

Kinetics of Oxygen Reduction on an Epitaxial Film of Palladium on Pt(111)<sup>†,‡</sup>V. Climent,<sup>§</sup> N. M. Marković, and P. N. Ross\*

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The kinetics of the oxygen reduction reaction on epitaxial thin films of Pd on Pt(111) was studied using the rotating ring-disk electrode technique. The results for the pseudomorphic monolayer of Pd are compared to those of the unmodified Pt(111) surface, both surfaces having nominally identical 2D structures. In an electrolyte containing a nonabsorbing anion, 0.5 M HClO<sub>4</sub>, the pseudomorphic layer of Pd has a somewhat lower (ca. factor of 2) activity than Pt(111). In an electrolyte containing an anion which is strongly adsorbing on Pt(111), 0.5 M H<sub>2</sub>SO<sub>4</sub>, the inhibition due to anion absorption is even greater on the pseudomorphic monolayer of Pd than on the unmodified Pt(111) surface. This additional inhibition is attributed to the difference in the potential of zero charge (pzc) between the two surfaces, the Pt(111) having the more positive pzc.

## 1. Introduction

The oxygen reduction reaction (ORR) is one of the most extensively investigated processes in electrochemistry.<sup>1</sup> Interest in the ORR has been driven primarily by the substantial technical need to develop electrocatalysts for the cathode in H<sub>2</sub>–air fuel cells. But this reaction is also a fundamental constituent of other electrochemical processes or technologies, such as corrosion in oxygenated aqueous solutions<sup>2</sup> or in air-depolarized electrosynthesis. Among the many catalysts examined, the platinum-group metals are of particular interest because platinum, palladium, and rhodium are the most active materials for the ORR in acidic electrolytes. Early kinetic and mechanistic studies were carried out on polycrystalline electrodes. For example, Tarasevich proposed that the reaction pathway for the ORR on all of the platinum-group metals is very similar, and that at low overpotentials the order of activity increased in the sequence Rh < Pd < Pt.<sup>3</sup> Tarasevich, also concluded that the kinetics were strongly dependent on the nature of the anion of the supporting electrolyte.<sup>3</sup> The understanding of the effect of anions on the kinetics of the ORR has recently been enhanced by studies with single-crystal surfaces.<sup>4,5</sup> Namely, with the advent of surface structural probes such as in-situ surface X-ray scattering (SXS),<sup>6</sup> complemented with the development of the rotating ring-disk electrode (RRDE) technique for use with platinum single crystals,<sup>5</sup> it has become possible to study the relationship between the surface structure, anion adsorbate structure, and the electrocatalytic activity of Pt(*hkl*) surfaces. These studies revealed that the structure sensitivity of the ORR arises primarily from structure-sensitive adsorption of anions in the supporting electrolyte, e.g., bisulfate,<sup>5a</sup> hydroxyl,<sup>5b</sup> and halides,<sup>5c</sup> that are not intermediates in the ORR. Consequently, these “spectator” adsorbates actually impede the kinetics. In contrast to Pt(*hkl*), however, there are no kinetic studies of the ORR on Pd(*hkl*) and Rh(*hkl*) surfaces. Electrochemical studies with Pd(*hkl*)

electrodes are relatively scarce because of the difficulties in surface preparation and stability caused by the absorption of hydrogen into the bulk lattice, e.g., the cycling of hydrogen in/out of the lattice causes disordering of the palladium single-crystal surface in the same way the oxide formation/reduction does with platinum single-crystal surfaces. To circumvent these problems, epitaxial Pd films on Pt(*hkl*) substrates have been recently used as a convenient substitute for massive Pd single crystals.<sup>7–11</sup> By the use of surface-sensitive techniques, e.g., by ex-situ low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES),<sup>10</sup> and most recently by in-situ SXS measurements,<sup>12</sup> it has been demonstrated that Pd can be deposited (either electrochemically or in ultrahigh vacuum (UHV)) on Pt(*hkl*) as uniform epitaxial metallic layer(s). The epitaxial growth of palladium on platinum single-crystal electrodes has allowed several groups to study both adsorption properties<sup>7–11</sup> as well as the electrocatalytic properties<sup>11</sup> of highly ordered Pd films on Pt(*hkl*).

In the present paper, we report an examination of the ORR on the Pt(111) electrode modified by epitaxial films of palladium, denoted hereafter as the Pt(111)–Pd system, employing the same procedures used in our recent study of the ORR on Pt(*hkl*) surfaces.<sup>5</sup> The results obtained with epitaxial films of Pd described herein will not necessarily be characteristic of bulk Pd(111). The epitaxial films of Pd we use here do not absorb hydrogen at potentials positive of the reversible hydrogen electrode (RHE). This was also true of thin (e.g., <10 ML) films of Pd on Au(*hkl*) surfaces.<sup>11</sup> When the Pd films on either Pt(*hkl*) or Au(*hkl*) are thicker than ca. 5–10 ML, hydrogen is absorbed at potentials positive of the RHE and the films may be expected to be characteristic of the bulk Pd surface of the same orientation. It is not clear why hydrogen is not absorbed into the thin films of Pd on Au or Pt. For Pt(*hkl*), the Pd films <5 ML are pseudomorphic, having the Pt lattice constant, but the strain is very small because the lattice constants differ by only 0.8%. Possibly the absence of absorption is due to the pinning of the first Pd layer to the Pt lattice, which does not absorb hydrogen, and the pinned layer prevents expansion of the topmost layers to accommodate hydrogen because the strain energy is too large. In any event, the results with the Pt(111)–

<sup>†</sup> Dedicated to Gabor Somorjai on the occasion of his 65th birthday and in recognition of his contribution to the physical chemistry of surfaces and interfaces.

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Pd system described herein may not be characteristic of bulk Pd(111) and should for the time being be considered a unique surface.

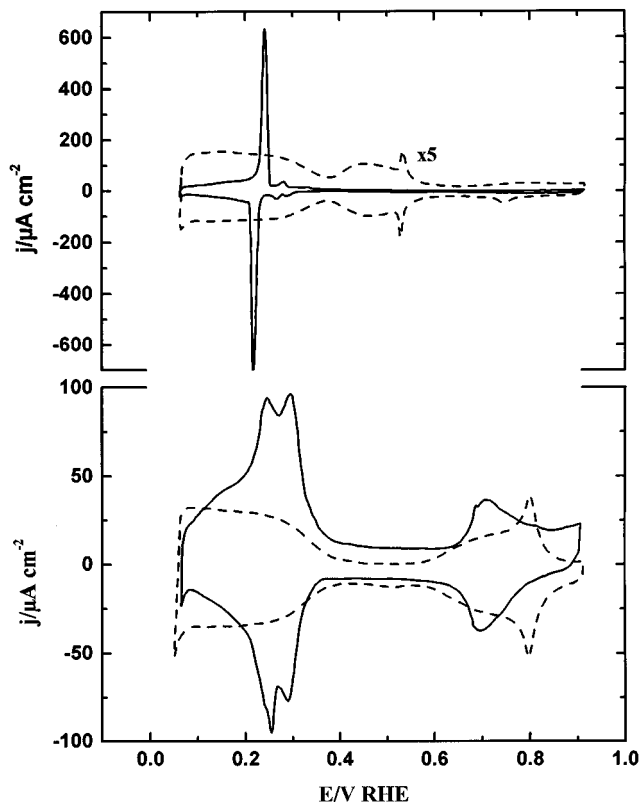
## 2. Experimental Section

The pretreatment and assembling of the Pt(111) crystal in an RRDE configuration was fully described in ref. 5. Briefly summarizing, before each experiment, the electrode was flame annealed and cooled in  $\text{H}_2 + \text{Ar}$  atmosphere. After that, the surface was protected with a droplet of ultrapure water and mounted into the disk position of an insertable RRDE assembly (Pine Instruments). The Pd film was deposited from a  $10^{-5}$  M PdO in 0.05 M  $\text{H}_2\text{SO}_4$  at 20 mV/s. The amount deposited was controlled by the continuous change of the voltammetric features, from those characteristic of Pt(111) to those characteristic of a pseudomorphic monolayer of Pd; for details including structural characterization, see refs. 7–11. After the completion of a monolayer of palladium, the electrode was rinsed with water and transferred to a second electrochemical cell containing a solution free of  $\text{Pd}^{2+}$ .

Solutions were prepared from  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  (Baker Ultrex), and PdO (Alfa Products), employing pyrolytically triply distilled water. The voltammetry was recorded in a solution deaerated by Ar (Air Products, 5N5 purity). All voltammograms were recorded at a sweep rate of 50 mV/s at room temperature. The polarization curves for the ORR were obtained in a solution saturated by oxygen (5N8 purity). Potentials were measured against a saturated calomel electrode but they are quoted vs the RHE throughout the paper. A bridge was placed between the reference electrode and the cell to prevent electrolyte contamination by  $\text{Cl}^-$ . A bipotentiostat (Pine Instruments, model AFRDE 4) was used for all of the RRDE experiments and all curves were recorded using a chart recorder.

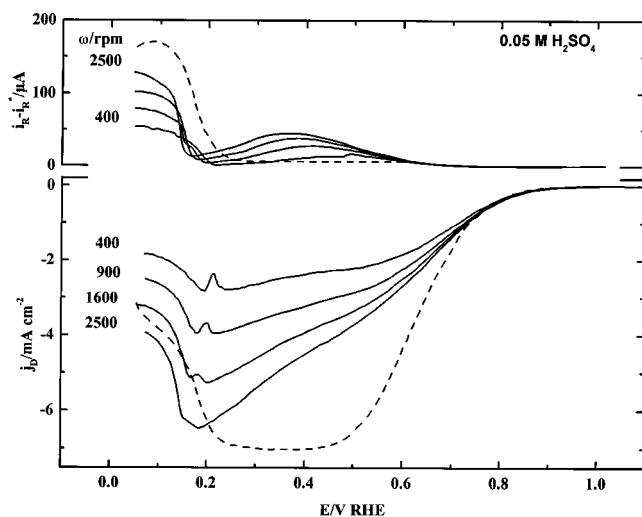
## 3. Results

**3.1. Cyclic Voltammograms.** Figure 1 shows the voltammograms corresponding to a Pt(111)–Pd electrode in 0.05 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{HClO}_4$  solutions. The voltammograms corresponding to the unmodified surfaces are also included for comparison. The current–potential curve of Pt(111)–(1 × 1) gives a distinctive voltammogram with a broad, nearly flat hydrogen adsorption/desorption region between  $0.05 < E < 0.375$  in both 0.05 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{HClO}_4$  that is indicative of hydrogen adsorption not accompanied by concomitant anion adsorption. At more positive potential, the “butterfly” peak is observed between 0.4 and 0.6 V in sulfuric acid solution and between 0.6 and 0.85 V in perchloric acid solution. These peaks are now understood to be anion adsorption pseudocapacitance: in 0.05 M  $\text{H}_2\text{SO}_4$  the adsorption/desorption of bisulfate anions;<sup>13</sup> in 0.1 M  $\text{HClO}_4$  adsorption/desorption of hydroxyl anions is most likely accompanied by desorption/adsorption of  $\text{Cl}^-$  anions.<sup>14</sup> Note that in sulfuric acid solution a small peak is also recorded at ca. 0.65 V. The position of this peak coincides with the “butterfly” peak observed in a perchloric acid solution, indicating that the peak at 0.65 in 0.05 M  $\text{H}_2\text{SO}_4$  may correspond to a filling-in by  $\text{OH}_{\text{ad}}$  on bisulfate-free Pt sites.<sup>15</sup> When a monolayer of palladium was deposited on the Pt(111) electrode, the voltammogram changed dramatically. In particular, the processes of hydrogen adsorption/desorption and bisulfate desorption/adsorption, which are well-resolved at the Pt(111) electrode in 0.05 M  $\text{H}_2\text{SO}_4$ , emerge into a single very sharp peak around 0.21 V at the Pt(111)–Pd surface (see Figure 1a). The charge under the peak ( $\approx 310 \mu\text{C}/\text{cm}^2$ ) is higher than the charge corresponding to the completion of a monolayer of

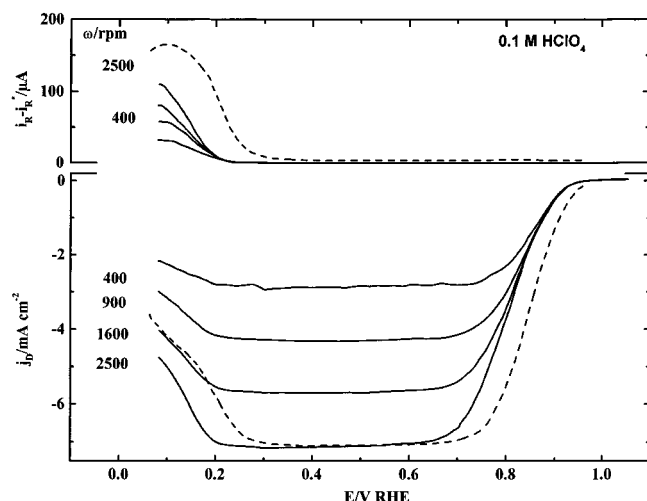


**Figure 1.** Cyclic voltammograms in argon-purged electrolyte: (top) 0.05 M sulfuric acid with Pt(111) (dash, current scale magnified by 5) and Pt(111) with a monolayer of Pd; (bottom) 0.1 M perchloric acid with Pt(111) (dash) and Pt(111) with a monolayer of Pd, 50 mV/s.

hydrogen (for any adsorbate, 1 ML is defined as one molecule/adatom adsorbed per Pt surface atoms, or  $1.5 \times 10^{15}$  molecules/ $\text{cm}^2$  (equivalent to  $\approx 240 \mu\text{C}/\text{cm}^2$ ), indicating that hydrogen adsorption/desorption is indeed accompanied by anion desorption/adsorption. Recently, charge displacement experiments confirmed that the difference between the charge which corresponds to the formation of a hydrogen monolayer, and the charge inferred under the voltammetry in the  $\text{H}_{\text{upd}}$  region (ca.  $90 \mu\text{C}/\text{cm}^2$ ), corresponds to adsorption/desorption of bisulfate anions.<sup>16</sup> Furthermore, the difference between the total charge in the  $\text{H}_{\text{upd}}$  potential region ( $\approx 330 \mu\text{C}/\text{cm}^2$ ) and the charge deduced for anion adsorption equals  $\approx 240 \mu\text{C}/\text{cm}^2$ , indicating that the Pt(111)–Pd surface is covered by 1 ML of  $\text{H}_{\text{upd}}$ .<sup>16</sup> It is interesting that in the same potential region the maximum charge associated with  $\text{H}_{\text{upd}}$  on Pt(111) is only  $160 \mu\text{C}/\text{cm}^2$  (0.66 ML). This implies that the adsorption energy of  $\text{H}_{\text{upd}}$  on the pseudomorphic Pd layer is higher than that on Pt(111), and/or the lateral repulsion between  $\text{H}_{\text{upd}}$  on the Pt(111)–Pd electrode is smaller than that on Pt(111). Figure 1a shows that a sharp peak at 0.23 V is followed first by a small peak around 0.26 V, and then with very narrow double-layer potential region. A peak at 0.26 V can be associated with the presence of small patches of a second Pd layer that are nucleated onto the first layer.<sup>7–10</sup> The fact that this peak is observed at the same potential as that for Pt(111) having various degrees of defects<sup>13c</sup> may indicate that the pseudomorphic Pt(111)–Pd film is *not* a defect-free surface. Figure 1a also revealed that a small peak at 0.65 V which is clearly observed in the “double-layer” potential region of Pt(111) completely disappeared in the voltammetry for the Pt(111)–Pd electrode. Both a complete disappearance of this peak as well as a collapse of the  $\text{H}_{\text{upd}}$  peak and the “butterfly” feature into a single sharp peak at a more cathodic potential than the bisulfate adsorption/desorption potential clearly indicate a strong



**Figure 2.** Current–potential curves for the ORR in oxygen-saturated 0.05 M sulfuric acid for the ring electrode (top) and for the disk electrode (bottom) of Pt(111) with a monolayer of Pd at various rotation rates; dashed curves are for an unmodified Pt(111) disk electrode at 1600 rpm. On positive sweep from 0.05 V at 50 mV/s.



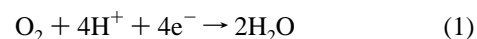
**Figure 3.** Same as Figure 2 in 0.1 M perchloric acid.

interaction of bisulfate anions with the Pt(111)–Pd surface. One would expect that the lower work function of the Pt(111)–Pd surface as compared to the unmodified Pt(111) will result in an enhanced adsorption of anions at the Pt(111)–Pd interface at fixed potential due to the fundamental relation between work function and the potential of zero charge (pzc).<sup>12</sup>

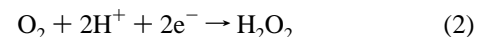
A close inspection of Figure 1b indicates that the adsorption of OH<sub>ad</sub> on the Pt(111)–Pd surface in 0.1 M HClO<sub>4</sub> occurs at a lower potential than on unmodified Pt(111) in the same solution. The negative shift (ca. 0.1 V) of the OH<sub>ad</sub> pseudocapacitive peak on Pt(111)–Pd vs Pt(111) is also an indication of a lower pzc. Note the dramatically different H<sub>upd</sub> features that are observed on the Pt(111)–Pd surface versus Pt(111) in both perchloric and sulfuric acid. These features were also noted in previous work.<sup>7–11</sup> The multiplicity of peaks is probably associated with defect sites created by initial formation of the second Pd layer. As we discuss below, both stronger interaction of anions with the Pt(111)–Pd surface vs Pt(111) as well as the defect sites created during the formation of pseudomorphic monolayer of Pd will have a significant effects on the ORR.

**3.2. ORR.** Figures 2 and 3 summarize a family of polarization curves for the ORR on the Pt(111)–Pd electrode in O<sub>2</sub>-saturated 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M HClO<sub>4</sub> solutions along with a

representative polarization curve recorded in the same solution but on Pt(111). For our purposes here, the ring electrode is potentiostated at 0.91 V, such that oxidation of H<sub>2</sub>O<sub>2</sub> which is produced on the disk electrode is under diffusion control. Consequently, H<sub>2</sub>O<sub>2</sub> can be quantitatively “collected” on the ring electrode. For Pt(111), starting at ca. 0.6 V and sweeping the disk potential negatively to 0.2 V, the ring currents were a very small fraction of the disk currents, implying that on the surface covered with adsorbed bisulfate anions oxygen reduction proceeds almost entirely through the direct 4e<sup>−</sup> pathway. The appearance of peroxide oxidation currents on the ring electrode begins at potentials negative of 0.2 V, and is concurrent with the adsorption of hydrogen on Pt(111). At the negative potential limit the limiting current corresponds exactly to a two-electron reduction of O<sub>2</sub>. We proposed that the change in the pathway of oxygen reduction from the four-electron reduction



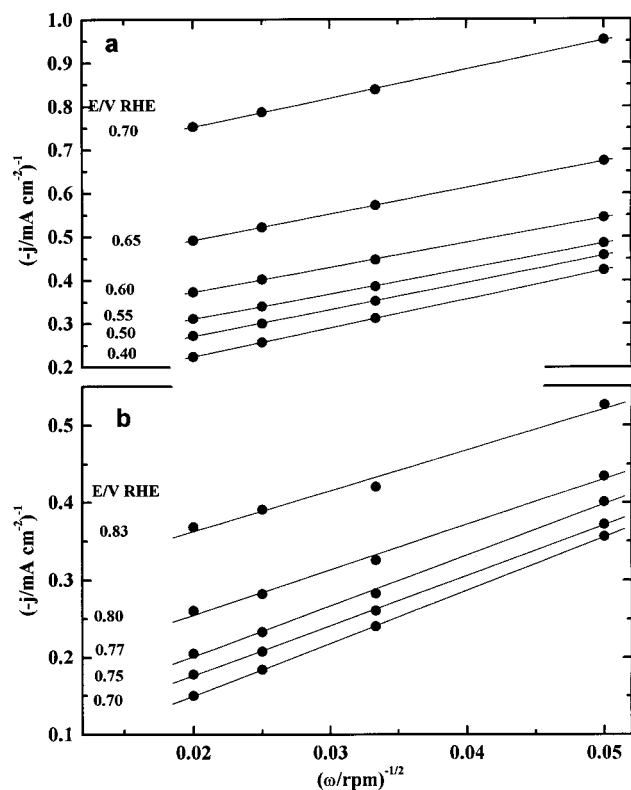
to the 2 e<sup>−</sup> reaction, leading to the formation of H<sub>2</sub>O<sub>2</sub>



in the hydrogen adsorption region is most likely related to the loss of adsorption sites which break the O–O bond.<sup>5</sup>

For the Pt(111)–Pd system, the ORR in 0.05 M H<sub>2</sub>SO<sub>4</sub> (Figure 2) is strongly inhibited below ca. 0.6 V. This is not a surprising result considering that the Pt(111)–Pd surface is mostly covered by strongly adsorbed bisulfate anions (see section 3.1), which can simultaneously suppress the initial adsorption of O<sub>2</sub> molecules and the formation of pairs of Pd surface atoms needed for the breaking of the O–O bond. Figure 2 clearly revealed that the formation of H<sub>2</sub>O<sub>2</sub> starts around 0.6 V, reaches maximum at ca. 0.38 V, and then monotonically decreases to zero around 0.2 V concurrent with the desorption of bisulfate anions. At the same time, the O<sub>2</sub> reduction currents increase to a diffusion-limiting value for ca. 3.7 electrons per O<sub>2</sub> molecule (see Figure 2). This implies that the ORR at Pt(111)–Pd–HSO<sub>4</sub> interface at 0.2–0.6 V proceeds via a “series pathway” with solution-phase peroxide formation.<sup>1</sup> Sweeping the potential more negative than 0.2 V, however, causes the O<sub>2</sub> reduction current to decrease again, and diffusion-limiting currents fall to a value indicative of a 2.5 e<sup>−</sup> reduction. As for the ORR on the Pt(111) surface,<sup>5</sup> in this potential region the kinetics of the ORR is determined by the surface coverage of H<sub>upd</sub>. On the basis of the foregoing discussion for Pt(111), the decrease in the rate of the ORR at the disk electrode, which parallels the increase in the peroxide oxidation currents on the ring electrode, is indicative of a change in the mechanism; e.g., from direct four-electron mechanism (eq 1) to a predominantly the 2.5e<sup>−</sup> reaction with the formation of bulk H<sub>2</sub>O<sub>2</sub> (eq 2). Note that in the same potential region (*E* < 0.2 V) the ORR at the Pt(111)–H<sub>upd</sub> interface is more inhibited than on the Pt(111)–Pd–H<sub>upd</sub> modified surface. Although the database is extremely limited, two possibilities may account for this phenomena: (i) A higher adsorption energy of H<sub>2</sub>O<sub>2</sub> on the Pt(111)–Pd surface as compared to the unmodified Pt(111) electrode acting as a catalytic driving force for the breaking of the O–O bond; or (ii) surface defects in the Pd film (see section 3.1), which can lead to an increase in the number of active sites required for dissociative adsorption of H<sub>2</sub>O<sub>2</sub> intermediates.

A comparison of the polarization curves of the ORR on Pt(111) and Pt(111)–Pd surfaces in 0.1 M HClO<sub>4</sub> is presented in Figure 3. As expected, due to stronger interaction of OH<sub>ad</sub> (an inhibitor spectator species), the activity of the Pt(111)–Pd



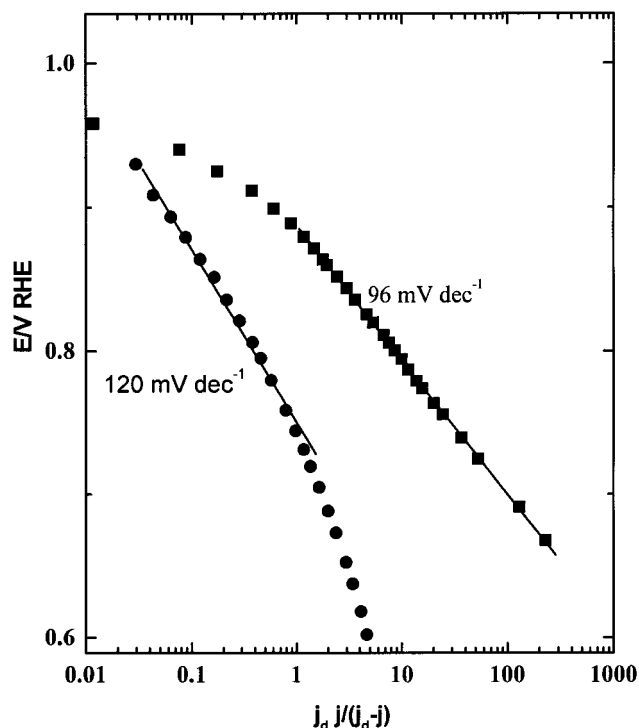
**Figure 4.** Levich-Koutecky plots for the ORR on the Pt(111)-Pd electrode in (top) 0.05 M sulfuric acid and (bottom) 0.1 M perchloric acid.

surface for the ORR is somewhat lower than with unmodified Pt(111), ca. factor of 2. In the potential region between  $0.85 < E < 0.7$  V, the continuous desorption of  $\text{OH}_{\text{ad}}$  is mirrored by the concomitant increase in the rate of the ORR, so at ca. 0.65 V, the  $\text{O}_2$  reduction current increases to a diffusion-limiting current for the  $4 e^-$  reduction. Note, that in the same potential range no peroxide was detected on the ring electrode, indicating that a pair of Pd sites is always available for the breaking of the O-O bond. This implies that the direct  $4e^-$  path (eq 1) is operative in this potential region. In contrast, the rate of the ORR starts to decrease with the increase of the surface coverage by  $\text{H}_{\text{upd}}$ , consistent with the quantitative  $2.5 e^-$  reduction of  $\text{O}_2$  in the potential region where 1 ML of  $\text{H}_{\text{upd}}$  is present on the surface. As we suggested above, free Pd sites required for a cleaving of O-O bond are blocked by  $\text{H}_{\text{upd}}$ , and the ORR proceeds predominantly via a “peroxide pathway” at  $E < 0.2$  V.

Figure 4 shows plots of  $j^{-1}$  vs  $\omega^{-0.5}$  for various electrode potentials (the so-called Levich-Koutecky plot). These plots for various potentials yield straight lines with intercept corresponding to the kinetic currents and the slope corresponding to the  $B$  values, e.g., from eq 3:

$$\frac{1}{j} = \frac{1}{nFkc_{\text{O}_2}} + \frac{1}{B\omega^{0.5}} \quad (3)$$

The experimental values of  $B$  ( $4.5 \text{ mA rpm}^{-0.5}$  in 0.05 M  $\text{H}_2\text{SO}_4$ , and  $4.3 \text{ mA rpm}^{-0.5}$  in 0.1 M  $\text{HClO}_4$ ) agree well with the theoretical values calculated for  $4 e^-$  reduction using literature data for  $\text{O}_2$  solubility, diffusion coefficient of  $\text{O}_2$ , and kinematic viscosity of electrolytes.<sup>5</sup> The linearity of the plots in insets of Figure 4 implies a first-order dependence in  $\text{O}_2$  kinetics on the Pt(111)-Pd surface. The Tafel plot (Figure 5) for the ORR on Pt(111)-Pd in 0.05 M  $\text{H}_2\text{SO}_4$  indicates that the Tafel slope is

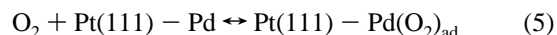


**Figure 5.** Tafel plot for the ORR on the Pt(111)-Pd electrode in (squares) 0.1 M perchloric acid and (circles) 0.05 M sulfuric acid.

$120 \text{ mV dec}^{-1}$  in the potential region above 0.7 V, with a transition to a very high value ( $\approx 400 \text{ mV dec}^{-1}$ ) below that. The Tafel slope of  $120 \text{ mV dec}^{-1}$  indicates that at low overpotentials the rate-determining step (rds) is the first charge-transfer step, eq 3.



Considering that a significant change in the Tafel slope usually implies a change in the rds, the transition in the Tafel slope below 0.7 V may represent a change in the rds from eq 3. According to Tarasevich,<sup>3</sup> the high Tafel slope of  $400 \text{ mV dec}^{-1}$  may correspond to the adsorption of molecular oxygen as the rds:



In contrast to sulfuric acid solution, in 0.1 M  $\text{HClO}_4$  a single linear Tafel slope (ca.  $96 \text{ mV dec}^{-1}$ ) was obtained in the entire potential range. Closely following our discussion for the ORR on Pt(111) in perchloric acid solution, we propose that, although the Tafel slope is different from  $120 \text{ mV dec}^{-1}$ , the rds for the ORR on the Pt(111)-Pd surface in 0.1 M  $\text{HClO}_4$  is also the first charge-transfer step; for more discussion of the ORR mechanism on Pt(*hkl*) electrodes, see refs. 5.

If the rate-controlling step is the first charge-transfer step, then, for the first-order dependence of the kinetics of the ORR found in this work, the general rate expression for the ORR can be given by<sup>5</sup>

$$i = nFkc_{\text{O}_2} (1 - \theta_{\text{ad}})^x \exp(-\beta FE/RT) \exp(-\gamma r\theta_{\text{ox}}/RT) \quad (6)$$

where  $n$  is the number of electrons,  $K$  is the rate constant,  $c_{\text{O}_2}$  is the concentration of  $\text{O}_2$  in the solution,  $\theta_{\text{ad}}$  is the surface coverage by adsorbed species; e.g.,  $\text{OH}_{\text{ad}}$ ,  $\text{O}_2$ ,  $\text{O}_2^-$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HSO}_4^-$ ,  $x$  is the number of Pt(Pd) sites occupied by the adsorbed species,  $i$  is the observed current,  $E$  is the applied potential,  $\beta$



and  $\gamma$  are the symmetry factors (assumed to be  $1/2$ ), and  $r$  is the rate of change of the apparent standard free energy of adsorption of oxygen-containing species with the surface coverage ( $\theta_{\text{ox}}$ ) of both reaction intermediates and  $\text{OH}_{\text{ad}}$ .<sup>17</sup> Equation 6 revealed that at the same potential and for the same partial pressure of  $\text{O}_2$  the rate of the ORR is determined by two terms: the preexponential term which is related with the fractional coverage of all adsorbed species, and the second exponential term which is directly related to the rate of change of free energy of adsorption of oxygen-containing species with its coverage. With the aid of eq 6, and on the basis of the observation that the adsorption of bisulfate anions on Pt(111)–Pd surface is much stronger than with unmodified Pt(111) electrode, it is possible to rationalize the strong inhibition of the ORR reaction in sulfuric solution at potentials above the bisulfate adsorption potential, 0.2 V. Hence, in this model the kinetics of the ORR on Pt(111)–Pd relative to clean Pt(111) is determined primarily by the preexponential  $(1 - \theta_{\text{ad}})$  term, but the absolute value of this term is not actually known for either surface. To examine the preexponential term further, we can compare the activities in 0.05 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{HClO}_4$ . Figures 2 and 3 show that the activity in perchloric acid solution (in the potential region above 0.8 V where kinetic currents can be observed in both electrolytes) is nearly 2 orders of magnitude higher than in sulfuric acid solution. This inhibition by bisulfate adsorption is even greater for Pt(111)–Pd than for unmodified Pt(111).<sup>5d</sup> Strong adsorption of bisulfate anion on Pt(111) is due at least in part to the symmetry match between the fcc (111) face and trigonal coplanar geometry of the oxygens of the sulfate anion.<sup>13c</sup> Following the same line of reasoning, stronger adsorption of bisulfate is due to the lower potential of zero charge on the geometrically identical pseudomorphic Pd monolayer. In order for the preexponential term to have an effect as large as 50–100-fold, the  $(1 - \theta_{\text{ad}})^x$  value must be on the order of 0.01, i.e., bisulfate anion adsorption leaves very few free Pd(Pt) sites on either the Pt(111)–Pd or Pt(111) surface.

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