Anodic Hydrogen Oxidation at Bare and Pt-modified Ru(0001) in Flowing Electrolyte – Theory versus Experiment

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ABSTRACT

This paper reports on electrochemical hydrogen oxidation at atomically smooth single crystal surfaces. These surfaces are considered as planar models for (bi)metallic nanoparticles that are commonly used as catalytically active electrode materials in low-temperature fuel cells. These samples are prepared in ultrahigh vacuum but are characterized under conditions of enhanced mass transport in hydrogen saturated electrolyte. The two examples shown in this paper are Ru(0001), which itself is rather inactive for hydrogen evolution and oxidation and thus reveals insights into the kinetically governed potential dependence of the reaction rates, and an atomically thin layer of Pt supported on Ru(0001). The latter surface turns out to be more active than bulk Pt electrodes. We show that both findings agree very well with predictions based on density functional theory in combination with a simple kinetic model.

INTRODUCTION

The electrode materials in low-temperature fuel cells are requiring electrocatalysts with an optimum performance for the respective reaction. For the oxidation of hydrogen at fuel cell anodes, Pt still is the best pure elemental electrode material. In order to reduce the cost for the fuel cell, however, there is a general interest in minimizing the required amount of Pt whilst keeping the anode performance high. One obvious approach is the attempt to use Pt containing alloys instead of pure Pt. Interestingly, such types of electrode materials not only require less Pt, they may even be superior to pure Pt in some aspects. This is particularly true for fuel cells that are not fed with pure H\textsubscript{2} but rather with a reformate gas that may contain traces of CO. It is known since long that the metal combination Pt+Ru is particularly useful for the fabrication of more CO tolerant electrocatalysts. The present paper, however, will concentrate on the principal reaction itself, i.e., the electrochemical hydrogen oxidation reaction. It will be shown that a single atomic layer of Pt vapor deposited onto a Ru(0001) substrate increases the activity by three orders of magnitude as compared to bare Ru(0001). Activities are compared via the kinetic exchange current density \( j_0 \) for the hydrogen evolution reaction \( \text{HER} \) \( \text{HOR} \). It will further be demonstrated that this behavior can be predicted by combining Density Functional Theory (DFT) data (from ref. \( ^5 \)) with a simple kinetic model (from ref. \( ^6 \)). This follows the approach by Greeley, Kibler, et al., who applied it on Pd monolayers deposited on various substrates. In contrast to the cited work, however, the experimental setup used in the present work not only allows for studies on the hydrogen evolution reaction but also on the hydrogen oxidation. After a description of this setup and the experimental procedures, the paper will first highlight some interesting aspects of the electrochemical behavior of Ru(0001) in H\textsubscript{2} saturated electrolyte. This is followed by a report on the HER \( \text{HOR} \) properties of a pseudomorphic Pt layer on Ru(0001) with a thickness of 1.08 ML, and finally by a comparison to predictions from theory, specifically, a DFT based volcano plot.
EXPERIMENT

Sample preparation. The experiments were performed in an ultrahigh vacuum electrolycrometry (UHV|EC) transfer system. The main UHV chamber (base pressure = $6 \cdot 10^{-11}$ mbar) is equipped with a home-built pocket-size scanning tunneling microscope (STM) and standard facilities for sample preparation and characterization such as an ion gun, a manipulator with a heater using radiation and optional electron bombardment, Auger electron spectroscopy (AES), and a quadrupole mass spectrometer for residual gas analysis. The transfer system itself is described in more detail in ref. The sample preparation was performed by cycles of Ar+ ion bombardment (sputtering) and annealing to temperatures >1100 K, followed by oxygen adsorption/desorption cycles and final annealing to ~1750 K to remove residual adsorbed oxygen. The sample temperature was measured by an infrared pyrometer (Impac Infratherm IGA 140). After the respective treatments, surface imaging by STM revealed atomically smooth terraces of 20–200 nm width, separated by monolayer steps (see Figure 1a). Atomically resolved images confirmed that possible surface contaminations were below the detection limit of AES (0.01 monolayers (ML; 1 ML = one adsorbate or foreign metal atom per substrate surface atom)).

Clean Ru(0001) surfaces were prepared by cycles of Ar+ ion bombardment (sputtering) and annealing to temperatures >1100 K, followed by oxygen adsorption/desorption cycles and final annealing to ~1750 K to remove residual adsorbed oxygen. The sample temperature was measured by an infrared pyrometer (Impac Infratherm IGA 140). After the respective treatments, surface imaging by STM revealed atomically smooth terraces of 20–200 nm width, separated by monolayer steps (see Figure 1a). Atomically resolved images confirmed that possible surface contaminations were below the detection limit of AES (0.01 monolayers (ML; 1 ML = one adsorbate or foreign metal atom per substrate surface atom)).

Platinum was evaporated from an electron beam evaporator (FOCUS EFM 3), with the substrate at 300 K and a deposition rate of about 0.25 ML min$^{-1}$. To attain an atomically smooth surface, the sample was subsequently flash annealed to 850 K. The resulting coverage was determined by quantitative evaluation of STM images and by AES.

Electrochemical measurements. For the transfer into the electrochemical cell the surface was protected by an oxygen adlayer, which was created by O$_2$ exposure at 300 K (10 L exposure). The sample was subsequently transferred into a pre-chamber that was kept at vacuum (10$^{-9}$ mbar) by a turbomolecular pump. After the transfer, the pre-chamber was separated by gate valves from the main chamber and from the turbo pump, respectively, and filled with clean N$_2$ to ambient pressure. Subsequently, a miniaturized electrochemical flow cell, which is made of KEL-F$^\text{®}$ and mounted on the top of a glass tube, was moved up into the pre-chamber through an opened gate valve and brought into contact with the single crystal from below. The single crystal electrode is then pressed to an O-ring gasket (diameter 6 mm, Kalrez$^\text{®}$) on the top of the flow cell by a small wobble stick, which also provides a direct electrical contact to the sample. The same contact tip also measures the sample temperature during the experiment, which was always at T = 297 K. The O-Ring ensures that only the well-defined, smooth part of the surface gets in contact with the electrolyte, which is crucial to avoid electrolyte contact with the sample edges. On the one hand, those might be contaminated by parasitically deposited foreign metals, and on the other hand the edges naturally expose different crystal facets than the main sample area. Those may dominate the overall electrocatalytic activity and then lead to an overestimation of the activity of the actually studied surface. For the kinetic measurements, it is important that the O-Ring allows to work with continuous electrolyte flow ($\sim$ 1 mL s$^{-1}$) for enhanced mass transport. This allowed to attain diffusion limited current densities close to those reached by a rotating disc electrode at 1600 rpm, e.g., at around 2 mA cm$^{-2}$ for the electrooxidation of H$_2$ on a Pt electrode. Cyclic base voltammograms (base CVs) were recorded either in a quiescent or in flowing 0.1 M HClO$_4$ (Mercks, Suprapur) electrolyte. A reversible hydrogen electrode (RHE), which was coupled to the cell via the electrolyte inlet, was used as a reference electrode. All potentials in this paper are given versus RHE. Considering the packing density of Ru(0001), one electron per surface atom is equivalent to a charge density of 0.253 mC cm$^{-2}$. Current and charge densities were divided by this factor to yield turnover frequencies and elementary charges per surface atom, respectively.
Figure 1. (a) STM image of a UHV prepared Ru(0001) single crystal surface; inset: atomic resolution. (b) Cyclic voltammograms of Ru(0001) in flowing H₂-saturated (dotted curve) and H₂-free (solid curve) electrolyte (0.1 M HClO₄, 10 mV s⁻¹). The dashed curve shows j(E) according to the Butler Volmer equation (see text).

Figure 2. Semi-log plot of the data in Figure 1b as used to determine transfer coefficient α and exchange current density j₀ (see text).

Figure 3. (a) STM image of a vapor deposited 1.08 ML Pt film on Ru(0001); (b) voltammogram of the surface in (a) in a flow of H₂ saturated 0.1 M HClO₄ electrolyte; scan rate 10 mV s⁻¹. The curve for Ru(0001) is plotted for comparison but nearly vanishes on this scale.
Results

The dotted line in Figure 1b depicts a cyclic voltammogram (CV) of a clean Ru(0001) surface in 0.1 M HClO₄ solution. This CV has been extensively discussed in previous publications.

Key facts are as follows. At 1.05 V, Ru(0001) is covered by 1 ML of adsorbed oxygen (O_{ad}). In a negative going scan, peak C’ reflects reduction of this adlayer towards 0.5 ML O_{ad}. Peak B’ most likely reflects the attachment of one H atom to each adsorbed O_{ad} via H^{+} reduction, i.e., Ru(0001) is covered by 0.5 ML OH_{ad} at a potential of 0.1 V. Below 0.1 V, an adlayer of H_{ad} becomes more stable than OH_{ad}, which gives rise to the sharp beak A’ that reflects the replacement of 0.5 ML OH_{ad} by 0.5 ML H_{ad}. In the positive going scan, peak A contains the charges of the reversed processes of B’ and A’, i.e., it reflects the replacement of 0.5 ML H_{ad} by 0.5 ML O_{ad}. The latter adlayer is only completed after peaks D and E. Peak C, finally, reflects an increase of the O_{ad} coverage up to 1 ML.

The sluggish replacement of the H_{ad} layer by OH_{ad} and O_{ad} in the positive going scan was previously ascribed to a homolytic pathway of water dissociation, specifically,

\[
\begin{align*}
H_{ad} + H_2O &\to H_3O^+ + e^- + \square \\
2 \square + H_2O &\to OH_{ad} + H_{ad}.
\end{align*}
\]

The square symbol \(\square\) marks a free adsorption site. The assumption of homolytic water dissociation was mainly based on an observed catalytic effect of Pt atoms and islands on the base voltammetry of Ru(0001). It was concluded that the Pt sites act as catalytic channels for the conversion of H_{ad} to H^{+} (or H_{3}O^{+}, see reaction 1) and vice versa. In this picture, reaction (2) in the absence of Pt becomes hindered by a too slow oxidation of its product H_{ad}.

In a flow of H_{2} saturated electrolyte, the CV only changes in the region E < 0.4 V, whereas peaks E, C, and C’ remain largely unaffected. In the region close to the RHE potential (E = 0), where the overall reaction

\[
H_2 + 2 H_2O \leftrightarrow 2H_3O^+ + 2e^-
\]

is (by definition) in equilibrium, the CV adopts a textbook-like Butler-Volmer profile. The positive branch of the curve reflects the H_{2} oxidation reaction (HOR) whereas the negative one belongs to the H_{2} evolution reaction (HER). Figure 2 depicts the HER/HOR CV in a semi-log plot. The straight lines for \(|E| > 0.75 \text{ V}\) confirm the exponential profile of the curves. From the slope of the anodic branch, we deduce a transfer coefficient \(\alpha=0.377\), which is equivalent to a Tafel slope of 165 mV / decade. Intersection with the j-axis yields an exchange current density of \(j_0 = 4.6 \mu A \text{ cm}^2\). The accuracy of these parameters can be verified by the dashed curve in Figure 1b, which plots the Butler Volmer equation

\[
f(E) = j_0 \left( \exp(\alpha(kT/e)E) - \exp((\alpha - 1)(kT/e)E) \right)
\]

using \(j_0 = 4.6 \mu A \text{ cm}^2\), \(\alpha=0.377\), \(kT / e = 0.0256 \text{ V}\) (at \(T = 297 \text{ K}\)). The value of \(j_0\) will be discussed in more below.

The CV in H_{2} saturated electrolyte supports the previous interpretation of peak A, which was attributed to a sluggish and mainly overpotential driven oxidation of H_{ad}. Thermodynamic driving force of the H_{ad} replacement is the even higher stability of OH_{ad} and O_{ad}, but if their formation is associated with new H_{ad} formation, the process is obviously damping its own progress. In the presence of continuous H_{2} supply, reaction (2) can be expected to be further hindered due to H_{ad} formation by H_{2} dissociation according to

\[
H_2 \to H_{ad} + H_{ad}
\]

which would shift the equilibrium in (2) towards the left hand side. In addition, reactions like
\[
\text{OH}_{\text{ad}} + \text{H}_{\text{ad}} \rightarrow \text{H}_2\text{O} \quad (5)
\]
\[
\text{O}_{\text{ad}} + 2\text{H}_{\text{ad}} \rightarrow \text{H}_2\text{O} \quad (6)
\]
would destabilize \(\text{O}_{\text{ad}}\) and \(\text{OH}_{\text{ad}}\) layers in potential regions where they are stable in the absence of an \(\text{H}_2\) supply. Hence, the continuous \(\text{H}_2\) supply shifts the region where \(\text{H}_{\text{ad}}\) is favoured over \(\text{OH}_{\text{ad}}\) or \(\text{O}_{\text{ad}}\) towards higher potentials. In this region, \(\text{H}_2\) oxidation is the predominant electrochemically visible process. In this picture, the sudden drop of the current at \(E > 0.25 \text{ V}\) indicates that reaction (1) becomes so fast in relation to the \(\text{H}_2\) supply that the steady-state number of vacancies in the adlayer eventually allows for a nucleation of the more stable \(\text{OH}_{\text{ad}}\) or \(\text{O}_{\text{ad}}\) phase.

A last interesting feature to be highlighted in the CV in \(\text{H}_2\) saturated electrolyte is the total absence of pseudocapacitive features at \(E<0.2 \text{ V}\). Peak B’ is “interrupted” in the negative going scan and the current “jumps” up to the HOR branch of the Butler-Volmer type curve. One may speculate that the further reduction of the \(\text{O}_{\text{ad}}\) layer towards \(\text{OH}_{\text{ad}}\) and the replacement by \(\text{H}_{\text{ad}}\) still take place, but that those processes involve \(\text{H}_{\text{ad}}\) formed by \(\text{H}_2\) dissociation instead of \(\text{H}^+\) discharge and are thus invisible in the CVs. In total, the continuous \(\text{H}_2\) supply and the concomitant chemical surface reactions shifts the “adlayer exchange potential”\textsuperscript{16} where \(\text{H}_{\text{ad}}\) becomes favoured over \(\text{OH}_{\text{ad}}\) (and vice versa) from 0.1 \text{ V} towards a point in the hysteresis interval 0.2 \text{ V} < E < 0.25 \text{ V}.

Figure 3a shows an STM image of the morphology of 1.08 ML Pt vapor deposited to Ru(0001). The morphology and (electro-)chemical properties of this and similar Pt films has been extensively discussed previously.\textsuperscript{10,11,16,18-20} In agreement with predictions by DFT,\textsuperscript{5,16,21} the surface in Figure 3a was found to have a largely featureless base CV. In particular, \(\text{H}_{\text{ad}}\) and \(\text{OH}_{\text{ad}}\) related features are shifted to lower and higher potentials as compared to Pt(111), respectively. This results from the compressive lattice strain due to the pseudomorphic growth in combination with the Pt-Ru bonds. Due to the higher reactivity of Ru, Pt is bound more strongly to Ru than to Pt. Hence, the bonding power of Pt for the interaction with adsorbing species is reduced (“vertical ligand effect”). More specific, the compressive lattice strain and the heterogeneous metal-metal bond both cause a downshift of the d-band, which in turn generally weakens the interaction with many adsorbates.\textsuperscript{5,18,21,22}

The weaker adsorption of hydrogen has the potential to further promote the HER|HOR at the Pt thin film as compared to the surface of bulk platinum. Figure 3b shows the CV of 1.08 Pt / Ru(0001) in a flow of \(\text{H}_2\) saturated perchloric acid solution (black curve). For comparison, the corresponding curve for bare Ru(0001) (i.e., the CV from Figure 1b) is plotted as red line into the same graph. Due to the much higher currents attained at the Pt film, however, the Ru(0001) related curve is hardly distinguishable from the \(j=0\) line. For the Pt film, an evaluation of the current density via a half-logarithmic plot does not appear feasible. Instead, we follow the procedure used by Markovic et al. in ref.\textsuperscript{23}, which evaluates the slope \(dj/dE\) in an interval of \(-0.01 \text{ V} < E < 0.01 \text{ V}\), i.e., just close to the equilibrium potential \(E = 0 \text{ V}\). We find a slope of 100 mA cm\(^{-2}\) V\(^{-1}\). According to \(j_0 = (kT/e) (dj / dE) = 8.617 \cdot 10^{-5} \cdot \text{V} \cdot \text{K}^{-1} \cdot 297 \text{ K} \cdot 100 \text{ mA cm}^{-2}\) we thus attain \(j_0 = 2.6 \text{ mA cm}^{-2}\). This is more than five times higher than the value reported for Pt(111) at 303 K (\(j_0 = 0.45 \text{ mA cm}^{-2}\)).\textsuperscript{23}

**DISCUSSION**

Qualitatively, the orders of magnitude that distinguish the HER|HOR exchange current densities at Ru(0001) with and without the Pt layer can easily be rationalized – the key factor is the high affinity of Ruthenium to all kinds of adsorbates, which in the case of \(\text{H}_2\) oxidation
means that Ru will readily dissociate H\textsubscript{2} and form H\textsubscript{ad}. The high stability of H\textsubscript{ad}, however, makes H\textsuperscript{+} formation comparably unfavourable, thus introducing a high barrier for this process and also the reverse one of forming H\textsubscript{2} out of 2 H\textsubscript{ad}. The optimum level of reactivity required for a catalyst to promote a certain reaction most effectively is commonly rationalized by the Sabatier principle, i.e., any catalyst should rather be too inert no too reactive. For HER|HOR at atomically smooth surfaces, Greeley, Kitchin and coworkers have suggested a simple kinetic model, which, in combination with adsorption energy values for H\textsubscript{2}, was already shown to have a good predictive capability. Apart from DFT calculated adsorption energies, the model only requires a single fit parameter, which is a pre-exponential factor derived from the known behavior of some pure metal surfaces. Figure 4 shows the volcano-curve that was used in the cited work. To use it as reference for the surfaces studied here, one needs the adsorption energies of H\textsubscript{2} on Ru(0001), 1 ML Pt/Ru(0001), and 2 ML Pt/Ru(0001). These have been calculated recently in a consistent data set, and the results were shown to successfully predict the potential dependent H\textsubscript{ad} formation in base CVs of Pt mono- and multilayers on Ru(0001). The required parameters are listed in Table 1. The table also shows the Gibbs free energies of hydrogen adsorption and the resulting predicted exchange current densities for HER|HOR. Both parameter sets were determined according to the procedures shown in ref. 

The points in Table 1 are represented by open circles along the line of the volcano plot itself. For Ru(0001) as very reactive surface, one has to expect a H\textsubscript{ad} coverage higher than 0.25 ML under conditions of H\textsubscript{2} in the solution. As an extreme case, one may expect a coverage slightly beyond 1 ML H\textsubscript{ad}, which according to ref. will make the adsorption energy less negative by at least 0.1 eV as compared to 0.25 ML H\textsubscript{ad}.

![Volcano plot showing the DFT predicted and measured exchange current densities for HER|HOR on various model surfaces (see text).](image-url)
Table 1. Enthalpies of adsorption $\Delta H_{ads}$ for $\frac{1}{2} H_2 \rightarrow H_{ad}$, free energies of adsorption $\Delta G_{H^*}$ on selected model surfaces, HER|HOR exchange current density $j_0$ according to theory and experiment (see text); $\Delta H_{ads}$ values according to DFT calculations in ref. 5 for $H_{ad}$ coverage of 0.25 ML (for the value at ~1.1 ML $H_{ad}$ on Ru(0001): see text); $\Delta G_{H^*} = \Delta H_{ads} (H_2) + 0.24$ eV. 6

| Surface          | $\Delta H_{ads}$ (eV) | $\Delta G_{H^*}$ (eV) | $j_0$ (HER|HER)/ theory (mA cm$^{-2}$) | $j_0$ (HER|HER)/ experiment (mA cm$^{-2}$) |
|------------------|------------------------|------------------------|---------------------------------------|------------------------------------------|
| Ru(0001) @ 0.25 ML $H_{ad}$ | -0.531                | -0.291                 | 0.0006                                | (H$_{ad}$ coverage unknown)              |
| Ru(0001) @ ~1.1 ML $H_{ad}$ | -0.431                | -0.191                 | 0.029                                 |                                          |
| Pt(111)          | -0.351                | -0.111                 | 0.65                                  | (ref. 23) 0.45                          |
| 2 ML Pt / Ru(0001)| -0.231                | +0.009                 | 20.9                                  | 2.1                                      |
| 1 ML Pt / Ru(0001)| -0.081                | +0.159                 | 0.1 (1.1 ML Pt)                       | 2.6                                      |

The value of $j_0$ measured for Ru(0001) lies between the predictions for high and low $H_{ad}$ coverage. This is indicated by the two full circles connected by a horizontal line on the left side of Figure 4. The horizontal line reflects the experimentally observed value for $j_0$, whereas the two terminating circles stand for the two extreme cases of the $H_{ad}$ coverage under reaction conditions, which go along with two different DFT based predictions for the adsorption energies. According to the prediction via the combination of refs 5 and 6, 2 ML Pt on Ru(0001) should have properties close to the optimum that one can achieve with planar model surfaces – very close to the prediction for a Pd monolayer on a PtRu alloy in ref. 7. 1 ML Pt on Ru(0001), however, should still be slightly less active than Pt(111).

For a quantitative comparison of the experimentally prepared 1.08 ML Pt surface with the DFT based predictions, however, one must consider that the STM data in Figure 3a reveals the coexistence of areas with local layer thicknesses of 0 ML, 1 ML, and 2 ML Pt. According to Table 1, the areas with locally 2 ML Pt should be expected to be much more active than those with 1 ML Pt, specifically, by a factor of more than 200. Hence, the 10 % of the surface that have a local Pt thickness of 2 ML will dominate the overall activity and should yield an exchange current density of 2.1 mA cm$^{-2}$ as surface average, in good agreement with the experimental value of 2.6 mA cm$^{-2}$. In Figure 4, the 1.08 ML Pt surface is represented by a short horizontal line that is terminated by two circles representing 1 ML and 2 ML Pt. The lines terminated by the open and closed circles represent the predicted and measured exchange current densities, respectively.

CONCLUSIONS

The electrochemical evolution and oxidation of hydrogen on Ru(0001) and on atomically thin Pt layers on Ru(0001) is strongly influenced by the strong and weak adsorption of hydrogen on these surfaces, respectively. The electrocatalytic activities, represented by the electrochemical exchange current densities, can be predicted by DFT based adsorption energies in combination with a simple kinetic model. That model predicts a volcano behavior of the exchange current density as a function of the Gibbs free energy of hydrogen adsorption. Ru(0001) has an exchange current density of coarsely 5 µA cm$^{-2}$ and a transfer coefficient of $\alpha=0.37$ for the hydrogen oxidation branch. The latter corresponds to a Tafel slope of 165 mV/decade. Ru(0001) covered by 1.08 atomic layers of Pt yields an exchange current density of 2.6 mA cm$^{-2}$. This activity is
higher than the one of Pt(111) by about a factor of five. The exchange current densities predicted by the DFT based volcano curve agree with the findings in this paper. This confirms the predictive capability of DFT for model systems where the experimental approach allows for a good control of surface composition and structure.

Furthermore, the presented data also revealed interesting insights into the potential dependent adlayer formation on Ru(0001). Only positive of 0.42 V, cyclic voltammograms in plain and H\textsubscript{2} saturated electrolyte become identical. In the potential window 0.25 V < E < 0.42 V, there is evidence for little but measurable H\textsubscript{2} oxidation superimposed to the potential dependent adlayer (trans-)formation. At E > 0.42 V, where the O\textsubscript{ad} coverage exceeds 0.5 ML, H\textsubscript{2} oxidation is completely suppressed. In the region E < 0.2 V, however, the voltammogram of Ru(0001) in H\textsubscript{2} saturated solution does not show any pseudocapacitive currents, but is totally dominated by the H\textsubscript{2} oxidation/evolution currents that form a textbook-like Butler-Volmer-type curve. If any significant changes in the adlayer take place at all in this regime, this could only occur via non-electrochemical surface reactions that are invisible in the CVs, e.g., by consuming H\textsubscript{2} in chemical surface reactions.

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