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Water on well-defined platinum surfaces : an ultra high vacuum and electrochemical study

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Citation

Niet, M. J. T. C. van der. (2010, October 14). *Water on well-defined platinum surfaces : an ultra high vacuum and electrochemical study*. Retrieved from <https://hdl.handle.net/1887/16035>

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*I didn't fail the test, I just found 100
ways to do it wrong.*

Benjamin Franklin
(1706–1790)

11

Water dissociation on well-defined platinum surfaces: the electrochemical perspective

Abstract We discuss three important discrepancies in the current interpretation of the role of water dissociation on the blank cyclic voltammetry of stepped platinum surfaces. First, for H adsorption both H-terrace and H-step contributions have been identified, whereas for OH adsorption only OH-terrace has been identified. Second, different shapes (broad vs. sharp) of the H-terrace and H-step peaks imply different lateral interactions between hydrogen adatoms at terraces and steps, i.e. repulsive vs. attractive interactions. Third, the H-step peak has a non-trivial pH-dependence of 50 mV_{NHE} per pH unit. We propose here a model that can explain all these observations. In the model, the H-step peak is not due to just ad- and desorption of hydrogen, but to the replacement of H with O and/or OH. The O : OH ratio in the step varies with step geometry, step density and medium. In alkaline media relatively more OH is adsorbed than in acidic media where more O is adsorbed. This would explain the anomalous pH dependence and provide a possible explanation for the higher catalytic activity in alkaline media for electro-oxidation reactions.

11.1 Introduction

The interface between a platinum electrode and an aqueous electrolyte solution is arguably the most frequently studied electrode–electrolyte combination in all of electrochemistry. The reactivity and dissociation of water at the platinum–aqueous electrolyte interface, in particular the effect of platinum surface structure, is of immense importance to electrocatalysis.¹⁹⁶ The electrochemical signature of the platinum–aqueous electrolyte interface is its blank cyclic voltammetry (CV). Its interpretation in terms of hydrogen adsorption or hydrogen underpotential deposition (H_{UPD}) (at potentials below ~ 0.35 V vs. RHE, reversible hydrogen electrode), double-layer region (at potentials between 0.35 and 0.6 V_{RHE}), and OH adsorption and/or oxide formation (at potentials above 0.6 V_{RHE}), with some of the border potentials depending on surface structure, electrolyte cation and anion, voltammetric scan rate, and scan direction, is well accepted and discussed in many textbooks.¹¹⁴ Much of our current understanding of the blank cyclic voltammetry of platinum comes from the many detailed experiments that have been carried out with single-crystalline platinum electrodes since the seminal work of Clavilier.^{197–202} These measurements have formed the basis for linking the platinum surface structure and surface species formed to the electrochemical response.

The first modeling attempts to compute current–voltage relationships based on a statistical-mechanical description of the platinum–solution interface date back to Armand and Rosinberg.²⁰³ This work was later taken further by others, and has led, for instance, to the conclusion that the adsorption of hydrogen at the Pt(111)/electrolyte interface is well approximated by a mean-field (or “Frumkin”) isotherm, implying relatively weak repulsive interactions between the adsorbed UPD hydrogen.^{99–101} Moreover, the hydrogen adsorption energy and the interaction energy between adsorbed hydrogens are very similar to those at the Pt(111)/ultra high vacuum (UHV) interface, as obtained either by experiment or by first-principles density functional theory (DFT) calculations.²⁰⁴ This result implies that apparently water has little influence on the adsorption properties of hydrogen on Pt(111).

The issue under specific consideration in this chapter is illustrated in figure 11.1, which displays the voltammetry of Pt(111) (a) and the stepped Pt(553) (b) and Pt(533) (c) surfaces in both acidic (perchloric) and alkaline solution. Crystallographically, the Pt($n,n,n-2$) surface is a surface consisting of n -atom wide terraces of (111) orientation and steps of (111) orientation, or $n-1$ atom wide terraces of (111) orientation and steps of (110) orientation. Electrochemically, the steps behave like (110)-type sites. Therefore, we shall consider the surface as having (110) steps in the rest of this work. The Pt($n+1, n-1, n-1$) surface consists of n atom wide terraces with (100) steps. Perchloric acid is chosen as the acidic electrolyte here as the influence of co-adsorbing anions should be absent or minimal. The voltammetry of Pt(111) in perchloric acid and sodium hydroxide (figure 11.1a) consists of two

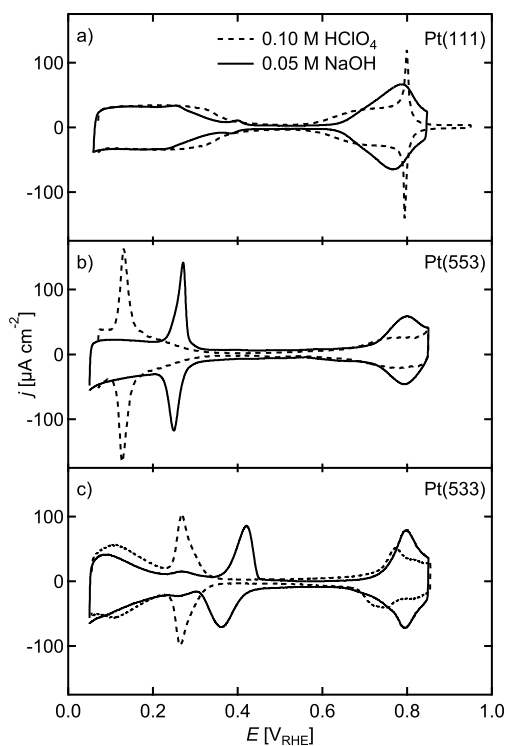
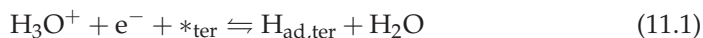


Figure 11.1 Cyclic voltammetry profiles of (a) Pt(111), (b) Pt(553), and (c) Pt(533) in 0.1 M HClO₄ solution and 0.05 M NaOH taken at 50 mV s⁻¹.

main peaks: a hydrogen adsorption-desorption feature (to be referred to as “H-ter” from now on) at 0.05–0.35 V_{RHE}, and a hydroxyl (OH) adsorption-desorption feature (to be referred to as “OH-ter” from now on) between 0.6 and 0.85 V_{RHE}. Note that the fact that both features occur at the same potential on the RHE scale implies a “trivial” pH dependence, *i.e.* a surface reaction involving one proton being exchanged with the solution per transferred electron. The fact that adsorbed hydrogen is formed in the H-ter feature has been confirmed using Fourier transform infra red (FTIR) spectroscopy^{190,205} (suggesting H to be adsorbed in the hollow sites), and the observed pH dependence is of course in complete agreement with a reaction of the type:



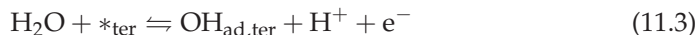
or



where “ter” stands for a (111) terrace site. In elegant thermodynamic work,

Jerkiewicz has shown that from the H-ter feature one can extract the H adsorption energy on Pt(111), and that this value agrees well with the value for H adsorption at the Pt(111)-vacuum interface.⁹⁹ Moreover, the shape of the H-ter feature is modeled well by a Frumkin-type isotherm implying weak repulsive interactions between the adsorbing hydrogens.^{99,183}

The feature termed OH-ter is less well understood, but is typically associated with the adsorption of OH from water dissociation²⁰⁶:



or



Adsorbed OH is very difficult to observe using FTIR spectroscopy (or any other vibrational spectroscopy, for that matter). From DFT calculations of OH co-adsorbed with water on Pt(111) and Rh(111),²⁰⁷ it is suggested that $\text{OH}_{\text{ad,ter}}$ would bind to a single surface atom with the O–H bond parallel to the metal surface in order to accommodate for hydrogen bond formation from a neighboring water molecule. Such a parallel adsorption mode would make this species invisible for IR spectroscopy. The observed pH dependence clearly agrees with reaction (11.3), and also the observed reversibility of the OH-ter feature strongly suggests that no further oxidation than to OH has taken place. From the charge associated with this feature in perchloric acid solution ($110 \mu\text{C cm}^{-2}$), one would estimate an $\text{OH}_{\text{ad,ter}}$ surface coverage of ~ 0.46 . In alkaline solution, the corresponding charge and coverage are $160 \mu\text{C cm}^{-2}$ and ~ 0.66 . Although the OH-ter features in acidic and alkaline solution occur in exactly the same potential region, the shapes of the features are different. In acidic solution, the feature is always associated with a sharp spike at $0.8 V_{\text{RHE}}$. No such sharp feature is observed in alkaline solution. The origin of the sharp feature was discussed by Berna *et al.*,²⁰⁸ who suggested that the broad and sharp peaks are associated with two different kinds of surface water, the exact molecular origin of which has so far remained elusive. Alternatively, it has been suggested that the sharp peak is associated with a disorder-order phase transition in the $\text{OH}_{\text{ad,ter}}$ adlayer, as these sharp voltammetric features are typically related to phase transitions in the adlayer.^{100,183} The phase transition would then be absent in alkaline media.

When comparing figure 11.1a to figure 11.1b, we observe that the introduction of steps of (110) orientation into the (111) surface leads to the appearance of *only one* additional voltammetric feature in both acidic and alkaline solution (steps of (100) orientation have a very similar influence, see figure 11.1c). Interestingly, the feature occurs at $0.125 V_{\text{RHE}}$ in 0.10 M HClO_4 solution, but at a higher potential ($\sim 0.26 V_{\text{RHE}}$) in 0.05 M NaOH solution. Traditionally, this feature is ascribed to the adsorption-desorption of hydrogen at the step, and we will therefore refer to it

as "H-step":



but clearly this reaction can NOT explain the observed "anomalous" pH dependence. Moreover, as we explained in a previous paper and chapter 10,¹⁰² the sharpness of this feature implies attractive interactions between adsorbed hydrogens, if indeed these are the only species adsorbing on the step. Attractive interactions seem somewhat unlikely, especially if these same interactions were concluded to be repulsive on the terrace. Therefore, the anomalous pH dependence and the peak sharpness strongly suggest that reaction (11.5) does not represent accurately what is really happening at the step.

Another anomaly related to the H-step feature that seemed to have been overlooked by many in the literature, is that it does not have an "OH-step" counterpart. If there are clear features related to H and OH adsorption on the terraces, and to H adsorption on the steps, then why is there no feature ascribable to OH adsorption on the steps? This question is especially pressing as the OH adsorbed in step and defect sites is believed by many (including ourselves) to be the active oxygen-donating species in many technologically important electrocatalytic oxidation reactions.¹²⁹ Given the great importance of this species, its voltammetric and spectroscopic invisibility becomes disturbing. . .

In this chapter we propose a model that is capable of reconciling many of the observed anomalies, including peak sharpness, anomalous pH dependence, and the absence of the OH-step feature. The model is partially based on assumptions that need further testing and confirmation, primarily by detailed spectroscopic and theoretical investigations. UHV modeling experiments of the co-adsorption of oxygen and water on stepped platinum surfaces, as described in chapters 4-6, support many of the assumptions made in the model. An additional attraction of the model is that, from a mathematical point-of-view, it is analytically solvable (albeit in a mean-field approximation for the adsorption on the terraces) with a clear physical meaning of all the physical parameters entering the model.

11.2 Experimental

Electrochemical experiments were conducted at room temperature in a two compartment electrochemical cell using a large area platinum counter electrode and a reversible hydrogen electrode (RHE) as a reference electrode, separated from the main compartment through a Haber-Luggin capillary. After initial boiling in sulphuric acid, the cell was boiled several times in water from an Elga Purelab Ultra system or a Millipore Milli-Q gradient A10 system (both 18.2 M Ω cm resistance) before each experiment.

0.05 M NaOH-solutions were prepared using NaOH pellets (Sigma-Aldrich, 99.998%). HClO₄ (Suprapur, 70%) and KClO₄ (pro analysis) were obtained from

Merck. The phosphate buffers with various pH's were prepared with a constant phosphate concentration of 0.10 M using a combination of ortho-phosphoric acid (Merck, Suprapur, 85%), anhydrous NaH_2PO_4 (Merck, Suprapur, 99.99%), anhydrous Na_2HPO_4 (Merck, Suprapur, 99.99%), and NaOH pellets. After each measurement the exact pH was determined with a pH-meter (Radiometer analytical, PHM 220) employing a GK2401C electrode head. All solutions were de-aerated by bubbling argon (BIP plus, 6.6, Air Products) through them. A blanket of argon was kept over the solution throughout the measurement.

Electrodes were prepared from a single crystal platinum bead oriented, cut and polished down to 0.25 μm with diamond paste as described in ref.²⁰² Before each experiment the electrode was flame annealed in an air-gas flame, cooled down in an Ar- H_2 (UltraPure Plus, 6.0, Air Products) reductive atmosphere and transported to the electrochemical cell under a protective droplet of de-aerated water. The electrode was brought in contact with the solution under electrochemical control.

All electrochemical measurements were performed using with a potentiostat (Autolab, PGSTAT 30 or PGSTAT 12) controlled by a computer. Since the electrodes have been cut at an angle α from the (111) plane, the geometric area (which has been measured) differs from the actual area available for adsorption through

$$A_{\text{act}} = \frac{A_{\text{geom}}}{\cos\alpha} \quad (11.6)$$

The resulting transferred charge has been corrected for this effect. All reported current densities have not been corrected for this effect.

11.3 Results

11.3.1 Pt[$n(111)x(110)$]

First we return to the H_{UPD} region of figure 11.1b, already discussed briefly in the Introduction, which shows the CVs of Pt(553) in acidic and alkaline solution. In acidic media (0.10 M HClO_4 , dashed line) a step induced feature appears at 0.125 V_{RHE} . This feature is completely reversible. In alkaline media (0.05 M NaOH, solid line) the feature has an identical shape, but has shifted to 0.26 V_{RHE} on the oxidative sweep. Moreover, the feature is less reversible than in acidic media, with the reductive sweep peak at 0.25 V_{RHE} . This lack of reversibility in alkaline media is in agreement with impedance spectroscopy measurements (chapter 10), which show a non-zero charge-transfer resistance in the H_{upd} region in alkaline solution.

Measurements comparing different step densities of steps with the (110) geometry in acidic media (0.5 M H_2SO_4 and 0.1 M HClO_4) showed that one electron is transferred per step platinum atom. Also on terrace sites a transfer of one electron per platinum atom is assumed, resulting in a reasonable double layer charging of 51 $\mu\text{C cm}^{-2}$.^{209,210}

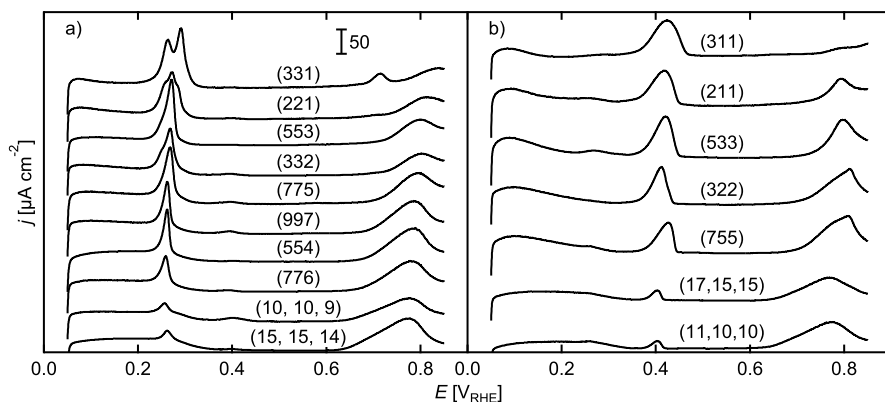


Figure 11.2 The oxidative sweeps of the (a) Pt[$n(111) \times (110)$] and (b) Pt[$n(111) \times (100)$] surfaces.

Figure 11.2a shows the oxidative sweeps of a series of Pt[$n(111) \times (110)$] electrodes with $n = 29, 19, 13, 9, 8, 6, 5, 4, 3,$ and 2 [Pt(15, 15, 14), Pt(10, 10, 9), Pt(776), Pt(554), Pt(997), Pt(775), Pt(332), Pt(553), Pt(221), and Pt(331)] in 0.05 M NaOH. We observe the step induced feature at $0.26 V_{\text{RHE}}$ for all surfaces. The magnitude of the feature increases with decreasing terrace width. For terraces ≤ 5 atoms a shoulder appears on the low potential side. On Pt(221) this develops into a three peak structure. On Pt(331) the peak at 0.26 V has diminished and the two shoulders are observed primarily.

According to the hard sphere model developed by Clavilier *et al.*^{209,210} the charge transferred per (110) step atom is given by

$$Q_{s,(110)} = 2e / [(n + 1/3)\sqrt{3}d^2], \quad (11.7)$$

where e is the electron charge, n the terrace length, and d the diameter of a platinum atom. In figure 11.3a the experimentally found charge (corrected for the cutting angle) is plotted against $1/(n + 1/3)$. On the dashed line one electron is transferred per step platinum atom (*i.e.* a slope of $241 \mu\text{C cm}^{-2}$). The deviation from a slope of one electron per atom varies with terrace width. The two longest terraces (29 and 19 atoms) lie on this line. For longer terraces (between 13 and 4 atomic rows) more charge is transferred than expected, with a maximum of 1.3 electrons transferred per step atom for Pt(775). The shortest terrace (2 atoms) appears to have less than one electron transferred per step atom.

11.3.2 Pt[$n(111) \times (100)$]

Next, we discuss the platinum surfaces with (100) steps. Figure 11.1c shows the CV of Pt(533) in acidic and alkaline solution as an example. For this step geometry the

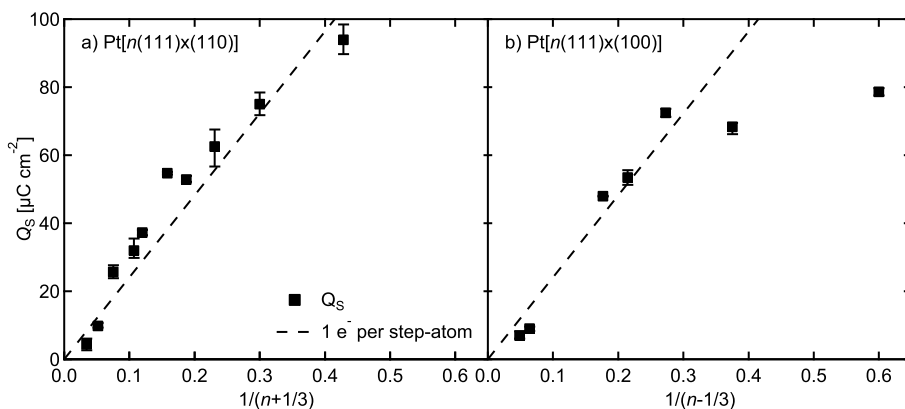


Figure 11.3 The charge transferred in the step-related feature for the (a) Pt[n(111)x(110)] and (b) Pt[n(111)x(100)] surfaces. The error bars represent the variation between measurements.

step induced feature is located at higher potentials than for (110) steps. In acidic solution it is located at $0.27 V_{\text{RHE}}$ and reversible. In alkaline media, however, the feature becomes irreversible with its oxidative sweep peak potential at $0.42 V_{\text{RHE}}$ and its reductive sweep peak potential at $0.36 V_{\text{RHE}}$. The shape of the peak is different as well, compared to the CV in acidic solution.

Measurements in acidic media ($0.5 \text{ M H}_2\text{SO}_4$ and 0.1 M HClO_4) on single crystals with varying (100) step density show that one electron is transferred per platinum step atom in the peak at $0.27 V_{\text{RHE}}$ ²¹¹. Figure 11.2b shows the oxidative sweeps of a series of Pt[n(111) × (100)] electrodes with $n = 21, 16, 6, 5, 4, 3,$ and 2 [Pt(11, 10, 10), Pt(17, 15 15), Pt(755), Pt(322), Pt(533), Pt(211), and Pt(311)] in 0.05 NaOH . We observe the step induced feature at $0.42 V_{\text{RHE}}$ for all surfaces. The peak intensity increases with decreasing terrace width. For some surfaces the peak is more "sawtooth-like" than for other surfaces. When multiple scans are taken the tilt of the sawtooth increases slightly for successive scans for all surfaces, but it is always more pronounced for some surfaces than others.

In figure 11.3b the experimentally found charges are plotted vs. $1/(n - 1/3)$, as suggested by the hard sphere model of Rodes *et al.*²¹¹:

$$Q_{s,(100)} = 2e / [(n - 1/3)\sqrt{3}d^2]. \quad (11.8)$$

The dashed line represents one electron transferred per platinum step atom (*i.e.* a slope of $241 \mu\text{C cm}^{-2}$). In contrast to the (110) step type data, the charge transferred is never significantly above one electron per platinum atom. For terrace widths up to 4 [$1/(n - 1/3) \approx 0.3$] the measured charges correspond roughly to one electron per platinum atom. For smaller terraces the charge transferred in the step-related peak appears to level off at $\sim 80 \mu\text{C cm}^{-2}$.

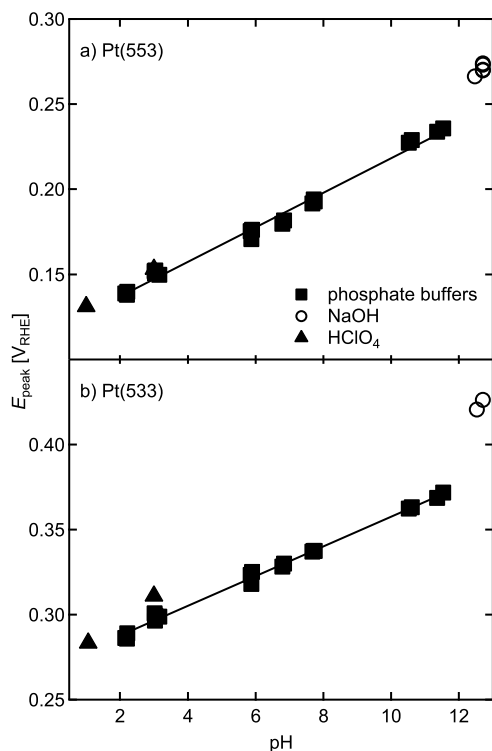


Figure 11.4 The pH dependence of the step-induced feature for (a) Pt(553) and (b) Pt(533) surfaces in various phosphate buffers, HClO₄ and NaOH.

11.3.3 pH-dependence

Figure 11.1 shows that the position of both step-induced features changes with pH. Figure 11.4 shows the position of the peaks in the oxidative sweep as a function of pH. It is clear from figure 11.2 that the peak position does not shift with terrace length. Therefore, two model surfaces are used in figure 11.4: Pt(553) for the Pt[*n*(111)×(110)] series (a) and Pt(533) for the Pt[*n*(111)×(100)] series (b). A series of phosphate buffers with constant molarity was used for this purpose. In order to exclude anion effects we have also included the peak positions in 0.1 M HClO₄ and a mixture of 0.1 M KClO₄ and 10⁻³ NaOH (pH=3) and, 0.05 M NaOH. For both surfaces the peak shifts linearly to higher potentials with increasing pH with 10 mV_{RHE} per pH unit, which corresponds to a shift of 50 mV per pH unit on the normal hydrogen electrode (NHE) scale. The peak positions in HClO₄ and KClO₄ are identical to what would be expected based on a fit through the phosphate buffer data. The NaOH data are not completely in line with the phosphate buffers, showing a slightly larger shift per pH unit, but do show the same trend. This slope of

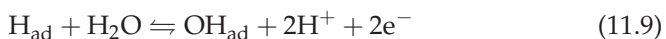
10 mV_{RHE} per pH unit has also been found for the (110) and (100)-related peaks on a polycrystalline platinum surface.²¹²

As a final remark, we would like to note that the total transferred charge in the peak in the phosphate buffers is the same for all pH values (not shown).

11.4 The model

Our attempts to explain the seemingly paradoxical observations outlined in the Introduction and partly illustrated in the foregoing Results section will be based on three model assumptions:

1. The sharpness of the H-step feature is due to the co-adsorption of H and OH, and the oxidative current associated with the feature is due to the replacement of H_{ad} by OH_{ad}, and vice versa for the reductive current. We showed previously that such a "replacement" process may lead to a sharp voltammetric feature with apparent attractive lateral interactions even if only repulsive interactions exist between the adsorbates themselves.¹⁹⁴ This model explained very well many aspects of the voltammetric features observed for a Pt(100) electrode in bromide-containing solution, in which adsorbed hydrogen is replaced by adsorbed bromide in a very sharp current peak. The further consequences of this model assumption will be discussed throughout the chapter. A further argument in favor of the formation of OH_{ad} in the H-step feature is the fact that the peak potential shifts negatively upon the presence of Li⁺ in the solution, a cation supposed to have a strong interaction with OH, whereas Li⁺ has no influence on the H-ter feature²¹³.
2. In order to explain both the pH dependence of, and the charge associated with the H-step feature (see the Results section), we will have to rule out a simple replacement reaction of the type:



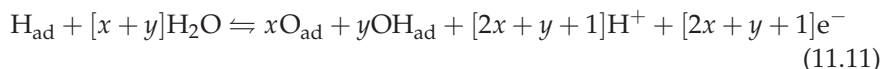
First of all, reaction (11.9) would predict a charge of 2 electrons per step site atom (if the maximum hydrogen and hydroxide coverage is unity), which is in disagreement with our data and existing experiments of Rodes and Clavilier.²⁰⁹⁻²¹¹ Second, reaction (11.9) predicts a "trivial" pH dependence of 60 mV/pH unit, which is in disagreement with the experimentally observed value of ca. 50 mV/pH unit we reported here. From a purely modelistic point-of-view, the first discrepancy can in principle be "fixed" by assuming stoichiometric coefficients different from 1 and/or a maximum H coverage in the step smaller than 1, and the second discrepancy by assuming that one of the surface-bonded species is able to store charge such that the ratio of protons over electrons exchanged during the reaction is different from 1. Purely

formally, one could write a reaction of the type:



where $x = i/j$, with i the stoichiometric number of hydroxides formed and j the stoichiometric number of adsorbed hydrogens involved in the reaction. In this reaction, δ should be interpreted as an electrosorption valency, not as a partial charge, and δ could be either positive or negative.

3. As an alternative to the somewhat artificial looking reaction (11.10), one may assume that H and OH are still not the only species involved in the H-step voltammetric feature. It is generally assumed that the Pt(111) surface is the only surface on which the formation of adsorbed OH and adsorbed O can be separated on the potential scale.¹³¹ On a different surface, or a step of (110) or (100) orientation, one could postulate:



The peak potential (on the RHE scale) corresponding to this reaction may in principle depend on pH if the ratio of O_{ad} over OH_{ad} , *i.e.* x/y , would depend on pH in a non-trivial way. In a general sense, reaction (11.11) expresses the idea that the more stable water dissociation product on a platinum surface other than (111) is O_{ad} , rather than OH_{ad} . As we will discuss in the next section, this is also in agreement with the modeling experiments in UHV described in chapter 4.

The reaction equations above can be combined with reaction 11.1 from the Introduction to derive an equation for the hydrogen coverages on the terrace and step sites as a function of potential. Details are given in our earlier papers and chapter 10.¹⁹⁴ The resulting equation that can be used to model the "hydrogen region" is:

$$j = \gamma_{\text{ter}}Fv \frac{d\theta_{\text{ter}}}{dE} + \gamma_{\text{step}}Fv \frac{d\theta_{\text{step}}}{dE} \quad (11.12)$$

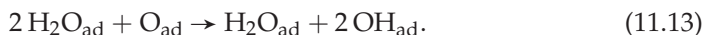
where θ_{ter} is the hydrogen coverage on the terrace, and γ_{ter} is the corresponding charge ("electrosorption valency") associated with hydrogen adsorption on the terrace, and where θ_{step} is the hydrogen coverage on the step, and γ_{step} is the corresponding total charge (including the possible adsorption/desorption of OH) associated with hydrogen adsorption/desorption on the step. The model assumes that the process occurring on the step can be modeled with only a single variable (since it involves only a single voltammetric peak), chosen to be the potential-dependent hydrogen coverage, with any other coverage (OH or O) following from the equilibrium expression for equation (11.10) or (11.11). F and E in equation (11.12) have their usual meaning.

Analytical expressions for θ_{ter} and θ_{step} as a function of potential ("isotherms") are given in the Appendix. The isotherm for θ_{ter} is essentially the "mean-field" or Frumkin isotherm, which has been shown to give a good approximation to the experimental voltammogram of Pt(111) as well as to exact Monte Carlo simulations.^{101,183} This isotherm is characterized by a relatively weak repulsive lateral interaction ($\epsilon_{\text{H-H,ter}}$, for the exact definition, see chapter 10) between the adsorbed hydrogens on the terrace. The isotherm for θ_{step} follows from the *exact* solution for a one-dimensional lattice gas with an effective nearest-neighbor interaction energy ($\epsilon_{\text{H-H,step}}$, defined and discussed in chapter 10). Fitting parameters of the model are the (effective) adsorption energies of hydrogen on the terrace and step, $\epsilon_{\text{ad,H-ter}}$ and $\epsilon_{\text{ad,H-step}}$, the (effective) lateral interaction energies $\epsilon_{\text{H-H,ter}}$ and $\epsilon_{\text{H-H,step}}$, and the (effective) electrosorption valencies γ_{ter} and γ_{step} .

11.5 Water dissociation on well-defined platinum surfaces: the UHV perspective

There have been many studies on the adsorption of water on platinum in ultra high vacuum, though most of them have focused on the closely-packed Pt(111) surface.⁶⁻⁸ The general consensus is that on Pt(111) water adsorbs molecularly at all coverages and temperatures (< 180 K). Scanning tunneling microscopy (STM) studies on an imperfect Pt(111) crystal show that water adsorbs preferentially on step sites, forming molecular chains.²⁸ Temperature programmed desorption (TPD) studies show a stabilization of the water monolayer by the presence of step sites.^{26,27}

The stability of O_{ad} vs. OH_{ad} on a platinum surface in ultra high vacuum can be studied by the co-adsorption of O_{ad} (obtained by dissociative adsorption of O_2) and H_2O . The co-adsorption of H_2O and O_{ad} on Pt(111) is known to produce OH_{ad} , which is incorporated in a hydrogen bonded network of $\text{H}_2\text{O}_{\text{ad}}$ and OH_{ad} ^{15,75,79} via



For surface coverages $\leq 0.25 \text{ ML } \text{O}_{\text{ad}}$, all O_{ad} participates in the OH formation,¹⁶ so that there is no O_{ad} left on the surface. H_2O is necessary to stabilize the formed OH species.^{16,80} Different structures can be produced by different $\text{O}_{\text{ad}} : \text{H}_2\text{O}$ ratios. High resolution electron energy loss spectroscopy (HREELS) on Pt(111) shows three separate $\delta(\text{OH}_{\text{ad}})$ peaks, associated with structurally different OH-groups.⁷⁸

We have shown in chapters 4–6 that on stepped surfaces (*i.e.* Pt(553) and Pt(533)), OH is probably not that easily formed as on Pt(111). When only the step sites are pre-covered with O_{ad} , additional high temperature peaks are observed in the TPD spectra, indicating OH_{ad} formation. However, upon also pre-covering terrace sites with O_{ad} these high temperature peaks become smaller and an additional peak is observed, characteristic of the recombinative desorption of OH_{ad} from (111) ter-

race sites. Moreover, the amount of exchange between pre-adsorbed O atoms and H₂O hardly increases even though over twice as many O atoms are present on the surface. This indicates that O_{terrace} is more prone to OH formation than O_{step}, leaving unreacted O atoms at step sites. We believe this observation supports that reaction (11.11) is the most realistic reaction to take place in step sites. Our UHV experiments would also suggest that (110) step sites would produce somewhat more OH_{ad} than (100) step sites (see chapter 4).

As far as co-adsorption of H and H₂O is concerned, H₂O is supposed to have a minor effect on the H adsorption properties on Pt(111).²⁰⁴ On the other hand, H pre-adsorbed on the stepped Pt(553) and Pt(533) surfaces can drastically alter the properties of co-adsorbed water in UHV (chapters 7–9).

Table 11.1 gives an overview of adsorption energies of O, H, and OH obtained under UHV conditions or from DFT calculations along with the maximum coverages of the species on (111) terrace sites and (100) and (110) step sites. On Pt(111) we observe an adsorption energy series of O > H > OH, with O binding the most strongly bound species.⁸⁰ Hydrogen adsorption shows two interesting features: it shows an adsorption energy series of (110)_{step} < (111)_{terrace} < (100)_{step} (*i.e.* it binds weaker to (110) steps than to (111) terraces) (see chapter 3) and the maximum surface coverage appears to be 0.5 at step sites, whereas it is 1 at terrace sites.^{57,63}

11.6 Discussion

In the blank CV of stepped platinum surfaces, the (110) step peak is located at lower potentials than the (100) step peak. This indicates that either H_{ad} is more strongly bound to (100) steps than to (110) steps and/or the co-adsorbant (OH_{ad}/O_{ad}) is more strongly bound to (110) steps. As shown in table 11.1, UHV experiments suggest that H_{ad} has a binding energy in the order of step₍₁₀₀₎ > terrace₍₁₁₁₎ > step₍₁₁₀₎ (see chapter 3). In this work we also observe a step binding energy in the order of step₍₁₀₀₎ > step₍₁₁₀₎ for both alkaline and acidic media. It is well known that the H_{upd}-H⁺ terrace peak is located at a position in agreement with the hydrogen binding strength in ultra high vacuum.⁹⁹ When we look at the possible co-adsorbants, both O and OH bind stronger to (100) steps than to (110) steps, whereas (remarkably) H₂O binds stronger to (110) steps (see chapter 3). This indicates that even though OH and O are likely candidates for co-adsorption, they do not seem to dominate the processes that determine the peak potential. Although H₂O appears to show the right energy trend, H₂O co-adsorption does not provide us with an oxygen donor needed at the surface to start CO oxidation at low potentials,¹³³ making it an unlikely candidate to be the only co-adsorbant.

In alkaline media the H-step peaks are observed at higher potentials compared to acidic media. The HClO₄ and NaOH data in figure 11.4 exclude anion effects as the source of this anomalous pH dependence. The peak shift indicates that H_{ad}

	(111) _{terrace}			(110) _{step}			(100) _{step}		
	H	OH	O	H	OH	O	H	OH	O
θ_{\max} [ML]	1.00 ^d	0.33 ^b	0.25 ^c	0.5 ^d	?	0.5 ^e	0.5 ^f	?	0.5 ^e
E_{ads} [eV]	-2.8 ^g -0.42 ⁱ	-2.4 ^g -2.51 ^j	-4.2 ^g	-0.47 ^h -0.41 ⁱ	-3.5 ^j	-5.66– -4.9 ^e	-0.84 ^h -0.59 ⁱ	?	-5.87– -5.10 ^e

Table 11.1 Maximum coverages and adsorption energies for H, OH and O on Pt(111) terraces, (110) steps, and (100) steps as obtained by UHV modeling experiments and/or DFT calculations. For the adsorption energies only references that compare either different surfaces or adsorbates have been included.

^aRef.⁵⁷ TPD

^bRefs.^{14,15,76,78,81,214,215} H₂O co-adsorption is necessary to stabilize the formed OH. The most stable structure is a OH/H₂O overlayer with a maximum coverage of 0.67 ML and a 1 : 1 ratio of H₂O and OH. The maximum coverage of this overlayer is 0.75 ML, but it is less stable.

^cRefs.^{32–34,40} From background dosing. Higher coverage states can be reached by extended temperature cycling,^{40,41} O-beam irradiation,⁴⁰ or exposure to NO₂.³³

^dChapter 3. No absolute values are given, but a similar θ_{H} is found as on Pt(533).

^eRef.³⁷ STM and DFT.

^fRef.⁶³ Estimated from TPD results and a calculation of the pumping speed of the molecular beam chamber for H₂. DFT calculations do show that it is energetically less favorable to cover the second half of the step sites with H_{ad}.⁶⁹

^gRef.⁸⁰ E_{ads} H vs. H.

^hChapter 3

ⁱRef.⁷⁰ vs. H₂.

^jRef.⁷¹

is more stable in alkaline media than in acidic media and/or that O/OH is less stable in alkaline media. As stated in assumption 3 of the model, the anomalous pH dependence can in principle be explained by assuming that the O : OH ratio in the steps varies with pH. From chapters 3–6 it is clear that OH_{ad} binds weaker to the surface than O_{ad} in UHV. The shift of the peak potential of the step-related features with pH suggests that the adsorption energy of the co-adsorbant decreases with increasing pH value. This could indicate that relatively more OH binds in alkaline media, *i.e.* oxidation to O_{ad} is less pronounced than in acidic media.

We would like to stress at this point that the potential of zero total charge (pztc) shifts with 60 mV_{NHE} per pH unit (0 mV_{RHE}) on Pt(111),¹⁹¹ whereas on Pt(110) a shift of around per 48 mV_{NHE} per pH unit (12 mV_{RHE}) has been observed¹⁹¹ (with a similar shift also observed for polycrystalline platinum²¹⁶). These values are very similar to the peak shift we observe, suggesting that the process causing the pH dependent peak shift and the pztc shift are probably related if not the same.

In alkaline media the H_{upd} peaks become irreversible, indicating a slower adsorption process than in acidic media both on terraces and steps (chapter 10). The peak for (100) steps is broader and appears more irreversible than for (110) steps. Under UHV conditions (100) steps are less susceptible to OH formation than (110) steps, favoring O_{ad} at step sites (chapter 4). If H₂O oxidizes all the way through to O_{ad}, it may be harder to react back (to H₂O), making the (100) peak more irreversible. In chapter 10 we showed, using impedance spectroscopy, that on Pt(111) the H adsorption process at the terraces is significantly slower in alkaline media than in acid media. This slow adsorption to both terrace and step sites below 0.5 V_{RHE} in alkaline media has been ascribed to the fact that hydrogen needs to be abstracted from H₂O rather than from H₃O⁺ (reactions 11.1 and 11.2).

As a final point we would like to discuss the total charge transferred in the step feature. If the feature is indeed due to the co-adsorption of H, O, and/or OH one would intuitively expect a charge transfer of two or more electrons per platinum atom. This is not what we observe: the largest amount of electrons transferred per platinum atom is 1.3, but typically we find values close to 1. In acidic media also a charge transfer of one electron per platinum atom is found.^{209–211} Table 11.1 provides us with a clue for this apparent discrepancy: in UHV a maximum coverage of 1 H atom per 2 platinum atoms has been suggested.⁶³ For oxygen the same maximum coverage is found.³⁷ For OH no maximum coverage is known. A maximum hydrogen coverage on steps of ~ 0.5 ML could possibly explain why both in acidic^{209–211} and alkaline (this work) media a charge transfer close to the one electron per platinum atom is found, even if reactions (11.10) and (11.11) require more than one electron (two if OH is the final product). Deviations from the exact line may be related to varying O : OH ratios, or the total amount of O containing species varying with step density.

The idea that H_{ad} desorption and OH_{ad} adsorption are not decoupled processes

on Pt(100) and Pt(110) is not new; see *e.g.* the discussion in ref.¹³¹ Marichev has recently discussed the evidence of OH adsorption in the hydrogen region of polycrystalline platinum.²¹⁷ Furthermore, Jerkiewicz *et al.*²¹⁸ have discussed the experimental evidence that on polycrystalline platinum, Pt—O is formed without any noticeable formation of an OH_{ad} intermediate.

11.7 Conclusion

We have discussed three important discrepancies in the current interpretation of the effect of water dissociation on the blank cyclic voltammetry of stepped platinum surfaces: First, for H adsorption both H-ter and H-step contributions are identified. For OH adsorption only OH-ter has been identified. Second, different shapes (broad vs. sharp) of the H-ter and H-step peaks imply different lateral interactions between hydrogen adatoms at terraces and steps, *i.e.* repulsive vs. attractive interactions. Third, the H-step peak has a non-trivial pH-dependence of 50 mV_{NHE} per pH unit. We have proposed here a model that can deal satisfactorily with these discrepancies. The H-step peak is not due to just ad- and desorption of hydrogen, but to the replacement of H with O and/or OH. This replacement process can straightforwardly explain the sharpness of the voltammetric peak, following the reasoning of ref.¹⁹⁴ The O : OH ratio presumably varies with step density and medium. In alkaline media it appears that relatively more OH is adsorbed in steps than in acidic media where more O is adsorbed, leading to a non-trivial pH dependence. We speculate that this could be the origin of the higher activity of platinum in alkaline media for oxidation reactions.

We find a charge transfer of maximally 1.3 electron per step platinum atom in alkaline media with the exact number varying with step density. Previously a charge transfer close to one electron per platinum atom was found in acidic media.^{209–211} Interestingly, both H and O have a saturation coverage of 0.5 ML on step sites in UHV^{37,63}. The model may explain the amount of charge transferred, if the maximum coverage of H in the step is close to 0.5 and the number of electrons transferred per H is 2 or more, as would be needed to make OH/O. A variation in the ratio and total amount of adsorbed oxygen species may explain the variation of the amount of charge transferred with step density.

Although we believe our model is a step forward in a consistent interpretation of the electrochemistry of water at well-defined platinum electrodes, an important aim for the future remains the quantification of the amount of OH_{ad} and O_{ad} at various surfaces as a function of potential and to establish which of the two species is the oxygen donor in electrocatalytic oxidation reactions.