

# LOCAL INSTABILITIES IN THE H<sub>2</sub> OXIDATION ON RHODIUM: STRUCTURAL EFFECTS

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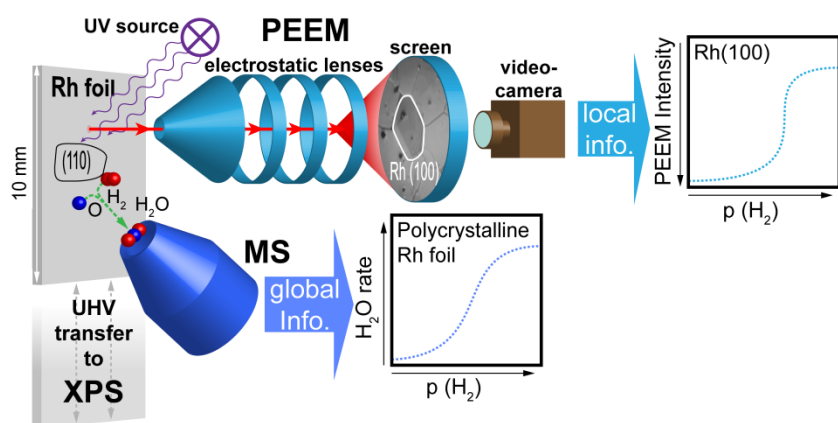
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## MOTIVATION

The catalytic H<sub>2</sub> oxidation is the deciding process in the energy conversion in hydrogen fuel cells. The only product of the reaction is water, therefore the importance of such “green” energy production increases continuously. To improve the efficiency of future generation fuel cells, a deeper understanding of the H<sub>2</sub> oxidation is desirable and thus, intensive theoretical and experimental studies are necessary. Until now, the H<sub>2</sub> oxidation was mainly studied on smooth single crystal surfaces of metals such as Pt, Pd, Rh<sup>[1]</sup>, whereas industrial catalysts are made of noble metal nanoparticles exhibiting different high Miller-index facets on their surface. It is therefore reasonable to create model systems with stepped (high Miller-index) surfaces. Recently, a self-sustained oscillating behaviour of the H<sub>2</sub> oxidation reaction was observed on a Rh foil exhibiting μm-sized stepped domains<sup>[2]</sup>. However, the observed turbulent-like spatiotemporal behaviour is complexly coupled over the whole sample. Therefore, to simplify the model system, we confine the stepped Rh surface, which seems to be necessary for oscillating reaction behaviour, to a small ca. 30 μm wide furrow-like region on a smooth Rh(111) single crystal surface.

## EXPERIMENTAL

For the present studies, a Photoemission Electron Microscope (PEEM) was used as a flow reactor for the H<sub>2</sub> oxidation reaction. In PEEM, the electrons photo-emitted from the studied surface as a result of the UV-light illumination create a strongly magnified, real-time image of the surface. This allows an *in situ* visualisation of surface processes on a μm-scale and a monitoring of ongoing catalytic reactions<sup>[3,4]</sup>. Recently, the novel “kinetics by imaging” approach was developed<sup>[5]</sup>, which links the catalytic activity of the imaged surface to the PEEM image brightness. This approach allows studying of the local kinetics on a μm-scale and thus revealing of structural effects.



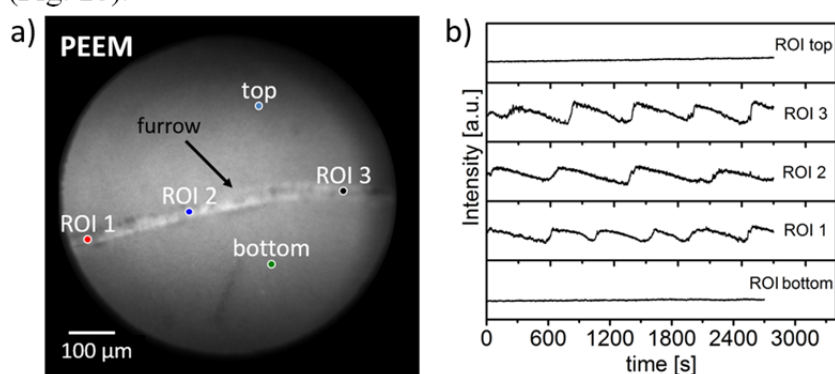
**Fig. 1:** Schema of the experiment: The PEEM is used as a flow reactor in the 10<sup>-6</sup> mbar pressure range. Apart of PEEM, the multipurpose UHV apparatus is equipped with XPS for chemical information and allows fast transfer of the Rh sample between XPS and PEEM under the reactive atmosphere. The MS is used for global kinetic measurements simultaneously to local kinetic measurements by PEEM.

The contrast mechanism of the PEEM is based on the work function of the imaged surface: low work function allows electrons to escape more easily and the PEEM image is bright, a high work function leads to a dark image. Since adsorbed H and O atoms change the work function, the state of the Rh surface (O or H covered, dark or bright, correspondingly) can be monitored by PEEM. In the experiment, the PEEM image is video-recorded and the digitized video-files are analyzed in order to collect the local kinetic information (Fig.1). The Rh sample was a 10x10 mm<sup>2</sup> Rh(111)

single crystal which was cleaned with  $\text{Ar}^+$  ion bombardment and annealed at 1177 K in UHV and at 777 K in  $5 \times 10^{-7}$  mbar of  $\text{O}_2$ .

## RESULTS AND DISCUSSION

The hydrogen oxidation reaction might exhibit self-sustaining oscillations of the reaction rate under stationary conditions. Since the reaction rate depends on the surface coverage, this should also oscillate between the O covered (low activity) and H covered (high activity). Such periodic changes are accompanied by surface pattern formation such as expanding spirals in the reaction front propagation<sup>[4]</sup>. In the present study, we focused on a furrow-like defect (Fig. 2a) exhibiting stepped Rh surfaces on its flanks. After the conditions were set where the polycrystalline Rh foil exhibited oscillating behaviour, variations in the image intensity could be observed within the furrow. When setting ROIs inside the furrow (Fig. 2a) and evaluating the image intensity within the ROIs over time, periodic changes in the local image intensity were detected (Fig. 2b). At the same time, the ROIs set outside the furrow ("ROI top" and "ROI bottom") did not register any intensity variation (Fig. 2b).



**Fig. 2:** a) PEEM snapshot during ongoing  $\text{H}_2$  oxidation at  $p_{\text{O}_2} = 1.1 \times 10^{-6}$  mbar,  $p_{\text{H}_2} = 8.4 \times 10^{-7}$  mbar and  $T = 433$  K. Regions of interest (ROIs) are marked where the local intensity was evaluated; b) Local intensity in marked ROIs over time. Oscillations are registered within the furrow but not on the smooth surface outside.

Since the observed oscillating behaviour is confined to the furrow, it seems like the stepped surface plays a decisive role in the appearance of oscillations. The oscillations can occur if two steady states are possible and a feedback mechanism switching between these steady states is provided. The steady states are the oxygen-covered (inactive) and the hydrogen covered (active) state of the surface. As the feedback mechanism, we assume the incorporation of oxygen under the Rh surface, i.e. formation of the subsurface oxygen. Such a periodic formation and depletion of the subsurface oxygen governs the sticking of oxygen and hydrogen and thus modulates the adsorption and the reaction in an oscillating way. However, the highly stepped Rh surface is necessary to form the subsurface oxygen. This is available on the flanks of the furrow, but not around the furrow where solely the smooth Rh(111) surface is located. In this way the oscillations are confined to the furrow.

## SUMMARY

We show that the oscillations in the  $\text{H}_2$  oxidation only occur within the mesoscopic furrow on the smooth Rh(111) surface. The furrow contains highly stepped surfaces on its flanks and it seems that these steps and defects are necessary for the appearance of oscillations, at least under present conditions. Periodic formation and depletion of subsurface oxygen on the stepped surface is assumed to serve as a feedback mechanism for the observed oscillating behaviour, but further studies are necessary to prove this assumption.

## REFERENCES

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