

**Experiment title:**Combined SXR – Mass Spectrometry based Operando Study of Electrochemical Stability of RuO₂-based Electrodes in the Oxygen Evolution Reaction**Keywords:** electrocatalysis, ruthenium dioxide, operando SXR, stability**Experiment****number:**

MA2635

Beamline: ID03	Date of experiment: from: 09.12.2015 to: 16.12.2015	Date of report: 29.02.2016
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Names and affiliations of applicants (* indicates experimentalists):**Dr. Jan Philipp Hofmann**^{1*}**Prof. Dr. Herbert Over**²**Prof. Dr. Emiel J. M. Hensen**¹¹ Laboratory of Inorganic Materials Chemistry, Dept. Chemical Engineering and Chemistry, Eindhoven University of Technology, Postbox 513, 5600MB Eindhoven, The Netherlands.² Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 17, 35392 Gießen, Germany**1. Stability of RuO₂(110) under oxygen evolution reaction conditions: preparatory lab studies: electroanalysis + OLEMS**

We performed preliminary (lab) experiments studying the structural stability of RuO₂(110)/Ru(0001) under high positive potentials in the oxygen evolution reaction in 0.5 M H₂SO₄. Additionally, we assessed the selectivity of RuO₂(110)/Ru(0001) with respect to the Cl₂ evolution reaction (CER) in aqueous electrolyte by setting up an electrolysis of 5M NaCl solution in 0.01M HCl.

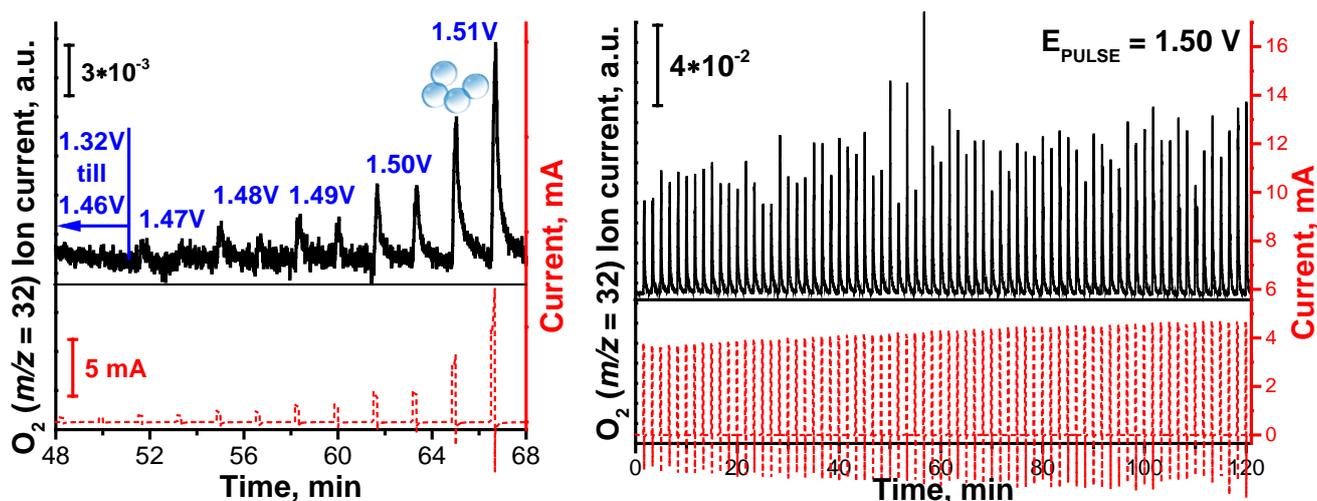


Figure 1. Combined OLEMS-chronoamperogram of RuO₂(110)/Ru(0001) (a) subjected to a stepwise increasing sequence of OER pulses and (b) its stability under repeatable OER pulsing recorded in 0.5 M H₂SO₄.

2. Combination of OLEMS with the *in-situ* electrochemistry cell at ESRF, ID03 – towards operando EC-SXRD/XRR/GISAXS

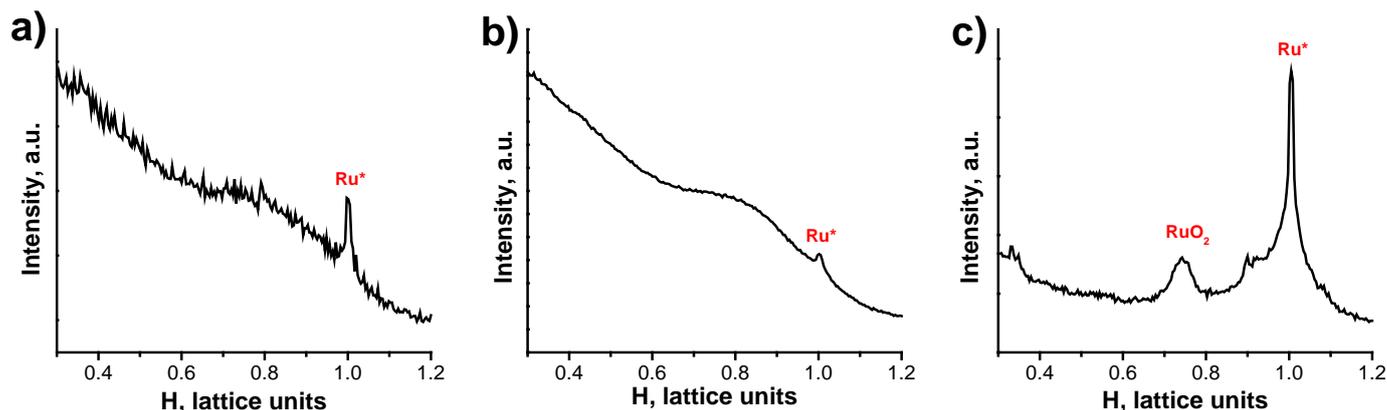


Figure 2. *H*-scan of samples a) $\text{RuO}_2(110)/\text{Ru}(0001)$ _Round-1 in electrolyte, b) $\text{RuO}_2(110)/\text{Ru}(0001)$ _Round-2 in electrolyte and c) outside the cell in Ar atmosphere. The reflexes at $H = 1.0$ belong to the underlying $\text{Ru}(0001)$ substrate, whereas the reflex at $H = 0.73$ are assigned to $\text{RuO}_2(110)$.

At ID03, we tried to acquire reference data of $\text{RuO}_2(110)/\text{Ru}(0001)$ samples prepared in advance at JLU Giessen. We observed a strong overlap of the oxide signal with the cell background resulting in its complete disappearance since it was buried under the broad feature ranging at 0.7–0.9 H units (Fig. 2 a, b). Thus, we took the crystal out of the cell and measured it in dry (inert gas) conditions (Fig. 2 c). Even though the signal of the oxide could be measured in inert gas, its intensity was too low to be observed under electrolyte. The quality of the prepared $\text{RuO}_2(110)$ and the substrate $\text{Ru}(0001)$ is thus very crucial for the electrochemical *in-situ* experiments, making a fresh preparation of the oxide at ESRF necessary.

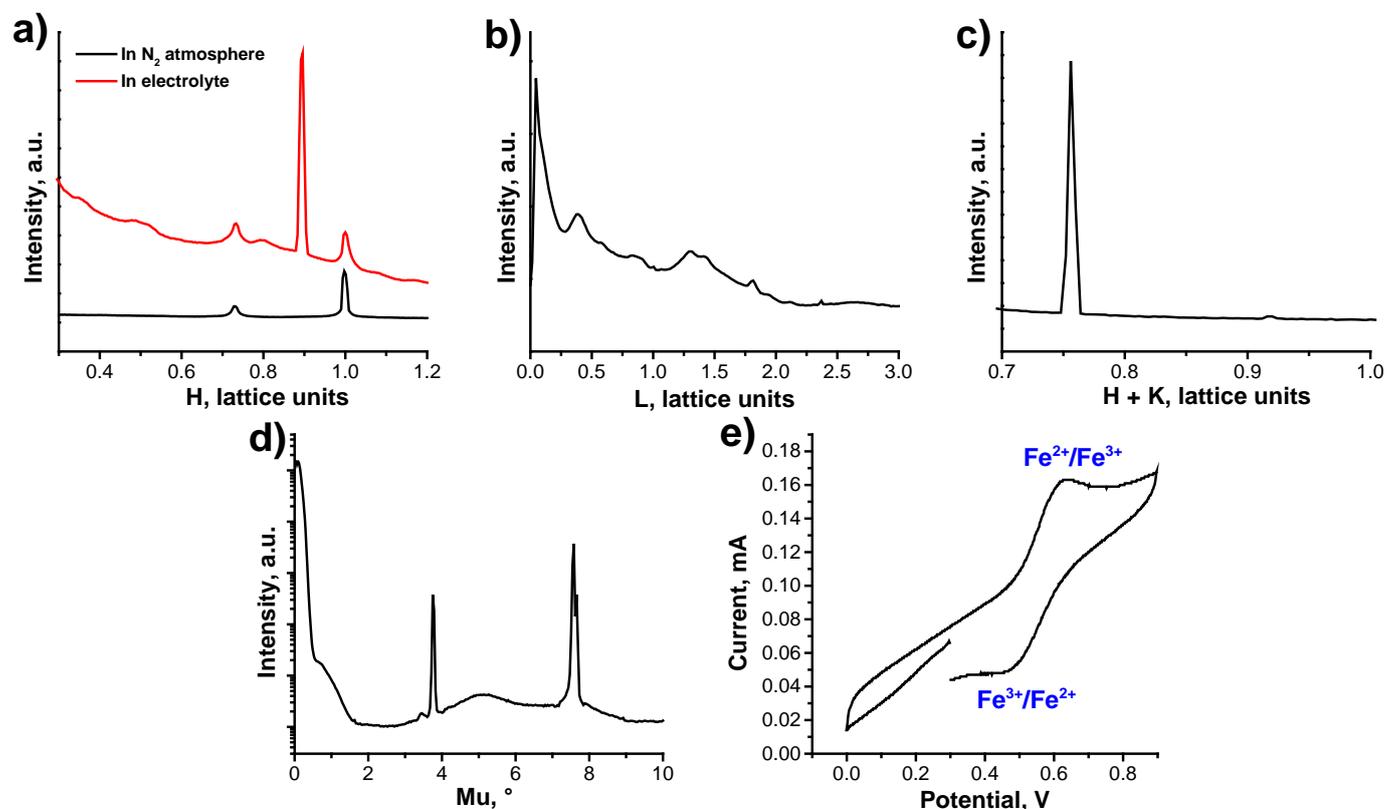


Figure 3. a) *H* scan conducted in N_2 atmosphere (black line) and inside the EC *in-situ* cell (red line), b) *L* scan, c) *H+K* scan, d) extended XRR and e) cyclic voltammogram of $\text{RuO}_2(110)/\text{Ru}(0001)$ electrode in 0.5 M H_2SO_4 .

Finally we succeeded to prepare a good RuO₂(110)/Ru(0001) sample at beamline ID03. Subsequently, we could record structural information in form of H, L, H+K scans and XRR (Fig. 3 a-d) in electrolyte. However, the electrochemical stability experiments were severely hampered by leakage of the cell resulting from the crystal shape and the way of mounting – we observed severe leakage especially visible in the cyclic voltammogram in form of reversible red-ox features of the Fe²⁺/Fe³⁺ couple (from a contact clamp) (Fig. 5 e). The current electrochemical cell at ID03 allows mounting of single crystals of all shapes, however, to be sure to have a leak-free setup, the use of *hat-shaped* crystals turned out to be crucial.

Since no hat-shaped Ru(0001) was available during beam time MA-2635, we would need to re-measure the stability experiments in a (shorter) follow-up beamtime. In conclusion, we could perform preliminary experiments. However, we were facing technical problems (which can easily be overcome in a next beamtime) so that we were not able to finish our original experiment. The preparation, X-ray structural analysis under electrochemical conditions as well as the mass-spectrometric product analysis have been set up and shown to work properly and reliably.