Journal of Applied Electrochemistry (2006) 36:1207–1214
DOI 10.1007/s10800-006-9179-y

Formic acid oxidation on Pd-modified Pt(100) and Pt(111) electrodes: A DEMS study

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Received 1 September 2005; accepted in revised form 2 March 2006

Key words: DEMS, formic acid, palladium, platinum single crystals, voltammetry

Abstract

Formic acid oxidation on palladium submonolayers on well-defined Pt(100) and Pt(111) electrodes has been studied using voltammetry and Differential Electrochemical Mass Spectrometry (DEMS). A combination of the two techniques allows a better understanding of the reaction taking place on the electrode surface. Thus, an exact correlation between the CO_2 mass signal and the current density in the voltammogram corresponding to the formic acid oxidation has been obtained. On palladium modified Pt(100) electrodes and in the potential region below 0.3 V, the currents in the positive scan are higher than those recorded in the negative scan. This diminution on the signal in the negative scan has been associated with CO_2 reduction to CO on the palladium adlayer. In addition, the CO_2 reduction reaction seems to take place on the border of the palladium islands. Finally, the adsorption of (bi)sulfate anions has an inhibiting behavior on the formic acid oxidation reaction.

1. Introduction

Formic acid oxidation on metal surfaces has been widely studied, not only covering fundamental aspects but also its possible application in fuel cell technology [1]. Among the different metal electrodes studied, platinum has shown the highest catalytic activity of all the pure metals for the oxidation. Formic acid oxidation on platinum takes place through a widely accepted dual path mechanism in which both paths are structure sensitive [2, 3]. One of them leads to direct formation of CO_2, whereas the other involves the formation of CO_{ads}, poisoning the metal surface.

Previous papers have demonstrated that the use of adsorbed adatoms as surface modifiers is an excellent alternative to improve the electrocatalytic activity of the metal substrate [4–23]. For example, a 40-fold increase in the currents at 0.5 V has been measured in the catalytic activity of Pt(111) when bismuth is adsorbed at coverage value of 0.28 [4, 23, 24]. However, in this case, the onset potential for formic acid oxidation remains essentially the same as that for the platinum substrate.

In relation to the potential range where formic acid oxidation takes place, Pt(hkl)/Pd surfaces appear as a more interesting alternative. Thus, Clavilier et al. performed formic acid oxidation experiments on well-defined Pt(hkl) electrodes modified with palladium adlayers, showing a clear synergetic effect [11]. In those previous works, palladium was deposited on Pt(hkl) substrates by using the so-called forced deposition method [11]. It was found that the growth of a second layer of palladium atoms takes place before the first layer is fully completed. Additionally, an improvement in the electrocatalytic activity on Pt(100) electrodes modified with Pd sub-monolayers was observed, with an onset potential as low as 0.12 V. The full palladium monolayer showed a somewhat smaller catalytic activity. On Pt(111) electrodes, no significant increase in electrocatalytic activity was reported when the palladium coverage was below the monolayer range [25–29]. When more than a monolayer was deposited, the onset potential for formic acid oxidation shifted to more negative potentials (0.2 V). On the other hand, Baldauf et al. used electrolytic deposition to form a Pd adlayer on Pt(hkl) electrodes. In all cases, the Pt(100)/Pd surface was clearly the most active toward formic acid electrooxidation [19]. This increase in activity was more significant as the Pd coverage increased above the monolayer range. The different method of adlayer preparation could be the origin of the observed differences, since the electrodeposition method seems to produce more uniform adlayers [25–29].

Thus, the aim of this work is to study formic acid oxidation on Pt(100) and Pt(111) modified with electrodeposited Pd using not only voltammetry but also Differential Electrochemical Mass Spectrometry

(DEMS) to analyze the formation of CO_2 during the oxidation process for the platinum substrates with different Pd coverages.

2. Experimental

Single crystal platinum electrodes, used as substrates, were oriented, cut and polished as described previously [30]. The quality of the electrode surfaces as well as the solution composition is known to be crucial. For this reason, the electrodes were annealed and cooled under a H_2+Ar reductive atmosphere. Three conventional electrochemical cells were used. In the first, the palladium adlayer was deposited from 10^{-5} M Pd^{2+} solution in 0.1 M sulfuric acid. Then, the electrode was rinsed with ultrapure water and immersed in the second cell, containing 0.5 M sulfuric acid, in which the characteristic voltammetric profiles were recorded. The voltammetric profiles reported here are the steady state ones, usually recorded after the second sweep and stable over several cycles. After the bimetallic electrode had been characterized, it was immediately transferred to the electrochemical cell containing a solution of 0.25 M formid acid (Merck pro analysis) in 0.5 M sulfuric acid where the electrocatalytic activity of the electrode was checked. The electrode contacted the solution at a constant potential of 0.1 V and was cycled between 0.06 and 0.85 V. This conventional electrochemical cell was connected trough a PTFE membrane with the mass spectrometer to perform both electrochemical and mass spectrometer experiments. A PTFE membrane (Gore-Tex, 75 μm mean thickness and 0.02 μm mean pore size) was employed to avoid entrance of solution to the mass spectrometer. A gold wire counter electrode was used in all electrochemical cells. All potentials were measured against a reversible hydrogen electrode (RHE).

DEMS was used to determine the CO_2 production from the oxidation of formic acid on the palladium modified Pt(hkl) electrode surfaces. The ionization chamber used in the DEMS experiments was pumped at 210 l s^{-1} with a turbomolecular pump (Pfeiffer) supported with a dry diaphragm pump (Pfeiffer) in order to avoid contamination from oil vapors. Due to the high pressure in the ionization chamber during the electrochemical experiments, a turbomolecular pump (60 l s^{-1}, Pfeiffer) supported with a dry diaphragm pump (Pfeiffer) differentially pumped the mass spectrometer analysis chamber. The quadrupole mass spectrometer (Prisma^{TM} QMS 100 M2, Pfeiffer) was connected to the analysis chamber and contained an electron multiplier/Faraday cup detector (Channeltron). The very short diffusion times from the cell to the detector ($<$ 1 s) allowed the measurement of the mass intensity of the products as a function of potential. The electrochemical cell was press fitted onto the membrane-flange assembly, with the membrane serving as the interface between the mass spectrometer main chamber at high vacuum and the electrochemical cell at atmospheric pressure.

The methodology employed for the Pd adlayer was similar to that previously reported [25–29, 31]. Very briefly, both Pt(100) or Pt(111) clean surfaces were immersed at 0.10 V in a 10^{-5} M $PdSO_4$ dissolved in 0.1 M H_2SO_4 in meniscus configuration. To control the coverage, the potential was continuously cycled at 50 mV s^{-1} between 0.06 and 0.85 V for the Pt(100) and between 0.06 and 0.95 V for the Pt(111). The voltammetric profiles recorded in this solution were used to estimate roughly the palladium coverage. The voltammogram was recorded until the desired value was obtained. Then, the electrode was transferred to a second cell containing only 0.5 M H_2SO_4 and free of Pd^{+2} cations. The value of the palladium coverage was calculated by recording the voltammetric profile in this cell [25, 29, 31]. The palladium coverage is defined the number of palladium atoms per platinum surface atom.

3. Results

3.1. *Pt(100)/Pd surfaces*

Figure 1 shows some of the voltammetric profiles obtained for the Pt(100) with different palladium coverage values. The characteristic adsorption peak of well ordered Pt(100) electrodes at 0.38 V progressively diminishes whereas a new sharp adsorption state at 0.16 V appears. This peak at 0.16 V is associated with the first adlayer of palladium atoms directly deposited on the Pt(100) substrate. For a perfect palladium epitaxial adlayer, it would be expected that the peak at 0.16 V increases until all the adsorption states associated to the Pt(100) electrode disappear. However, a new feature appears at 0.26 V while the peak at 0.38 V has not been completely suppressed. This new peak is associated with the growth of palladium in second, third and further layers, indicating that the growth of the second layer has started prior to the completion of the first layer. Previous work has shown that the use of the adsorption and subsequent reductive stripping of NO layer on a reasonably covered palladium surface is an excellent technique to obtain a Pt(100) electrode fully covered by a epitaxial palladium monolayer [25, 31]. However, this methodology was not employed in this work. Owing to the low amounts of palladium deposited in the present study, it can be assumed that palladium deposition is restricted to the first and second layer. By measuring the charge under the peaks at 0.16 and 0.26 V it is possible to determine the amount of Pd in the first and second layers [25, 29, 31].

The peaks at 0.16 and 0.26 V on the palladium adlayers are associated to the competitive adsorption of the (bi)sulfate anions and hydrogen [29], hydrogen being adsorbed at potentials negative to the peak, whereas the adsorption of the anions takes place at potential more positive than the peak potential. On the Pt(100)

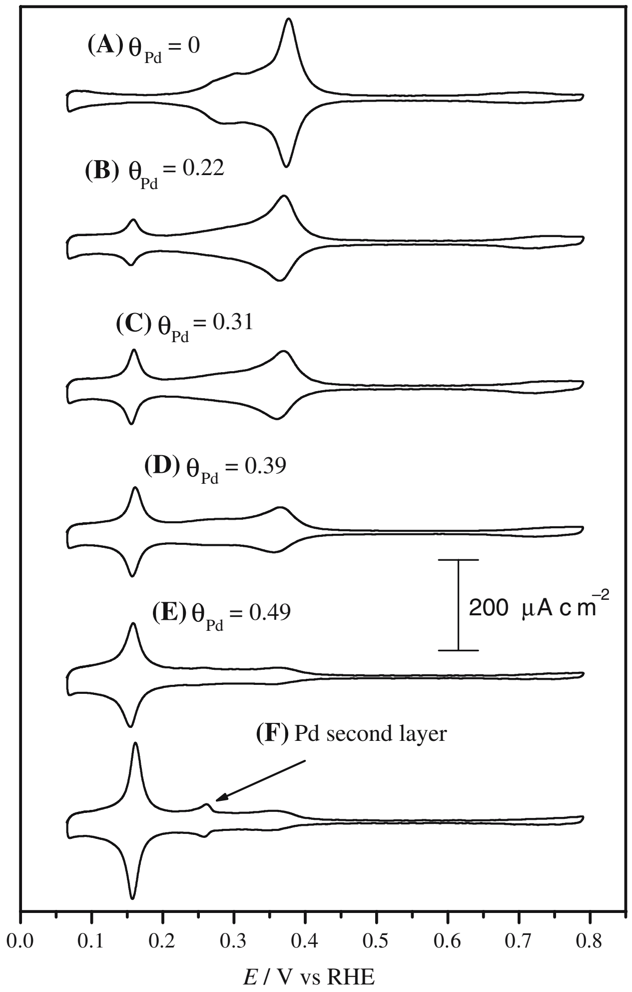

Fig. 1. Voltammetric profiles of the palladium modified Pt(100) electrodes with different palladium coverages in 0.5 M H_2SO_4. Scan rate: 50 mV s^{-1}.

electrode, the peak at 0.36 V is also associated with the competitive adsorption of the anions and hydrogen. Therefore, adsorption of (bi)sulfate anions takes place on the palladium adlayer at potentials more negative than that obtained for Pt(100) electrodes, i.e., the (bi)sulfate adsorption at a given potential is stronger on palladium than on platinum. This stronger adsorption may have an effect on the formic acid oxidation.

The voltammetric profiles recorded for the oxidation of formic acid on the "so-prepared" palladium modified Pt(100) surfaces are reported in Figure 2. For the Pt(100) electrode, the typical voltammogram is observed. For the positive scan, no current is measured since the surface is almost completely poisoned by CO formed at the immersion potential (0.1 V). At potentials above 0.8 V, the CO adlayer is oxidatively stripped, giving rise to a clean Pt(100) surface. In the negative scan, the current rises as the potential is made more negative, until a maximum current is obtained at ca. 0.42 V. From this point, adsorbed CO is formed again. The build up of the CO blocks the surface for the direct oxidation of formic acid and the oxidation current diminishes until negligible values are obtained at ca. 0.3 V.

For the palladium modified Pt(100) bimetallic electrodes, a new feature at ca. 0.2 V is observed in the positive scan which grows as the palladium coverage increases Simultaneously, the oxidation signal in the negative scan associated with the Pt(100) free sites diminishes. This indicates that the oxidation signal below 0.3 V is associated with the formic acid oxidation on the palladium adlayer. In the potential region below 0.3 V, the currents in the positive scan are higher than those in the negative scan, thus suggesting the absence of significant poisoning of the palladium covered area in the initial positive scan. The small differences in the signal for the negative scan with respect to the positive one has been tentatively associated with the reduction of CO_2 formed at positive potential to CO on the palladium covered areas [11]. The buildup of CO partially blocks the surface and, therefore, lower currents are recorded. The region in the voltammogram above 0.4 V corresponds to the oxidation of CO on the palladium free areas of the electrode. The voltammetric profile in this region shows the same behavior as that obtained for the unmodified Pt(100) electrode. However, currents in this region diminish as the palladium coverage increases, especially in the negative scan.

DEMS was employed to follow CO_2 formation during formic acid oxidation. To achieve this, the electrode was pressed against the Teflon membrane that leads to the vacuum chamber and the voltammogram and mass signal for CO_2 were recorded simultaneously. Thus, whereas the voltammetric profiles recorded simultaneously show both the contribution associated to the Pt(100) surface and the electrochemical signal from the Pt wire, the mass spectrometer signal obtained is exclusively due to the single crystal face. Figure 3 shows the CO_2 mass signal corresponding to the palladium modified electrodes of Figure 1. The CO_2 mass signal follows the corresponding voltammetric profiles for formic acid oxidation showed in Figure 2 (obtained in the meniscus configuration). With the present DEMS setup, it is not possible to calibrate the apparatus since the amount of CO_2 trapped by the vacuum chamber depends on the gap between the electrode and the membrane. Thus, two different experiments with the same voltammetric profile for formic acid oxidation may yield a different increase in the CO_2 mass signal. However, for a single experiment, an exact correlation is obtained between the CO_2 mass signal and the current density in the voltammogram. Therefore, the comparison between the voltammetric profiles of Figure 2 and the corresponding CO_2 mass signal indicates that the mass signal is exclusively due to formic acid oxidation on the single crystal surface without significant perturbations from the Pt wire, and only the formic acid oxidation to CO_2 is giving rise to the measured current density.

Using the DEMS and voltammetric data, the formic acid oxidation on these electrodes can be analyzed. First, the only significant changes between the

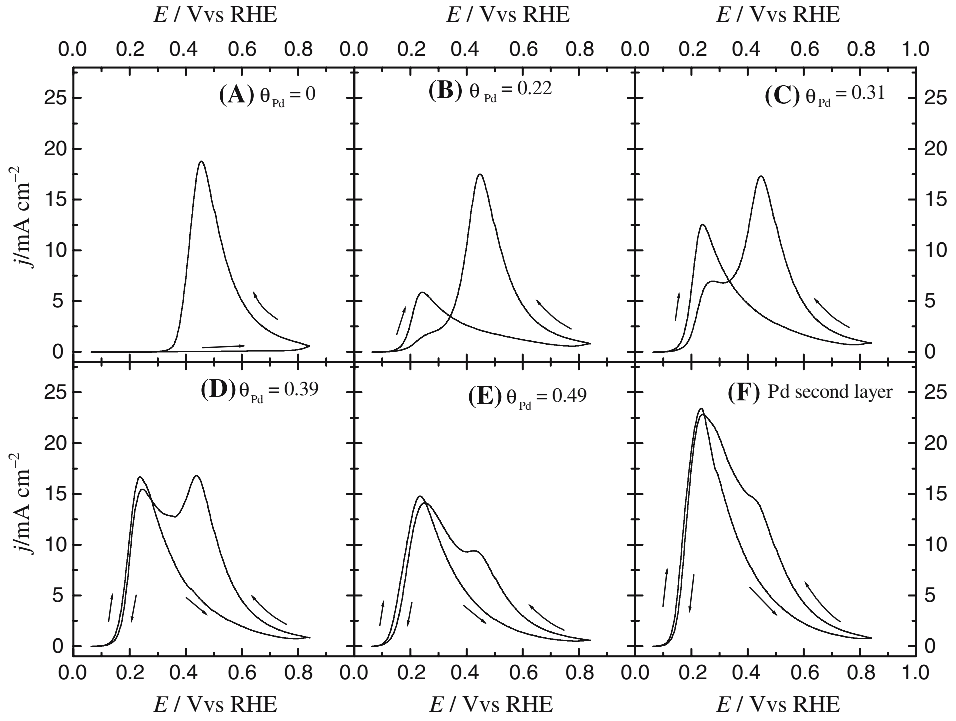

Fig. 2. Voltammetric profiles of the palladium modified Pt(100) electrodes with different palladium coverages in 0.25 M HCOOH + 0.5 M H_2SO_4 solution. Scan rate: 20 mV s^{-1}.

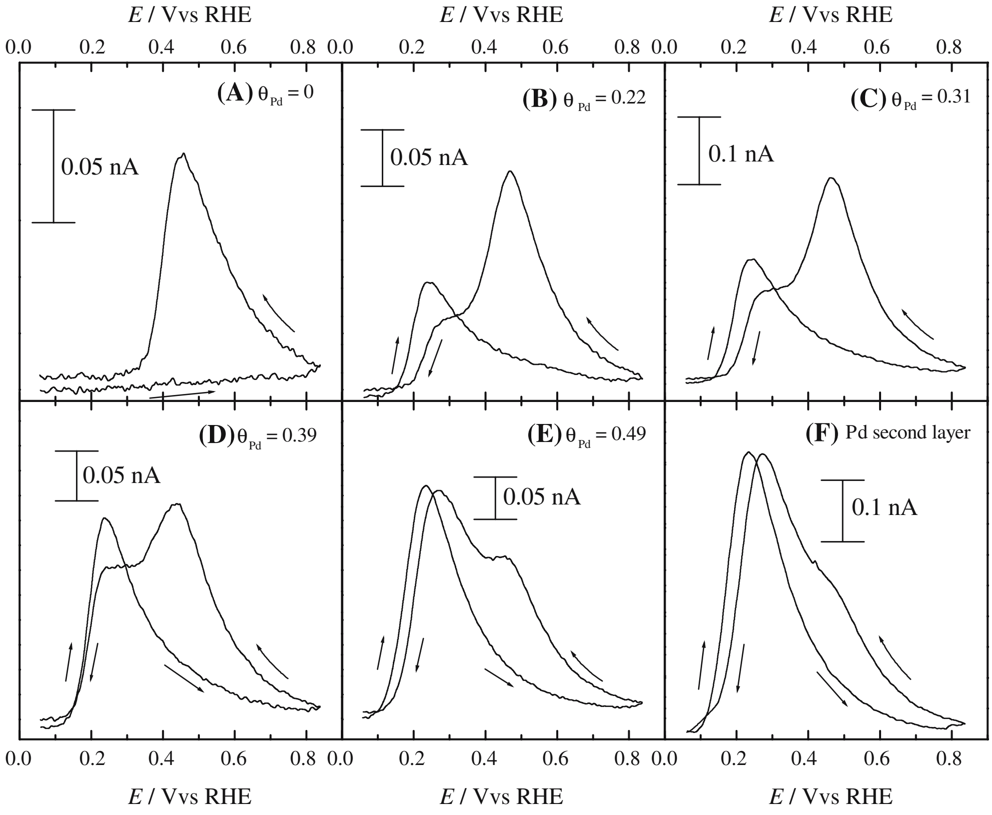

Fig. 3. Mass signal (m/z = 44, CO_2) as a function of the applied potential of the palladium modified Pt(100) electrodes with different palladium coverages in 0.25 M HCOOH + 0.5 M H_2SO_4 solution. Scan rate: 20 mV s^{-1}.

voltammetric current density and the CO_2 mass signal are observed in the potential region were formic acid oxidation on the palladium adlayer takes place. In the mass signal of Figure 3(B) and (C), the difference between positive and negative scans below 0.3 V is significantly smaller than that measured in the corresponding voltammetric profiles. If CO_2 reduction is taking place at these potentials on the palladium adlayer, an oxidation-reduction process is taking place simultaneously on the electrode surface. Therefore, the total current measured will be smaller than that corresponding to formic acid oxidation. When the electrode is pressed against the membrane, the pumps of the vacuum chamber force the diffusion of the CO_2 molecules away from the electrode surface, and reducing the possibility of their reduction to CO. This leads to higher mass signals for CO_2 than those expected from the voltammetric profile in the meniscus configuration and agrees with the spectroscopic observation of the reduction of CO_2 to CO on palladium [11].

When examining the difference in the current for formic acid oxidation on the palladium adlayer in the positive and negative scans, it can be seen that the difference diminishes as the palladium coverage increases and is almost non-existant for palladium coverages higher than 0.5. If the CO_2 reduction took place in any palladium atom of the adlayer, it would be expected that the difference in the positive and negative scans were always the same, irrespective of the coverage. As aforementioned, this difference becomes smaller as the coverage increases. In order to explain this fact, some special sites have to be associated with the reduction of CO_2. It can be proposed that the reduction of the CO_2 takes place only on palladium adatoms neighboring free platinum atoms. Since the palladium adlayer grows in islands, this means that the reduction occurs only in the island borders. Thus, the ratio of palladium atoms in the borders of an island to the total palladium adatoms diminishes as the adatom coverage increases. Therefore, the diminution of the current in the negative scan becomes smaller as the adatom coverage increases and for high adatom coverage values is almost negligible.

The anions also seem to play an important role in the oxidation of formic acid. The onset of (bi)sulfate adsorption on a perfect Pt(100) electrodes takes place at potentials above the peak at 0.38 V [32] and the maximum coverage is reached when all hydrogen has been completely desorbed. The onset of the bisulfate adsorption on the palladium adlayer is displaced towards negative potentials, and therefore, (bi)sulfate adsorption is stronger on the palladium adlayer. At potentials above 0.2 V, formic acid molecules have to compete with (bi)sulfate anions in order to be oxidized. As the potential is made more positive, the adsorption of (bi)sulfate anions is stronger and the current for formic acid oxidation diminishes. For the unmodified Pt(100) surface, the diminution in the oxidation current starts when the maximum (bi)sulfate coverage has been obtained, i.e, above 0.4 V. A similar situation is observed for the palladium adlayer, i.e., the diminution of the oxidation current occurs when hydrogen has been completely desorbed and replaced by the anions, thus corroborating the inhibition effect of the anions adsorbed on the electrode surface.

3.2. *Pt(111)/Pd surfaces*

Pt(111)/Pd surfaces were prepared using the same procedure as that employed for Pt(100). Figure 4 shows the results obtained. The couple of sharp peaks at 0.20 V increases in height as the amount of palladium increases. These peaks are associated to the deposition of palladium on the first layer. The growth of the peaks at 0.20 V is accompanied by a uniform diminution in the characteristic Pt(111) adsorption states. When more than a single layer of palladium is deposited, the peak at 0.20 V begins to decrease and a second contribution at higher potentials (0.25–0.26 V) appears (Figure 4(E)). This latter contribution is related to the deposition of palladium adatoms onto the first adlayer. Finally, Figure 4(F) shows the voltammetric profile corresponding to Pd coverage with more than a monolayer. The second adsorption state at 0.26 V in the positive going is scan now well-developed. However, there are still some parts of the electrode with only one layer, since the peak at 0.2 V is visible.

Figure 5 shows the voltammetric profiles for formic acid oxidation obtained for the different Pt(111)/Pd surfaces. For the Pt(111) electrode, the typical voltammogram is obtained. The small difference in the currents recorded in the positive and negative scans around 0.5 V is associated with a small amount of poison formed at the initial potential. When palladium is deposited on the Pt(111) electrode, the behavior is completely different from that obtained for Pt(100) electrodes. In this case, the oxidation current at 0.5 V decreases as the amount of palladium increases and no other signal can be observed for the oxidation of formic acid on the first palladium adlayer. Nevertheless, it is important to note the close coincidence of the current for the positive and negative scans when palladium is deposited, suggesting the complete absence of poisoning. Since the poison formation is associated with defect sites [33], the absence of hysteresis indicates that the defect sites have all been covered by the palladium adatoms. When more than one palladium monolayer is deposited (Figure 5(F)), the situation changes. In this case, a new oxidation peak is obtained at 0.3 V, which is associated with the oxidation of formic acid on the palladium multilayer.

The voltammetric profiles obtained here are in agreement with those previously reported by Clavilier et al. [11] but significantly different from those reported by Kolb et al. [19]. Kolb et al. showed a pronounced hysteresis between the two different scan directions as well as a well-defined peak at -0.05 V vs SCE. In addition, they found two oxidation peaks at 0.3 and 0.45 V vs SCE for surfaces ranging between 0.5 and 1 monolayer of electrodeposited Pd. Nevertheless, for surfaces with coverages higher than one monolayer (Figure 5(F)), the voltammetric profile observed is similar to those reported by Kolb et al. for surfaces containing 2 and 3 monolayers of Pd on Pt(111).

Figure 6 shows the CO_2 mass signal obtained for the corresponding Pt(111)/Pd surfaces. As before, the mass signal corresponding to CO_2 formation has a profile

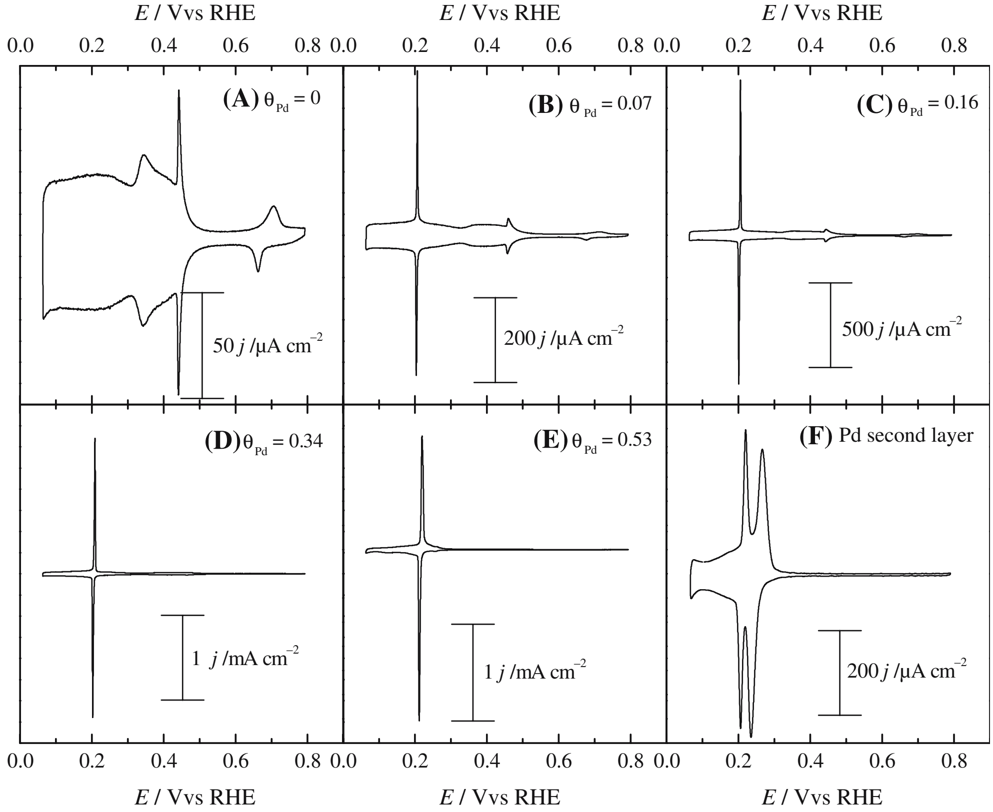

Fig. 4. Voltammetric profiles of the palladium modified Pt(111) electrodes with different palladium coverages in 0.5 M H_2SO_4. Scan rate: 50 mV s^{-1}.

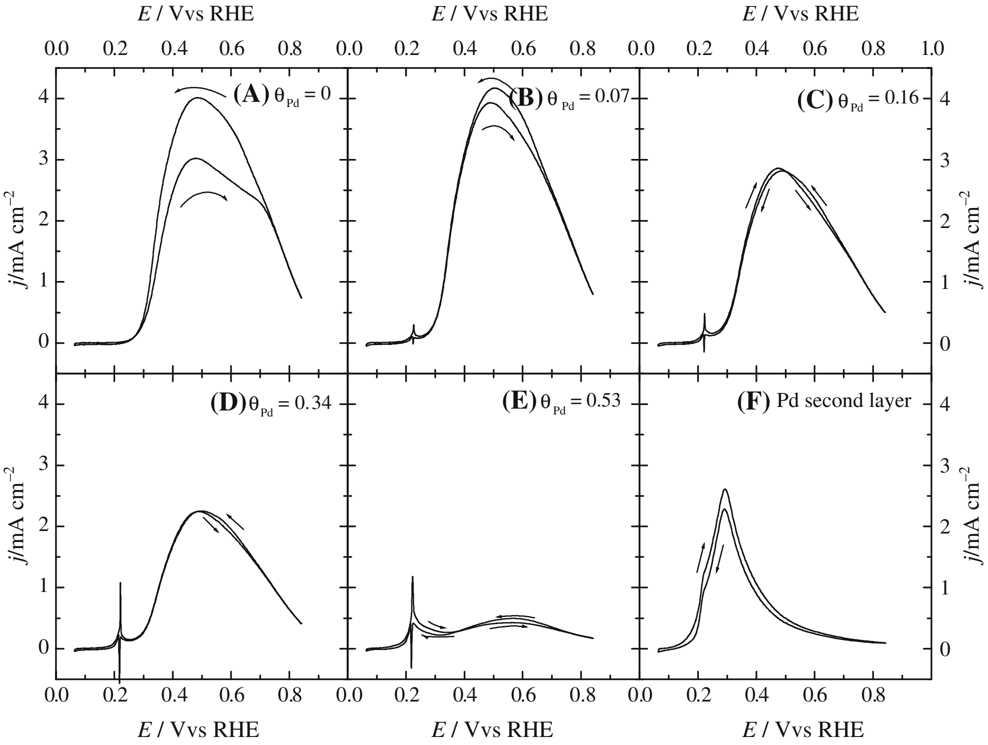

Fig. 5. Voltammetric profiles of the palladium modified Pt(111) electrodes with different palladium coverages in 0.25 M HCOOH + 0.5 M H_2SO_4 solution. Scan rate: 20 mV s^{-1}.

very similar to that obtained in the voltammetric study. Thus, as the amount of palladium increases, the oxidation current decreases. Only when the Pd coverage is higher than one monolayer, is a new oxidation current at lower potential observed. In this case, no differences in the positive and negative going scans in the multilayer

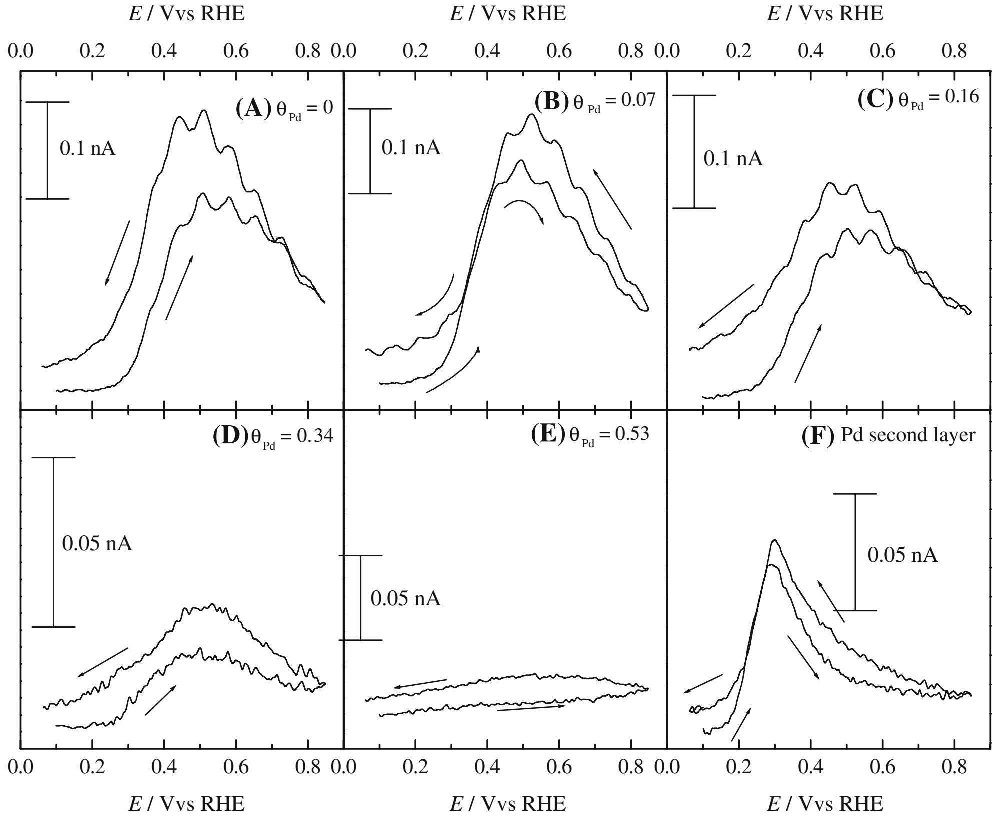

Fig. 6. Mass signal (m/z = 44, CO_2) as a function of the applied potential of the palladium modified Pt(111) electrodes with different palladium coverages in 0.25 M HCOOH + 0.5 M H_2SO_4 solution. Scan rate: 20 mV s^{-1}.

palladium deposit are observed, indicating that CO_2 reduction is not occurring.

For these electrodes, the adsorption of anions also has an inhibiting effect on the oxidation of formic acid. For the Pt(111) electrode, currents decrease above 0.5 V, which coincides with the potential at which the full (bi)sulfate layer is formed [34]. In the case of the palladium multilayer, the peak at 0.26 V corresponds to the competitive adsorption of hydrogen and (bi)sulfate [29] and the maximum coverage is obtained at 0.3 V, when hydrogen has been completely displaced by the anions. At this potential, the current for formic acid starts to diminish as a consequence of the formation of the anion adlayer on the electrode. As the potential is made more positive, the adsorption of the anion becomes stronger and lower currents for formic acid oxidation are recorded.

Acknowledgements

This work was performed in the framework of projects BQU2003-03877, BQU2003-4029 from McyT (Spain), and GV04B688 from GV (Spain).

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