

## The Oxygen Reduction Reaction on Thin Palladium Films Supported on a Pt(111) Electrode

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The oxygen reduction reaction (ORR) in acid and alkaline solutions is investigated on thin Pd films ( $0 < \theta_{\text{Pd}} < 1.5$  ML) supported on a Pt(111) electrode. In 0.1 M KOH, the general form of the current vs  $\theta_{\text{Pd}}$  relationship for the ORR has a volcano shape, with the maximum catalytic activity exhibited by a surface modified with 1 ML of Pd. However, if the amount of Pd deposited exceeds 1 ML, the reaction is inhibited and 1.5 ML of Pd are less active than unmodified Pt(111). In 0.1 M HClO<sub>4</sub>, none of the Pd films are more active than Pt(111). In solution containing Cl<sup>−</sup> (ca.  $10^6$ – $10^{-5}$  M), the inhibition on the Pt(111)–Pd electrode is much more severe than on bare Pt(111) due to stronger anion adsorption on Pd. We present an interpretation of the kinetics of the ORR on Pt modified by thin Pd films in alkaline and acid solution based on the electronic properties of the Pd films and how the electronic properties effect specific anion adsorption, the formation of OH<sub>ad</sub> and the adsorption of the reaction intermediates.

## 1. Introduction

With the advent of ex-situ and in-situ surface-sensitive probes and the development of new experimental methods for surface preparation, it has become possible to establish relationships between the macroscopic rate of an electrochemical reaction and the surface structure/composition of metal surfaces at an atomic level.<sup>1</sup> The prominent examples are the hydrogen evolution/oxidation reaction (HER/HOR),<sup>2,3</sup> oxidation of CO,<sup>4–6</sup> and the oxygen reduction reaction (ORR)<sup>7,8</sup> on single-crystal metal surfaces. These studies revealed that all of these reactions are structure-sensitive processes, the structure sensitivity arising primarily from structural-sensitive adsorption of anions in the supporting electrolyte, i.e., bisulfate,<sup>9</sup> hydroxyl,<sup>10</sup> and halides.<sup>11,12</sup> It was proposed that these “spectator” adsorbates actually impede the kinetics by blocking the active surface sites for the adsorption of the reactants and the active intermediates. This is consistent with the so-called secondary structure sensitivity observed in gas-phase catalysis, where some secondary process in the reaction mechanism leads to site blocking.<sup>13</sup> Until recently, electrochemical studies with Pt(*hkl*)-bimetallic surfaces have been very scarce. In the last five years, however, thin transition metal films supported on Pt(*hkl*) have been studied in great detail in order to establish a link between physical properties of a surface and its electrocatalytic activity.<sup>14–23</sup> The morphology and stability of Pd films on Pt(111) were examined by utilizing in-situ SXS<sup>22</sup> and FTIR<sup>20,23</sup> measurements. SXS studies demonstrated that electrochemically deposited films are pseudomorphic, whereby the Pd atoms occupy commensurate Pt sites such as to continue the ABC stacking of the Pt(111) substrate. These films are rather stable between the hydrogen evolution and the oxide formation potential region, showing no sign of hydrogen absorption characteristic for bulk Pd and also

observed for a 3D Pd island deposited on Pt(*hkl*) with  $\theta_{\text{Pd}} > 1$  ML.<sup>24</sup> For increasing coverage beyond 1 ML, Pd deposition on Pt(111) follows the Stranski-Krastanov pseudomorphic growth mode, e.g., 3-dimensional pseudomorphic crystalline Pd islands begin to aggregate after *one* smooth Pd monolayer is formed on the Pt substrate.<sup>22</sup> FTIR characterization of Pt(111)–CO<sub>ad</sub> modified with Pd ( $0 \text{ ML} < \theta_{\text{Pd}} < 1 \text{ ML}$ ) was used as an indirect method to establish whether Pd forms 2D islands or whether Pd atoms disperse on the surface much more randomly, as seen for the deposition of Bi on transition metals.<sup>25</sup> The appearance of separate C–O stretching bands, corresponding to CO adsorbed on Pt and Pd, indicated that Pd atoms cluster into islands and that Pt and Pd behave according to their own surface chemistry. From these results, one would expect a gradual change in the catalytic properties of Pt(111)– $\theta_{\text{Pd}}$  electrodes, from those characteristic of pure Pt(111) to those which are characteristic for Pt(111) covered with 1 ML of Pd. In a recent paper it has been shown that this is in fact the case for the HER/HOR,<sup>26</sup> i.e., the *i* vs  $\theta_{\text{Pd}}$  relationship has a volcano shape with the maximum catalytic activity exhibited by the Pt(111) surface modified with 1 ML of Pd.

In this study, the Pt(111)–Pd system is used to demonstrate how the energetics of spectator species and the intermediates formed in the ORR are affected by interfacial bonding and energetic constraints produced between Pd pseudomorphic films ( $0 < \theta_{\text{Pd}} < 1.5$  ML) and the Pt(111) substrate. As a background for the discussion, the surface-coverage sensitive adsorption of hydrogen, oxygenated species, and anions is presented. After summarizing the voltammetric curves, it will be shown that the kinetics of the ORR in alkaline solution varies with Pd surface coverage, with the maximum catalytic activity exhibited for Pt(111) modified with one Pd monolayer. To elucidate the importance of specifically adsorbing anions on the rate of the ORR, selective results for the ORR on a Pt(111)–Pd surface in the presence of Cl<sup>−</sup> will be shown and discussed. Considering that high-surface-area catalysts are often synthesized from halide-containing educts and that trace levels of chloride may

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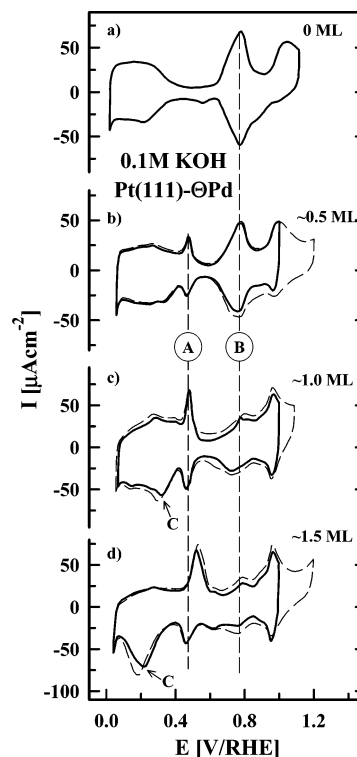
also be present in the water contained in the fuel cell feed-stream, the effect of  $\text{Cl}^-$  on the catalytic activity is not only important from a theoretical point of view, but also of great practical importance.

## 2. Experimental Section

The pretreatment and mounting of the Pt(111) single crystal ( $0.283 \text{ cm}^2$ ) in a rotating ring disk electrode (RRDE) configuration was fully described previously.<sup>9</sup> In short, following crystal cleaning by flame annealing in a hydrogen flame and cooling in a mild stream of argon, the crystal was protected by a drop of ultrapure water, transferred to, and mounted into the disk position of an insertable disk electrode assembly (Pine Instruments). Subsequently, the electrode was transferred into the electrochemical cell. For the electrochemical deposition of palladium, the clean flame-annealed sample was subjected to a potential cycling between  $0.05 < E < 0.9 \text{ V}$  in a  $0.05 \text{ M H}_2\text{SO}_4 + 5 \times 10^{-6} \text{ M Pd}^{2+}$  solution (Baker Ultrex) with a sweep rate of  $50 \text{ mV/s}$ . The amount of Pd deposited was controlled by monitoring the continuous change of the voltammetric features from those characteristic of bare Pt(111) to those of a pseudomorphic monolayer of palladium. The palladium coverage, indicated in the text, is calculated using a calibration curve established by plotting the charge densities in the  $\text{H}_{\text{upd}}$ -region of the CVs of UHV-prepared  $\text{Pt(111)}-x \text{ Pd}$  surfaces against the Pd coverage  $x$  as determined by low-energy ion scattering (LEIS).<sup>20</sup> After the electrochemical Pd deposition, the electrode was rinsed with ultrapure water and transferred into a thermostated standard three-compartment electrochemical cell for kinetic measurements. The electrode was immersed into the Ar-purged electrolyte (Ar: Bay Gas Research Purity) under potentiostatic control at  $\approx 0.1 \text{ V}$ , and the quality of the film was checked by cyclic voltammetry. For measuring the oxygen reduction reaction the electrolyte was subsequently saturated with oxygen for about 5 min.

For the ORR measurements the ring electrode was potentiostated at  $1.3 \text{ V}$  in order to oxidize  $\text{HO}_2^-$  (alkaline solution) or  $\text{H}_2\text{O}_2$  (acid solution) which is produced on the disk electrode under diffusion control. Consequently, peroxide was quantitatively collected on the ring electrode. It is well-known that, in alkaline solution at positive potentials, oxide formation inhibits the kinetics of the ORR and consequently the reduction currents recorded in the positive-going and negative-going sweep are slightly different. Therefore, for the sake of comparability of the different data collected, a strict procedure was applied for recording the polarization curves. Before beginning the measurement the electrode was held for 30 s at the start potential, the positive potential limit, then the potential was swept with a scan rate of  $50 \text{ mV/s}$  to the negative potential limit and directly back to the positive potential limit. Shown in the figures, and used for the kinetic analysis of the data, e.g., the Levich-Koutecky plot or the Tafel plot, are always the polarization curves of the *positive-going* potential sweep. This procedure has the advantage that the polarization curves are obtained from the ORR on the initially "bare" metal surface, i.e., the reaction is not perturbed by preexisting surface oxides.

Sulfuric acid and perchloric acid solutions were prepared from concentrated acid (Baker Ultrex, and EM Science Suprapure), whereas potassium hydroxide solution was prepared from pellets (Aldrich Semiconductor Grade). All solutions were diluted using triply pyrodistilled water. The reference electrode for the electrochemical cells was a saturated calomel electrode (SCE) separated from the working electrode compartment by a closed electrolyte bridge in order to avoid chloride contamination. All

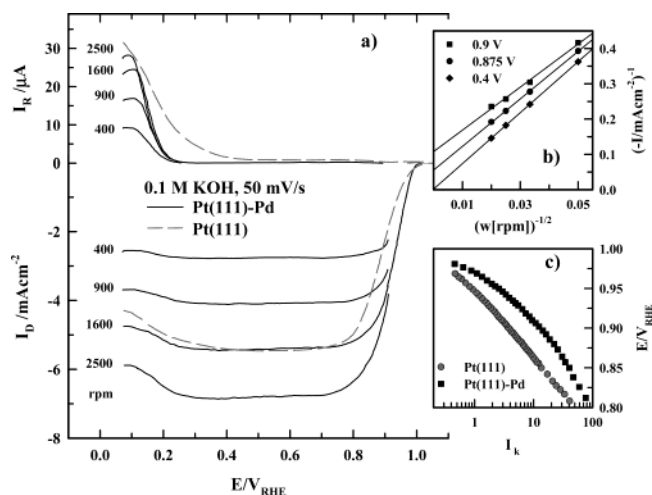


**Figure 1.** Cyclic voltammetry of  $\text{Pt(111)}-x \text{ ML Pd}$  electrodes recorded in  $0.1 \text{ M KOH}$  (sweep rate  $50 \text{ mV/s}$ ) at room temperature; (a)  $x = 0$ ; (b)  $x \sim 0.5$ ; (c)  $x \sim 1$ ; (d)  $x \sim 1.5$ .

potentials shown in the text, however, refer to the reversible hydrogen electrode in the same solution, calibrated from the reversible potential for the hydrogen evolution/oxidation reaction.

## 3. Results

**3.1. Cyclic Voltammetry in Alkaline Solution.** To illustrate how the systematic increase in the Pd surface coverage of a  $\text{Pt(111)}-x \text{ Pd}$  electrode affects its electrochemical properties in alkaline solution, in Figure 1 the cyclic voltammogram of bare Pt(111) is compared to the voltammograms of three different  $\text{Pt(111)}-x \text{ Pd}$  surfaces with  $x \sim 0.5$ ,  $x \sim 1.0$ , and  $x \sim 1.5$ , respectively. Whereas in the voltammogram of bare Pt(111) the hydrogen underpotential deposition is clearly separated by a double layer region from the potential region where adsorption of oxygenated species ( $\text{OH}_{\text{ad}}$ ) takes place (peak B at about  $0.75 \text{ V}$ , see Figure 1a), on electrodes (partially) covered with palladium a second peak (A) is discernible at about  $0.55 \text{ V}$  (see Figure 1b–d). This peak we assigned previously to  $\text{OH}^-$  adsorption on Pd surface atoms.<sup>20</sup> Consequently, due to the higher oxophilicity of palladium on  $\text{Pt(111)}-x \text{ Pd}$  surfaces  $\text{OH}^-$  adsorption on Pd atoms shifts to lower potentials compared to  $\text{OH}^-$  adsorption on Pt sites. Note, that for  $\Theta_{\text{Pd}} \geq 1 \text{ ML}$  still a small peak (B) of  $\text{OH}^-$  adsorption on Pt(111) is visible in the CV, indicating that 3D growth may start slightly before the completion of one Pd monolayer. Furthermore, it can be seen that on a Pd-modified electrode hydrogen desorption is extended to more positive potentials, reflecting the strong interaction of Pd atoms with  $\text{H}_{\text{upd}}$ . As a consequence, the  $\text{H}_{\text{upd}}$  and  $\text{OH}_{\text{ad}}$  potential regions are not clearly separated from each other anymore, a fact which limits the accuracy of any determination of the adsorption isotherms of  $\text{H}_{\text{upd}}$  and  $\text{OH}_{\text{ad}}$  considerably, as is also the case, for example, for cyclic voltammetry of Pt(100) in alkaline solution.<sup>27</sup> A second characteristic of the shown voltammograms is that, in the Pd coverage region of  $\Theta_{\text{Pd}} \leq 1$



**Figure 2.** (a) Polarization curves for the ORR on a Pt(111)-1 ML Pd disk electrode and corresponding peroxide oxidation current on the ring electrode in 0.1 M KOH at different rotation rates; 50 mV/s; 293 K; (b) corresponding Levich-Koutecky plot at 0.9 V, 0.875 V, and 0.4 V; (c) Tafel plot of the true kinetic current at 1600 rpm, for comparison data for Pt(111) under the same conditions are included as well.

ML, the overall charge associated with the  $H_{\text{upd}}$  process increases with  $\Theta_{\text{Pd}}$ , as already reported for acid<sup>20,21</sup> and alkaline solution,<sup>20</sup> reaching a maximum value of about 1 ML  $H_{\text{upd}}$  for a complete palladium film of monatomic thickness on Pt(111). Figure 1d displays an important new observation, namely, that for  $\Theta_{\text{Pd}} > 1$  ML in the *negative-going* sweep a reduction peak (C) is discernible in the  $H_{\text{upd}}$  region. Compared to the CV with  $\Theta_{\text{Pd}} \sim 1$  ML, it is clear that peak C is very pronounced and with opening the potential window at the positive limit this peak increases further and shifts negatively. Regarding the voltammograms at high potentials compared to the highly irreversible oxide formation on bare Pt(111), oxide formation on the thin palladium film is a more reversible process as confirmed by in-situ SXS.<sup>24</sup> Comparing the CV of the surfaces with  $x \sim 1$  and  $x \sim 1.5$ , it can be seen that in the latter case no indications of a double-layer region can be found anymore. The charges at positive potentials are increased for the case of  $x \sim 1.5$ , indicating an increased oxide formation if Pd islands are deposited. A further inspection of Figure 1d reveals that the  $H_{\text{upd}}$  potential region is rather asymmetrical, indicating that hydrogen adsorption and hydrogen desorption take place at two “different” surfaces.

**3.2. Oxygen Reduction Reaction in Alkaline Solution.** On the thus characterized palladium films the oxygen reduction reaction was investigated. A family of polarization curves of the ORR on a Pt(111)-1 ML Pd electrode in  $O_2$ -saturated 0.1 M KOH solution at room temperature is summarized in Figure 2. It can be seen that the shape of the polarization curves recorded at different rotation rates is similar to those already known for Pt(111).<sup>27</sup> In short, beginning at the positive potential limit only small reduction currents can be observed on the disk electrode, indicating the slow kinetics of the ORR. Sweeping the potential in a negative direction, the current increases rapidly and only a narrow potential region of kinetic-diffusion controlled current densities is observed before reaching the diffusion-limited current density  $I_D$ . Below ca. 0.3 V, the disk current decreases again, and simultaneously peroxide is detected on the ring electrode (see Figure 2a), whereas in the potential region positive of 0.3 V essentially no peroxide is detected.

Comparing the polarization curve of the Pd monolayer and the bare Pt(111) electrode (dashed curve, rotation rate 1600 rpm) recorded under the same experimental conditions, two charac-

teristics are obvious. First, the potential region of mixed kinetic-diffusion control on Pt(111)-1 ML Pd is shifted (compared to Pt(111)) about 50 mV toward *higher* potentials, making the former surface the most active surface for the ORR in alkaline solution so far. Secondly, less peroxide is always produced on the palladium film than on bare Pt(111). For a complete kinetic analysis of the ORR on the thin palladium film in Figure 2b, a Levich-Koutecky plot, derived from the data in Figure 2a, is shown.  $I^{-1}$  vs  $\omega^{-1}$  yields straight lines with an intercept corresponding to the kinetic current  $I_k$ . From the slope of the straight lines, B factors between  $3.93 \times 10^{-2}$  and  $4.6 \times 10^{-2}$  mA/rpm<sup>-1/2</sup> are obtained. These values fit well with the theoretical value of  $3.99 \times 10^{-2}$  mA/rpm<sup>-1/2</sup> for a four-electron reduction using literature data for  $O_2$  solubility,  $c_0 = 1.21 \times 10^{-3}$  mol/L, viscosity  $\nu = 1.0008 \times 10^{-2}$  cm<sup>2</sup>/s, and oxygen diffusivity  $D = 1.86 \times 10^{-5}$  cm<sup>2</sup>/s.<sup>28</sup> A similar value,  $4.0 \times 10^{-2}$  mA/rpm<sup>-1/2</sup>, was found for bare Pt(111) under the same conditions.<sup>27</sup> In Figure 2c, finally, the Tafel plots of the mass-transport corrected currents  $I_k$  on both surfaces are shown. The currents  $I_k$  are calculated using eq 1:

$$I_k = \frac{I \times I_D}{I_D - I} \quad (1)$$

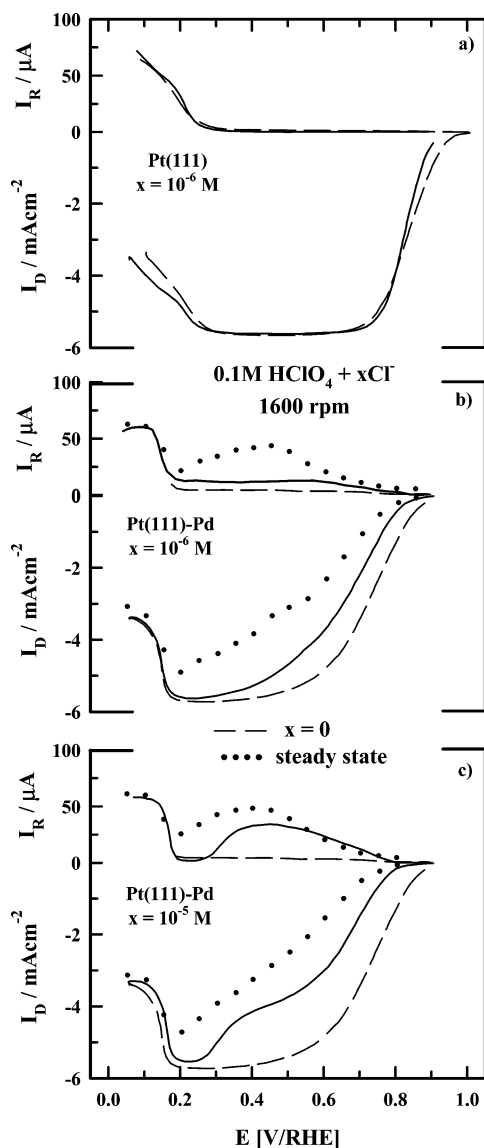
Apparently the Pd-modified Pt(111) electrode is much more active for the ORR than the unmodified Pt(111) surface (note the logarithmic scale), and by comparing the kinetic current densities at 0.9 V, an activity improvement of a factor of about 4 can be observed. Note, however, that in contrast to bare Pt(111) on Pt(111)-Pd, no linear dependence is found between  $\log I_k$  and the applied potential  $E$ . In the potential region of mixed kinetic-diffusion control for Pt(111) a constant (negative) Tafel slope of ca. 85 mV per decade (mV dec<sup>-1</sup>) is observed. For Pt(111)-Pd, however, no straight line can be fitted to the data. In principle, the tangent at each point has a different slope. Yet, for a rough estimation of the *range* of the Tafel slopes observed in the potential region of 0.925 V <  $E$  < 0.975 V, a negative Tafel slope with ca. 50 mV dec<sup>-1</sup> is calculated, whereas in the potential region of 0.80 V <  $E$  < 0.90 V a negative Tafel slope of ca. 100 mV dec<sup>-1</sup> is obtained.

To demonstrate the effect of the palladium coverage on Pt(111) on the reactivity of the surface in Figure 3a, the polarization curves of the ORR on Pt(111)- $x$ Pd electrodes, with  $x \sim 1$  and  $x \sim 1.5$  are compared to the unmodified Pt(111) at a rotation rate of 1600 rpm. Interestingly, while Pt(111)-1 ML Pd is more active than bare Pt(111), the activity of the initially highly active palladium film *re-decreases* even below the activity of the unmodified Pt(111) electrode if more than one monolayer of palladium is deposited. This finding is summarized in Figure 3b where the activities of the different Pd films at a fixed potential of 0.9 V are plotted against the palladium surface coverage. The data indicate a “volcano like” dependency with a maximum in the activity for a full Pd monolayer. The structures of the different Pd films as derived in previous measurements are given as a ball model. Summarizing, it is found that the Pd monolayer without island formation exhibits special properties.

**3.3. Oxygen Reduction Reaction in Perchloric Acid Solution Containing Cl<sup>-</sup> Anions.** In this section the focus lies on the inhibiting effect of specifically adsorbed anions on the kinetics of the ORR. These measurements are motivated by the fact that in previous investigations it was found that in acid solution Pt(111)-1 ML Pd is always *less* active for the ORR than bare Pt(111).<sup>21</sup>







**Figure 4.** Polarization curves for the ORR and corresponding peroxide oxidation current on the ring electrode in 0.1 M HClO<sub>4</sub> containing different amounts of chloride; 50 mV/s, 293 K. Dashed line, no chloride added; full line, 10<sup>-6</sup> M (a, b) and 10<sup>-5</sup> M HCl (c) added, respectively; thick dots represent steady-state currents after 1 min coming from the negative potential limit.

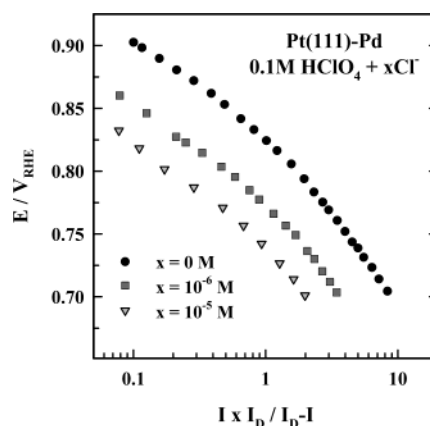
the addition of the first electron to O<sub>2,ad</sub> to form a superoxide radical:



and the rate expression is then:<sup>1</sup>

$$I = K(1 - y\Theta_{\text{ad}})^x \times \exp\left(\frac{-\Delta G_{\theta}^*}{RT}\right) \quad (3)$$

where  $I$  is the observed current, the constant  $K$  represents all structure/composition insensitive parameters,  $\Theta_{\text{ad}}$  is the total surface coverage by anions ( $\Theta_{\text{anions}}$ ) and OH<sub>ad</sub> ( $\Theta_{\text{OHad}}$ ),  $y$  is the number of Pt sites blocked by adsorbed spectator species,<sup>37</sup>  $x$  is the order of active sites (either one or two), and  $\Delta G_{\theta}^*$  is the standard free energy of activation. The rate of the change of the apparent standard free energy of adsorption at zero coverage ( $\Delta G_{\theta}^*$ ) with the surface coverage is given by  $\Delta G_{\theta}^* = \Delta G_0^* + r\theta_{\text{ad}}$ .<sup>31,32</sup> In the following sections, we will use the serial reaction



**Figure 5.** Tafel plots of the kinetic current densities of the ORR on Pt(111)-Pd in 0.1 M HClO<sub>4</sub> containing different amounts of chloride; rotation rate, 1600 rpm; scan rate, 50 mV/s.

pathway and rate expression (eq 3) to analyze the effects of various factors on the kinetics of the ORR on Pt(*hkl*)-Pd surfaces.

**4.1. Electrochemical Properties of the Pt(111)-Pd System in Perchloric Acid Solution: Effects of Cl<sup>-</sup>.** The experimental results presented in the previous sections clearly demonstrated that even a trace amount of chloride has a strong inhibiting effect on the ORR. There are two general observations concerning the kinetics of the ORR on Pt(111) and Pt(111)-Pd surfaces:

(i) For the Pt(111)-Cl<sub>ad</sub> system, it is clear that, although Cl<sub>ad</sub> inhibits the initial adsorption of O<sub>2</sub> molecules on Pt(111), it does *not* affect the pathway of the reaction, see Figure 4a. Therefore, a 4e<sup>-</sup> reduction for the ORR on the Pt(111)-Cl<sub>ad</sub> electrode is operative on the surface positive of the H<sub>upd</sub> potential region. Figures 4b and 4c show that even in the presence of relatively small amount of Cl anions, i.e., 10<sup>-6</sup> M in Figure 4, the onset of the ORR is exceptionally deactivated on Pt(111)-Pd. A further inspection of Figures 4 reveals that, in contrast to the Pt(111)-Cl<sub>ad</sub> system, the ORR at the Pt(111)-Pd/CO<sub>ad</sub> interface is always accompanied quantitatively by H<sub>2</sub>O<sub>2</sub> oxidation currents on the ring electrode and proceeds under steady-state conditions as a 3.5e<sup>-</sup> reduction over the potential range of 0.3 <  $E$  < 0.7 V. The key to resolving the effect of Cl<sub>ad</sub> on the kinetics and reaction mechanism of the ORR on Pt(111)-Pd vs Pt(111) is to be found in understanding the relationship between the strength of metal-Cl<sub>ad</sub> interaction and the effect of Cl<sub>ad</sub> on the rate of O-O bond breaking and/or bond making. Details about the Pd-Cl interaction have been recently discussed,<sup>33</sup> and here only a brief summary will be given. These experiments were carried out in perchloric acid, i.e., the “main” anion present in solution was the perchlorate anion, ClO<sub>4</sub><sup>-</sup>, which interacts with the surface as confirmed by surface-enhanced infrared absorption spectroscopy (SEIRAS).<sup>34</sup> However, by recent RDE experiments it has been concluded that in addition to perchlorate, even in “ultrapure” perchloric acid solution, chloride is present as a trace impurity.<sup>33</sup> Whereas its adsorption on Pt(111) is almost invisible in cyclic voltammetry (at this concentration) the interaction of Cl<sup>-</sup> with Pd is so strong, that even very small chloride concentrations (ca. 10<sup>-7</sup> M) can control the adsorption of H<sub>upd</sub> and OH<sub>ad</sub> as well as the kinetic rate of CO oxidation. The strong interaction of anions with Pd is well-known, e.g., higher bond energies are found in PdCl compounds than are established in PtCl compounds.<sup>28</sup> In sulfuric acid solution, sulfate adsorption is shifted to lower potentials on Pt(111)-Pd compared to Pt(111),<sup>35</sup> in agreement with the slightly lower potential of zero charge (pzc) (and the lower work function, respectively) of Pd resulting in a strong inhibition of

the ORR on the former surface.<sup>21</sup> Since also the Pd–Cl<sub>ad</sub>/Pd–ClO<sub>4,ad</sub> interaction is stronger than the Pt–Cl<sub>ad</sub>/Pd–ClO<sub>4,ad</sub> interaction,<sup>33</sup> it is reasonable to propose that the adsorption of both perchlorate and chloride is enhanced on the former surface and thus the number of metal sites required for adsorption of O<sub>2</sub> and the breaking of O–O bond are reduced on Pd in comparison with Pt. As a consequence, and in agreement with the Pt(*hkl*)–Br<sub>ad</sub> system<sup>11</sup> and the Pt(111)–Pd system in sulfuric acid,<sup>21</sup> the onset of the ORR on Pt(111)–Pd is shifted negatively and peroxide is produced in the same potential range, see Figures 4b and 4c. Notice that in the H<sub>upd</sub> potential region (*E* > 0.3 V), the ORR is strongly inhibited by H<sub>upd</sub>, and corresponds *only* to a 2e<sup>−</sup> reduction at the negative potential limit on all surfaces.

(ii) Figure 5 shows that, as at Pt(111)–HSO<sub>4,ad</sub>,<sup>9</sup> Pt(*hkl*)–Cl<sub>ad</sub>,<sup>12</sup> and Pt(*hkl*)–Br<sub>ad</sub>,<sup>33</sup> interfaces, independent of the chloride concentration a single Tafel slope of ca. 120 mV dec<sup>−1</sup> is deduced from the kinetic analyses of the ORR on Pt(111)–Cl and Pt(111)–Pd–Cl surfaces. The value of the Tafel slope appears to be consistent with the supposition that the standard free energies of adsorption of the reaction intermediates are not affected by the adjacent Cl<sub>ad</sub> and/or ClO<sub>4,ad</sub>, and thus the term  $\Delta G_\theta^*$  in eq 3 becomes a constant factor.<sup>12</sup> As a consequence, the kinetics of the ORR on Pt(111) in the solution containing chloride anions is *completely* determined by the availability of free Pt sites, i.e., the (1 −  $\Theta_{ad}$ ) coverage-dependent term in eq 3.

**4.2. Electrochemical Properties of the Pt(111)–Pd System in Alkaline Solution.** For the ORR in alkaline solution, the process of oxide formation is of eminent importance and will therefore be discussed first in this section. Since the interpretation of the base CVs of Pt(111) and Pt(111)–Pd electrodes in alkaline electrolyte has been described in our previous studies in detail,<sup>20</sup> here we review that interpretation only briefly for completeness. Recall that the structure of electrochemically deposited thin Pd films on the Pt(111) electrode has been studied by SXS technique.<sup>22,24</sup> Ranging from the submonolayer regime to 1 ML, it has been found that the Pd grows via pseudomorphic island formation, whereby the Pd atoms occupied commensurate Pt sites such as to continue the ABC stacking of the Pt(111) substrate. These films were rather stable between the hydrogen evolution and the oxide formation potential region, showing no sign of hydrogen absorption characteristic for bulk Pd. For an increasing coverage beyond 1 Pd monolayer, Pd deposition on Pt(111) follows the Stranski–Krastanov pseudomorphic growth mode, whereby three-dimensional pseudomorphic Pd islands begin to aggregate after (close to) one smooth monolayer of Pd is formed on the Pt substrate. Figure 1 shows that the systematic palladium deposition up to 1.5 ML has the effect of gradually modifying the voltammetric response of Pt(111) such that the intensity of the ‘butterfly’ feature (peak B) is almost lost at about 1.5 ML Pd, a reversible peak develops at 0.45 V (peak A), and an asymmetric peak appears in the hydrogen adsorption region (peak C). It has been suggested that peak A corresponds to the initial adsorption of OH<sup>−</sup> on Pd sites, consistent with the slightly more negative value of the pzc of palladium relative to platinum.<sup>28</sup> The systematic change in the voltammetry with increasing Pd surface coverage may also be gleaned from the inspection of the true oxide potential region (*E* > 0.88 V) which, although known not to introduce defects into the surface atoms of a palladium monolayer,<sup>22</sup> does give rise to an alteration of peak C. As the palladium coverage increases and/or as the positive potential limit is increased, a slight shift of peak C to more negative values is observed in the hydrogen UPD potential region. Consequently, a higher

palladium monolayer and/or a higher the positive potential limit results in a stronger interaction of oxide with the surface, and a greater shift of the reduction of this oxide to more negative potentials can be observed. Again, continuous potential cycling between 0.05 and 1.2 V does not lead to changes in the cyclic voltammetry<sup>22,24</sup> for a palladium monolayer, indicating a lack of structure transformation (surface roughening) of the surface, as found for bare Pt(111). Therefore it was proposed that a surface oxide rather than a bulk oxide is formed on the Pd monolayer.<sup>22</sup> In what follows, it is suggested that it is the loss of the exceedingly stable (toward bulk oxide formation) Pd–Pt interface when depositing Pd multilayer which leads to the ‘volcano’ shape in the relationship between the kinetics of the ORR and the Pd surface coverage.

The first correlation between the kinetics of the ORR and the surface coverage of chemisorbed oxygen-containing species, historically termed ‘oxide’, was established on a polycrystalline platinum electrode. In this study, Tarasevich<sup>36</sup> proposed that the transition in the Tafel slope is directly related to the surface coverage of ‘oxide’ and its effect on the adsorption of O<sub>2</sub>. Very recently, by eliminating the surface heterogeneity of a polycrystalline Pt electrode with single-crystal electrodes, our group gained new insight into the relationship between the surface coverage of OH<sub>ad</sub> and the kinetics of the ORR.<sup>9</sup> It was proposed that the best fit of experimental data can be obtained simply by introducing both site-blocking (preexponential) and energetic (exponential) components in eq 3. We present here an interpretation of the kinetics of the ORR on Pt modified with thin Pd films in alkaline solution on the basis of the hypothesis that the key to understanding the activity of the Pt(111)–Pd surfaces for the ORR is how the Pd adatoms affect the formation of OH<sub>ad</sub> and the adsorption of O<sub>2</sub> and the reaction intermediates. We do not claim, however, that our analysis here is definitive. In fact, it is just a model relating the kinetics of the ORR with both (1 −  $\Theta_{OH}$ ) and  $\Delta G_\theta^*$  components in eq 3.

Figure 2 reveals that the general form of the *i* vs  $\Theta_{Pd}$  relationship for the ORR on Pd-modified Pt(111) has a volcano shape, with the maximum catalytic activity exhibited by a surface modified with 1 ML of Pd. Although on Pd surface atoms the initial adsorption of OH<sup>−</sup>, which acts as a site blocking species, is shifted toward more negative potential compared to Pt atoms (see Figure 1), palladium deposition up to 1 ML increases the rate of the ORR. This is a strong indication that the effect of (1 −  $\Theta_{OH}$ ) term, which leads to a decrease in activity, is compensated by the  $\Delta G_\theta^*$  component in eq 3. We propose, therefore, that the kinetics of the ORR on the Pt(111)–Pd submonolayer film are enhanced due to electronic effects resulting in an optimized adsorption energy of O<sub>2</sub> and the radical anion intermediates O<sub>2</sub><sup>−</sup>, HO<sub>2</sub><sup>−</sup> on Pd atoms.

However, if the Pd coverage exceeds 1 ML, the catalytic activity decreases (Figure 2) and a surface covered by ca. 1.5 ML of Pd is even less active than unmodified Pt(111). To explain this change in reactivity, on the basis of cyclic voltammetry we postulate an increase in the ‘oxide’ binding energy on 3D Pd islands and/or an enhanced irreversible ‘bulk oxide’ formation on the 3D Pd bulk phase (see model in Figure 2). We conclude, therefore, that a Pd *monolayer* on Pt(111) has a unique stability toward oxide formation due to the Pd–Pt interface and that the kinetics of the ORR on Pt(111) modified with a Pd *multilayer* is lowered predominantly due to the (1 −  $\Theta_{OH}$ ) preexponential term, as is the case in acid solution. Theoretical aspects of the relationship between the electronic structure and the reactivity of thin Pd films deposited on Pt(111) are, however, required in order to fully understand the



trends in atomic/molecular chemisorption of oxygen containing species and the reaction intermediates formed during the ORR. Therefore, for a more complete understanding of the unique properties of Pt(111)–Pd measurements of the electronic structure are in planning.

## 5. Conclusion

The oxygen reduction reaction on thin Pd films electrochemically deposited on Pt(111) is investigated in acid and in alkaline solution. The amount of Pd deposited is varied between  $0 < \theta_{\text{Pd}} < 1.5$  ML. In 0.1 M HClO<sub>4</sub>, the pseudomorphic Pd monolayer has a lower activity (by the factor of ca. 2) than Pt(111). In solution containing Cl<sup>−</sup> (ca.  $10^6$ – $10^{-5}$  M), the inhibition on the Pt(111)–Pd electrode is much more severe than on bare Pt(111) due to a strong anion adsorption on Pd. In contrast, in 0.1 M KOH the activity of Pt(111) can be enhanced by Pd. In alkaline solution, the general form of the current vs  $\Theta_{\text{Pd}}$  relationship for the ORR has a volcano shape, with the maximum catalytic activity exhibited by a surface modified with 1 ML of Pd. If the amount of Pd deposited exceeds 1 ML, the catalytic activity re-decreases and a surface covered by ca. 1.5 ML of Pd becomes even less active than unmodified Pt(111).

To interpret the kinetics of the ORR on Pt modified by thin Pd films in alkaline as well as in acid solution, it is proposed that the key to understanding the activity of the Pt(111)–Pd surface lies in analyzing two main contributions: the amount of specific anion adsorption on the surface, and thus the number of reaction sites; and electronic effects influencing the adsorption energy of O<sub>2</sub> and the radical anion intermediates. Therefore, in acid solution the Pt(111)–Pd surface is less active than bare Pt(111) due to enhanced anion adsorption, whereas in alkaline solution, where only OH anions are present, for  $\theta_{\text{Pd}} < 1$  ML this effect is compensated by an optimized adsorption energy of O<sub>2</sub>, O<sub>2</sub><sup>−</sup>, HO<sub>2</sub><sup>−</sup> on Pd atoms.

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