



	Experiment title: Influence of electrochemical environment on the surface structure of magnetite (001)	Experiment number: CH-5314
Beamline: ID08	Date of experiment: from:06/06/18 to: 12/06/18	Date of report: 05/03/20
Shifts: 18	Local contact(s): Helena Isern and Linus Pithan	<i>Received at ESRF:</i>
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Introduction

Metal oxides been proposed as an alternative to precious metal electrocatalyst for reactions of technological interest such as the oxygen reduction reaction (ORR), the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER)¹. Fundamental understanding of the atomic scale structure of metal oxide surfaces under reaction condition is crucial to model the electrochemical reactions and optimize the catalyst design. However, despite of their catalytic relevance, atomic scale studies of metal oxide surface structure under reaction conditions still remains a challenge due to instability of the surfaces under reaction conditions and the fact that most of traditional surface-sensitive techniques require ultrahigh vacuum (UHV) conditions, which are far from real reaction conditions. The aim of the study was to determine the electrochemical potential region in which magnetite surface reconstruction is stable.

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. Magnetite surface was prepared in a UHV sample preparation chamber available in the ID03 beam line by sputtering with Ar⁺ and annealing of the sample in presence of a base O₂ pressure of 10-5 mbar. LEED patterns were adquire in order to check surface quality after preparation. Latter on, the sample was transfered to the EC mounted in the Xray beam.

Results The aim of the experiment was to establish the stable electrochemical region for magnetite reconstruction in 0.1M NaOH. A potential control to the UHV-prepared Fe₃O₄(001) sample was established at an initial potential of 0.20 V, (potential is in the middle of the double layer region). Under these initial conditions the sample exhibits a moderate surface roughness, according to measurements of the Fe₃O₄(001) CTRs (data not shown), which is comparable to previous achievements found for reconstructed Fe₃O₄(001) surfaces under UHV conditions². From this stable value positive and negative electrochemical potentials were tested. Fig. 1a shows the electrochemical current (green) and simultaneously obtained superstructure intensity (blue) during a potential cycle from 0.20 to 0.90 V and back at 20 mV/s. The intensity in the negative sweep is constant down to 0.20 V. Below this potential, the intensity gradually decreases until the peak completely disappears at about 0.80 V indicating the lifting of the reconstruction at negative potentials. In a similar experiment on a second sample, a series of stepwise potential excursions to successively more negative values was applied. In each of those excursions, the potential was first changed stepwise from 0.20 V to the negative potential limit, kept there for a time period of 10 s and then stepped back to 0.20 V. The resulting superstructure intensity after each excursion is plotted in Fig. 1b. In contrast to the behavior in the negative potential range, the reconstruction is remarkably stable at more positive potentials, where oxygen evolution commences. Potential cycles into this regime showed only minor changes in the intensity of the reconstruction rods (Fig. 2a). Furthermore, at a fixed potential of 0.9 V, corresponding to OER current densities of >2 mA/cm², the intensity only slightly decayed over a time period of 45 min (Fig. 2b); on the average by about 0.7% per minute.

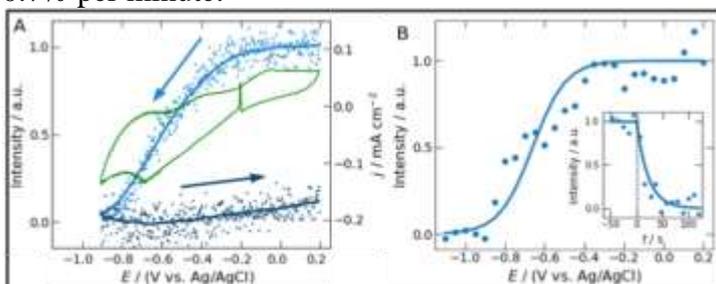


Figure 1. Potential dependence of the relative x-ray intensity changes (measured at (1,2,1.3)) showing the progressive lifting of the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction in 0.1 M NaOH at potentials negative of -0.20 V. (a) relative intensity changes (blue) and simultaneously measured electrochemical current density (green) during a potential cycle from 0.2 to -0.8 V and back at sweep rate of 2mV/s. Arrows indicate the direction of the potential scan. (b) Intensity at (1,2,1.3), measured at 0.20 V after the potential had been kept for 10 s at a more negative potential, which in the course of the experiments was lowered in 50 mV steps down to -1.10 V. In an independent experiment on a fully reconstructed sample (inset), the time-dependent (1,2,1.3) intensity changes after a potential step from 0.20 to -0.80 V (at $t = 0$ s) were monitored, illustrating the fast lifting of the reconstruction (characteristic time constant $\tau_{0.80V} = 22$ s).

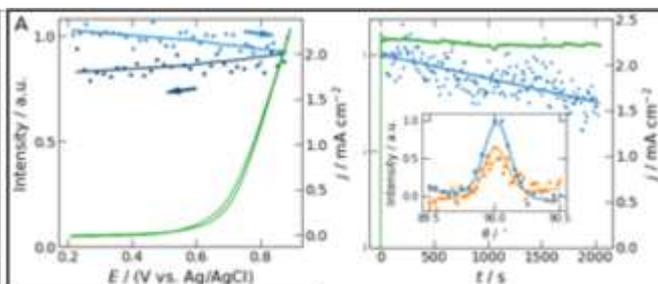


Figure 2. Potential dependence of the relative x-ray intensity (dots) measured at (0,3,0.5) showing the stability of the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction deep in the OER regime in 0.1 M NaOH. The electrochemical current (green line) was recorded simultaneously. Arrows indicate the scan direction (20 mV/s). (b) Time dependence of the normalized x-ray intensity at a constant potential of 0.90 V (dots) and current (green line). Inset: azimuthal scans of the (0,3,0.5) rod before (blue line) and after (orange line) the sample was kept for 1000 s at 1.00 V, where the OER reaches a current density of ≈ 10 mA/cm².

Conclusion This work demonstrates that electrochemical studies of well-defined oxide single crystal electrodes are possible by combining sample preparation in UHV with structure-sensitive in situ / operando methods, such as surface X-ray diffraction. We specifically could show that under suitable transfer conditions, specifically high pH and electrochemical controlled potentials above -0.2 V, the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction of Fe₃O₄(001) is maintained, and both positive and negative potential limits before killing the reconstruction were established.

References [1] Védrine, J. C. *ChemSusChem* **12**, 577-588, doi:10.1002/cssc.201802248 (2019).
 [2] Arndt, B. *Surface Science* **653**, 76-81, doi:https://doi.org/10.1016/j.susc.2016.06.002 (2016).