the reciprocal space. This suggest the absence of long range order of Fe and NiFe anodic oxides prepared in these conditions. On the other hand,

we could determine how the oxide forms by measuring the bcc Fe and fcc NiFe CTRs before and after the potential step into the oxidation regime. An example of such investigation is shown in **Fig. 1**: the in-plane grain size and thickness of a 10 ML (2 nm) bcc Fe(110) film undergo major changes upon Fe oxidation and reduction indicating a significant modification of the layer morphology. Similar behaviour has been observed in the case of a 16 ML fcc NiFe(111) layer.

In the second procedure, we directly deposited Fe₃O₄ on Au(111) in 2 M NaOH + 10mM FeCl₃ + 12 mM triethanolamine using a reflux cell at 80°C using the same procedure as in Ref [2]. A film with an equivalent thickness of 20 nm of Fe₃O₄ was deposited on Au(111) at a potential of $-1 V_{Ag/AgCl}$. The deposition is performed ex-situ in a separate cell and then the sample is transferred into the XRD cell. The structure of the oxide was characterised by CTRs. We found a (111)-oriented Fe₃O₄ in epitaxy with the substrate and no signature of other Fe oxide and oxi-hydroxides phases. After filling the cell with 0.1 M NaOH to investigate the OER, we performed 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 peak on the detector frame was fitted in order to obtain the out-of-plane strain (in black) and film thickness (in red) as a function of potential (**Fig. 2**). The lattice is slightly compressed and the thickness significant decreases towards more positive potentials. These reversible structural changes are correlated with clear reversible changes of the optical reflectivity (in dark blue). All these modifications are mainly taking place at the onset of the OER as given by the electrochemical current (in green). This trend was reproducible. The full datasets are presently analyzed in details to get better insight into these processes.

Conclusion

We succeeded in preparing Fe oxide films in our in-situ XRD cell starting with ultrathin epitaxial Fe films deposited on Au(111). Although these films seems not well crystallized we could obtain insight into the mechanisms of oxide formation by analyzing the modification of the Fe Bragg peaks during oxidation/reduction cycles. In addition, we successfully measured simultaneously electrochemical data, SXRD, and optical reflectivity during the water splitting reaction on Fe oxide film. This achievement was possible by the successful development of an experimental procedure for the preparation of epitaxial Fe₃O₄(111) films on Au(111), which employed deposition in a reflux cell and subsequent transfer into the XRD cell. Preliminary data analysis showed potential dependent changes in the strain and the thickness of a thin film.

References

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

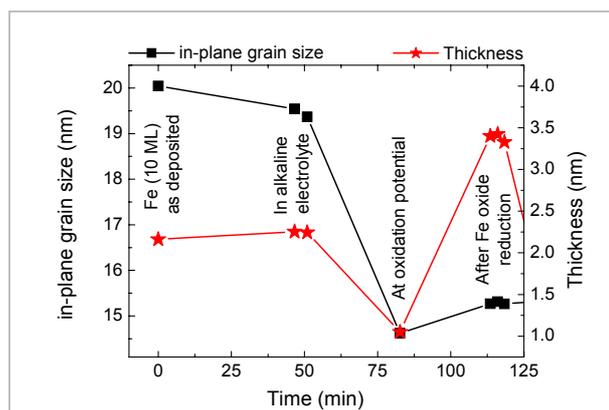


Fig. 1: In plane grain size and layer thickness (as determined from the Fe(10-1) peak at different steps of the Fe layer formation in acidic electrolyte and oxidation and reduction in alkaline electrolyte. Upon oxidation, the in-plane grain size and layer thickness decrease. Upon oxide reduction, the in-plane grain size does not recover whereas the layer thickness completely recovers and increases to a value even larger than the original thickness indicating a significant morphology change after one oxidation/reduction cycle.

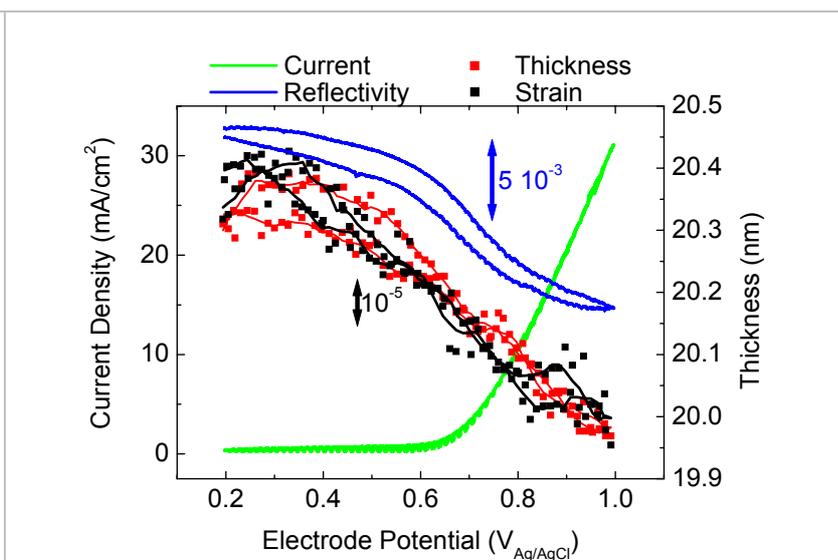


Fig. 2: strain (black with the black arrow scale) and thickness (red) of 20 nm thick Fe₃O₄ film deposited on Au(111) as a function of applied potential in the oxygen evolution regime. These data were obtained by fitting the Fe₃O₄(044) peak and are correlated with the increase in electrochemical current (green), caused by the onset of the oxygen evolution, and concomittant changes in the optical reflectivity (blue with the blue arrow scale). Notice the reversibility of structural changes.