



Experiment title:

Operando SXR – Mass Spectrometry Study of RuO₂(110)/Ru(0001): Identifying Stability Issues in the Oxygen Evolution Reaction

Keywords: electrocatalysis, ruthenium dioxide, in-situ SXR, stability

Experiment number:

MA3073

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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.

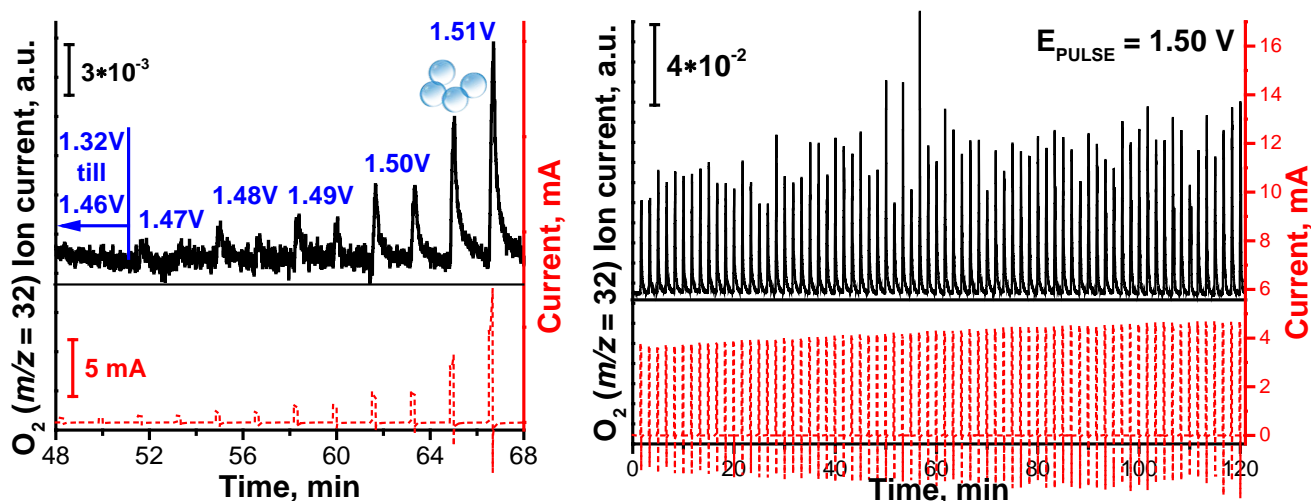


Figure 1. Combined OLEMS-chronoamperogram of RuO₂(110)/Ru(0001) (a) subjected to a stepwise increasing sequence of OER pulses and (b) its stability under repeatable OER pulsing recorded in 0.5 M H₂SO₄.

2. Potential-dependent stability of RuO₂(110) in 0.5 M H₂SO₄. In-situ synchrotron study by means of XRR and H, L scans.

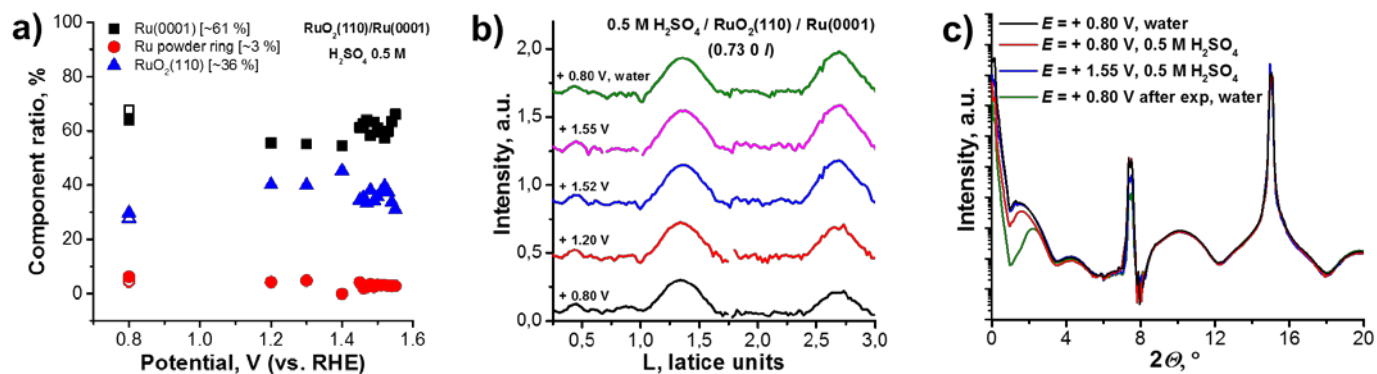


Figure 2. a) Integrated areas of RuO₂(110), Ru(0001) and Ru powder ring components appearing in H scans; b) selected L scans recorded at different potentials during the experiment; c) selected specular and off-specular XRRs recorded at different potentials during the experiment.

At ID03, we studied the stability of RuO₂(110)/Ru(0001) samples (prepared in advance at JLU Giessen) under applied anodic potential pulses. In the first experiment, we utilized 0.5 M H₂SO₄ as electrolyte to run the O₂ evolution reaction (OER). Despite common believe in RuO₂(110) instability under the OER conditions, we did not observe any significant changes of its in- and out-of-plane crystallinity in the range of applied potentials (Fig. 2 a, b). Performed H scans revealed three components attributed to RuO₂(110) ($H_1 = 0.726 \pm 0.006$), Ru(0001) ($H_2 = 0.998 \pm 0.006$) and a Ru powder ring ($H_3 = 0.870-0.930$) (Fig. 2 a). The ratio between the components was found to be constant. Appearance of Ru powder rings was observed prior to the applied EC treatment and thus we could conclude that domains of polycrystalline Ru were initially present on the fresh crystal. The thickness of the RuO₂(110) domains was derived from an analysis of the L scans and found to be constant throughout the experiment (1.3 ± 0.1 nm) (Fig. 2 b). This value is consistent with previously published data. We also analyzed XRRs and found that the roughness of the electrode was not largely affected by the applied anodic treatment (Fig. 2 c). Intensity fluctuations in the specular XRR region were found to be unsystematic and thus more likely to be originated from the extensive gas production or variation in the beam alignment.

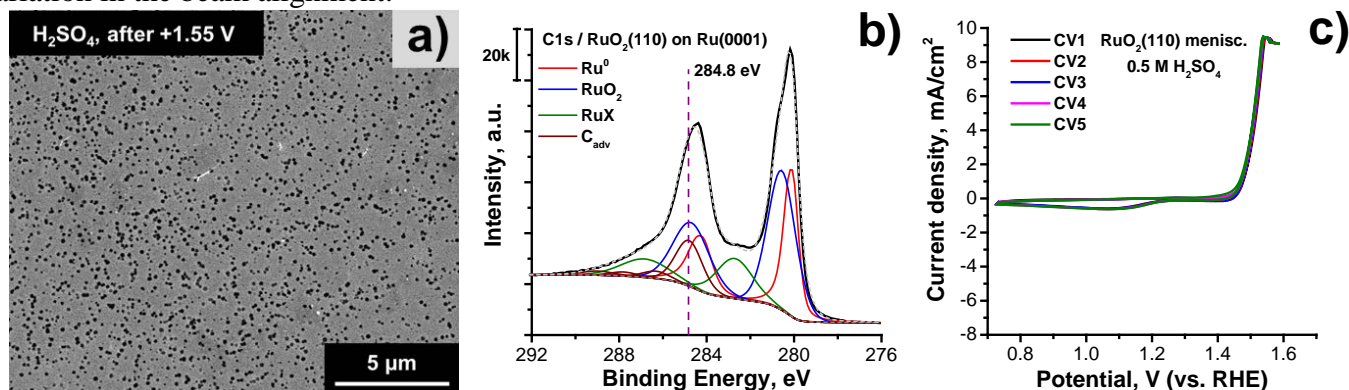


Figure 3. a) Scanning electron micrograph; b) combined C1s/Ru3d XP spectrum and c) cyclic voltammograms of RuO₂(110)/Ru(0001) electrode treated with anodic potential pulses in 0.5 M H₂SO₄.

After the beamtime, we performed additional *ex-situ* characterization of the spent RuO₂(110)/Ru(0001) electrodes. SEM measurements revealed significant pitting of the electrode surface (11.2 % of the total electrode area) caused by the applied electrochemical treatment (Fig. 3 a). The average diameter of these features was determined to be 150 nm. However, based on the synchrotron data recorded at ID03, an impact of those features on the surface crystallinity was not observed. Chemical structure of the electrode was also preserved, as it can be seen from the XPS measurements showing presence of the peaks attributed to Ru⁰,

RuO₂ and RuX (most likely, Ru(OH)₃, hydrated form) (Fig. 3 b). CV measurements conducted in hanging meniscus mode (only surface was in the contact with electrolyte) did not show the presence of Ru⁰ on the surface of the electrode (Fig. 3 c).

3. Potential-dependent stability of RuO₂(110) in 0.5 M HCl. In-situ synchrotron study by means of XRR and H, L scans.

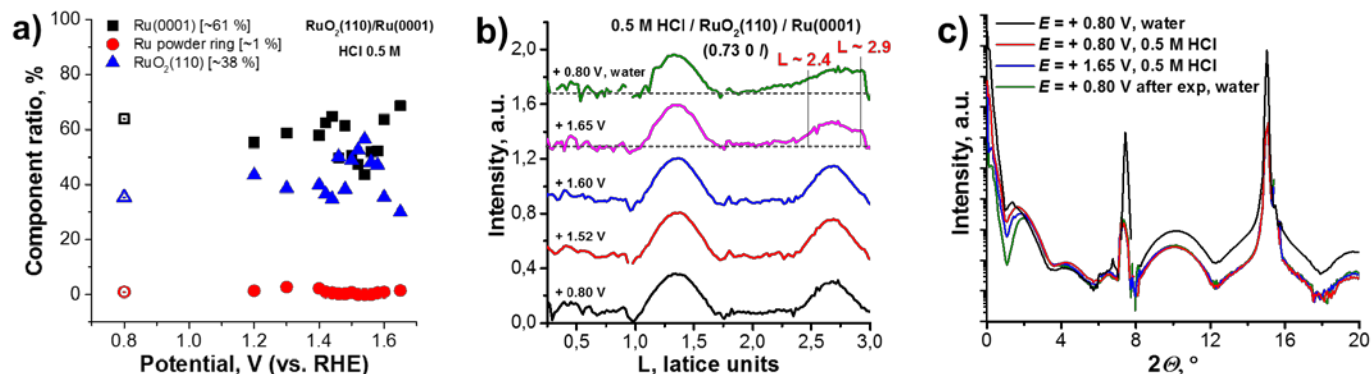


Figure 4. a) Integrated areas of RuO₂(110), Ru(0001) and Ru powder ring components appearing in H scans; b) selected L scans recorded at different potentials during the experiment; c) selected specular and off-specular XRRs recorded at different potentials during the experiment.

In the second experiment, we utilized 0.5 M HCl as electrolyte to initiate simultaneous Cl₂/O₂ evolution reaction (CER/OER, respectively). Similar to the previous experiment, H scans revealed 3 components: RuO₂(110) ($H_1 = 0.727 \pm 0.005$), Ru(0001) ($H_2 = 0.997 \pm 0.005$) and Ru powder ring ($H_3 = 0.884-0.931$) (Fig. 4 a). Ru powder rings were also found on the untreated electrode and thus its appearance is not related to the applied electrochemical treatment. Starting from $E = +1.43$ V, a reversible decrease of Ru(0001) intensity accompanied by a proportional reversible increase of RuO₂(110) intensity was observed in H scans. The fact of reversibility of these changes and extensive CER expected at this potential range made us think that those changes are most likely attributed to Cl₂ production rather than change in the electrode's crystallinity. The size of RuO₂(110) domains was derived from an analysis of the L scans and found to be constant throughout the experiment (1.2 ± 0.1 nm), similar to the previous experiment (Fig. 4 b). However, we also observed the disturbance of the $L = 2.7$ peak at the last two potentials ($E = +1.65$ V and $E = +0.8$ V (recorded in H₂O)). This is most likely related to an overlap with an artefact line appearing at the same region of 2D detector as the signal from RuO₂(110) appears (Fig. 5 a). Also, it can be attributed to a small electrolyte leak which we noticed at the end of the experiment. This leak yielded contamination of the sample surface with elements of the contact plate, including Cu, Zn, Sn and also Si from the sealings (Fig. 5 b). We also analyzed XRRs and found that roughness of the electrode was not largely affected by applied anodic treatment (Fig. 4 c). Intensity fluctuations in specular XRR region were found to be unsystematic and thus more likely to be originated from the extensive gas production or variation in the beam alignment.

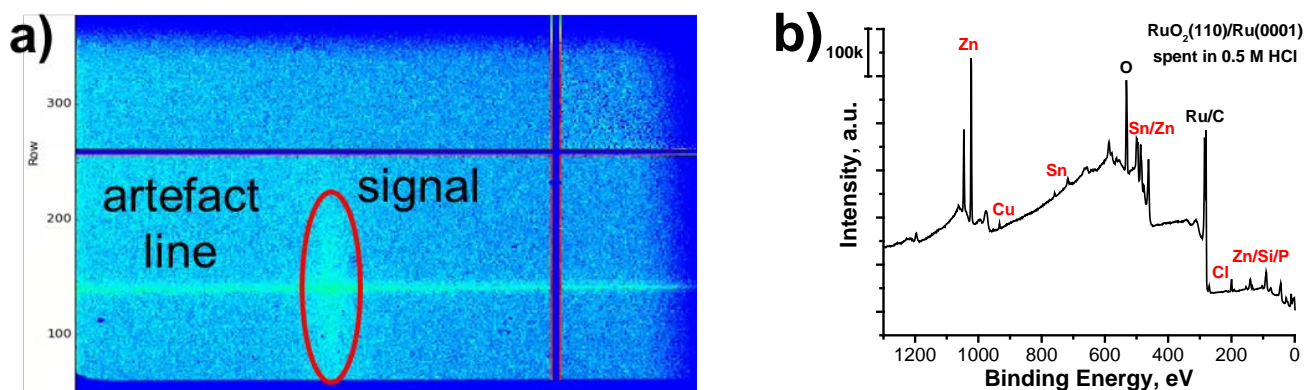


Figure 5. a) An example of the signal overlapping with an artefact line of (yet) unidentified origin; b) survey XP spectrum of RuO₂(110)/Ru(0001) treated with anodic potential pulses in 0.5 M HCl.

SEM measurements of the spent RuO₂(110)/Ru(0001) revealed similar pitting of the electrode surface (13.0 % of the electrode area) caused by the applied electrochemical treatment (Fig. 6 a). However, the average diameter of these features appeared to be higher (220 nm) compared to the previous experiment (being 150 nm). Despite the surface pitting, we did not observe irreversible changes in crystalline structure of RuO₂(110) by any of the synchrotron techniques utilized at ID03. Chemical structure of the electrode – as far as it concerns Ru speciation – was found to be similar to the previous sample, as it can be seen from the XPS measurements showing presence of the same peaks attributed to Ru⁰, RuO₂ and RuX (most likely, Ru(OH)₃, hydrated form) (Fig. 6 b). CV measurements conducted in hanging meniscus mode did not show presence of Ru metal on the electrode surface and thus Ru powder ring signal observed in H scans can rather be attributed to the rim of the crystal (Fig. 6 c). Moreover, it was found that potential cycling in the studied potential window leads to appearance of 2 reduction peaks most likely attributed to reduction of Cl₂ ($E = + 1.36$ V) and other Cl species strongly bound to RuO₂ ($E = + 1.15$ V).

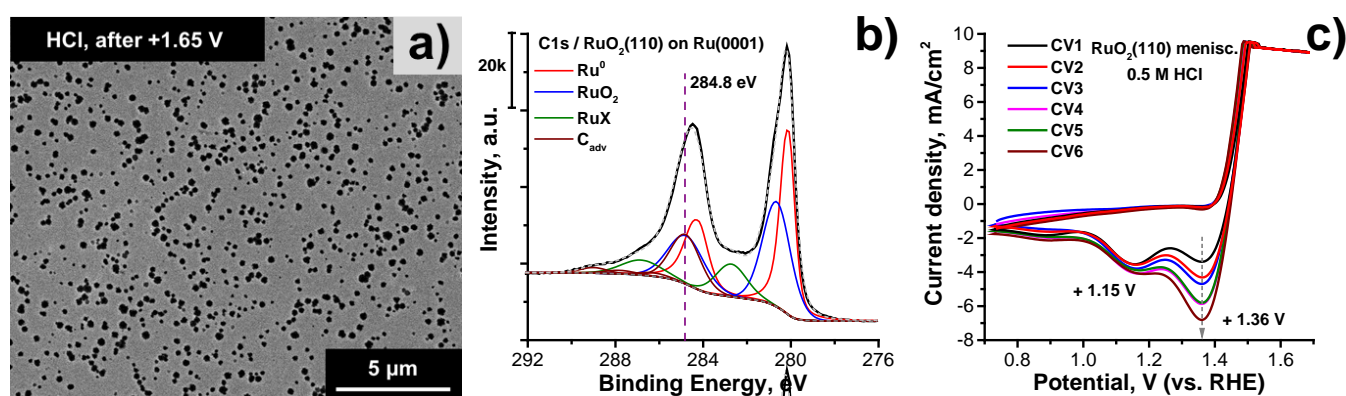


Figure 6. a) SE micrograph; b) combined C1s/Ru3d XP spectrum and c) cyclic voltammograms of RuO₂(110)/Ru(0001) electrode treated with anodic potential pulses in 0.5 M HCl.