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Catalityc effects of ruthenium and osmium spontaneous deposition on platinum surfaces toward methanol oxidation

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Abstract

The influence of ruthenium and osmium spontaneous deposition on polycrystalline platinum in sulfuric acid was studied by conventional electrochemical techniques. The inhibition of the hydrogen adatom voltammetric profile by the foreign adatoms was used to calculate the degree of surface coverage of ruthenium, osmium, and a mixture of both metal ions from solutions of different composition. Methanol adsorption and oxidation were compared on bare platinum, platinum/ruthenium, platinum/osmium, and ternary compounds, considering the efficiency of methanol oxidation per hydrogen adatom displaced by the foreign metal on platinum.

Keywords: Ruthenium; Osmium; Platinum; Electrocatalysis; Voltammetry

1. Introduction

Electrochemical energy conversion is a topic of technological importance, with main developments arising from novel anodic electrocatalysts. The efficiency of these electrochemical devices is mostly conditioned by the surface topography and composition of the substrates, which in the case of fuel cells are platinum or platinum alloys [1,2]. However, the development and characterization of poison-resistant catalysts is of tremendous interest in this technology. The microscopic structure of these electrode surfaces is also required to complement the understanding of the electrochemical reactivity developed from these modified platinum electrocatalysts [3].

The influence of the surface structure of electrodes in processes involving anodic oxidation of fuels is a topic of fundamental studies during the past decades [4,5]. The main advances have been achieved due to the progress in the use of single crystal electrode surfaces in electrochemical studies and the development of surface sensitive hybrid techniques for the in situ and ex situ analysis of the electrocatalytic processes [6–9].

A number of procedures have been proposed to change the structure and composition of electrode surfaces in fuel cells. Underpotential deposition and surface decoration of different metal atoms on platinum electrocatalysts lead to enhanced surface reactivity upon anodic oxidation of fuels such as methanol [10–13]. The study of early-stage metal deposition has a long tradition in electrochemistry, being a process mainly governed by the nature of the substrate and foreign metals and by the electrode potential. In spite of the equilibrium potentials with the new metal being easily reached, underpotential deposition produces dramatic changes in the electrode surface properties [14–16].

Ruthenium and osmium deposition on platinum are of special interest for methanol anodic oxidation on fuel cells

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and were first reported in the early sixties [17,18]. Among the different ways to deposit ruthenium or osmium on platinum [17–22], spontaneous deposition is attractive because of its simplicity and the fast surface concentration plateau reached after several seconds. However, some confusion between this chemisorption process and underpotential deposition has occurred in the literature [23–25]. Despite the reversible behavior of underpotential deposited non-noble metals on noble metal substrates, the films formed by spontaneous deposition normally do not dissolve easily from the metal surface. They are very stable and normally change to stable hydroxides and oxides when the electrode potential is increased. In the case of ruthenium, osmium, palladium, rhodium, etc. the work function of the foreign metal is not required to be higher than that of the substrate.

The focus of this paper is on ruthenium, osmium, and their combined depositions on platinum because of their well-known catalytic activity in a variety of surface reactions and complex formations [25–28]. Even so, all of them were focused on their effect on methanol oxidation in solution, without considering the role of adsorption prior to oxidation. Therefore, the study of sub- or monolayers of ruthenium or osmium on platinum allows us to understand the role of the surface composition of the electrocatalysts on the methanol oxidation. In this sense, interesting and fundamental papers have been performed about ruthenium and osmium deposition on platinum single and polycrystalline (pc) surfaces [5,6,8,29]. The ex situ examination of the electrode surfaces by STM images, specially in the case of Pt(111) surfaces, at the submonolayer levels shows the formation of islands [30] with maximum 0.20 ML coverage for ruthenium (at 120 s of exposure) and 0.15 ML coverage for osmium (at 60 s of exposure). Depending on the osmium coverage the island diameter varies from 2 to 5 nm [6], but in the case of ruthenium [30] the islands appear to be uniformly distributed along the surface, with an average value of 3 nm. The island density increases with ruthenium coverage values, but in the case of osmium there is no optimum island size [6,7]. On the other hand, the knowledge on the foreign metal adatom concentration and the nature of the deposited species at potentials of interest is important for the understanding of the mechanism of methanol oxidation. Thus, interfacial and surface analysis techniques were used for this purpose [8,9,31] but normally for electrodeposited and melted phases of these metals with platinum.

An understanding of methanol adsorption and oxidation processes on modified platinum electrodes can lead to a deeper insight into the relation between surface structure and reactivity in electrocatalysis. It is well known that the main impediment in the operation of a methanol fuel cell is the fast depolarization of the anode in the presence of traces of adsorbed carbon monoxide. The promotion effect has been mainly discussed based on either the "ligand effect" [32] or the "bifunctional effect" [33].

The adsorption of methanol will be mostly on platinum free sites:

$$\mathrm{Pt} + \mathrm{CH_3OH} \leftrightarrow \mathrm{Pt(CH_3OH)_{ad}}. \tag{1}$$

After increasing the electrode potential methanol adsorbates oxidize to [33,34]:

$$\mathrm{Pt(CH_3OH)_{ad}} \leftrightarrow \mathrm{Pt(HCO)_{ad}} + 3\mathrm{H}^+ + 3e^-, \tag{2}$$

$$\mathrm{Pt(HCO)_{ad}} \leftrightarrow \mathrm{Pt(CO)_{ad}} + \mathrm{H}^+ + e^-. \tag{3}$$

The bifunctional mechanism proposes that a foreign metal, M, promotes water decomposition at lower potentials,

$$\mathrm{M} + \mathrm{H_2O} \leftrightarrow \mathrm{M(OH)_{ad}} + \mathrm{H}^+ + e^- \tag{4}$$

or

$$\mathrm{M} + \mathrm{H_2O} \leftrightarrow \mathrm{M(H_2O)_{ad}}. \tag{5}$$

These species also promotes the complete oxidation of the organic adsorbate by a recombination of these species (from reactions (2) and (3) and reactions (4) and (5)) through a Langmuir–Hinshelwood mechanism [35]. For example,

$$\mathrm{Pt(CO)_{ad}} + \mathrm{M(OH)_{ad}} \leftrightarrow \mathrm{CO_2} + \mathrm{H}^+ + e^- + \mathrm{Pt} + \mathrm{M}. \tag{6}$$

According to the ligand effect, the energy level of the modified substrate is changed to weaken the bond energy of the carbon monoxide adsorbate to facilitate its oxidation.

The best choice of the alloying or co-deposited elements depends on which step of the latter mechanism is the rate-determining step (normally reaction (6)). Since different results have been obtained with ternary and quaternary combinations of these metals with rhodium, molybdenum, and iridium [3,35,36], we have explored the methanol adsorbate formation and oxidation on some metal combinations.

2. Experimental

Electrochemical experiments were carried out at room temperature in a microflux three-electrode cell using different pc platinum wires as working electrodes. The electrochemical setup was completed using a large-area platinum counterelectrode and a reversible hydrogen reference electrode (RHE). The 1 M H_2SO_4 supporting electrolyte was prepared from J.T. Baker reagent with Millipore treated water (18.2 MΩ cm resistivity). The real surface area of the pc platinum electrodes ranges from 0.22 to 0.28 cm^2. They were calculated from the integration of the hydrogen adatom voltammetric profile after double-layer correction. All potentials in the text are referred to the RHE scale.

The 0.5 mM ruthenium-containing solution was prepared from $\mathrm{RuCl_3{\cdot}3H_2O}$ (Aldrich–Sigma) in 0.2 M sulfuric acid, whereas the 0.5 mM osmium-containing solution from $\mathrm{OsCl_3{\cdot}}x\mathrm{H_2O}$ (Aldrich–Sigma) in 0.2 M sulfuric acid solutions. They were used as a source of ruthenium and osmium aquo-complex ions, respectively. They were prepared without local large salt concentrations in order to avoid precipitations and polymerization. The immersion time (considered as the time in contact with the metal-containing solution) for ruthenium was 120 s and for osmium was 60 s. The calculation of the degree of surface coverage (θ) by the foreign metal on pc platinum reaches 0.25 ML. Also a solution composed by 0.5 mM ruthenium-cation + 0.5 mM osmium-cation in 0.2 M sulfuric acid was used to prepare the ternary Pt/Ru/Os surfaces. Ternary Pt/Ru/Os systems were prepared as follows:

Method 1 (Pt/Ru/Os): a first ruthenium spontaneous deposition was performed after a 120 s immersion in an acidic 0.5 mM Ru^{3+} solution, followed by osmium deposition during a 60 s immersion in an acidic 0.5 mM Os^{3+} solution.

Method 2 (Pt/Os/Ru): a first osmium spontaneous deposition was performed by 60 s immersion in an acidic 0.5 mM Os^{3+} solution, followed by ruthenium deposition during a 120 s immersion in an acidic 0.5 mM Ru^{3+} solution.

Method 3 (Pt/Ru-Os): simultaneous osmium + ruthenium spontaneous deposition by immersion in an acid solution of 0.5 mM Os^{3+} + 0.5 mM Ru^{3+}. The immersion times were specified in the text in each case.

Methanol solution oxidation was studied by chronoamperometric plots at 0.70 V on each modified platinum surface and by linear sweep voltammetry scanning the potential from 0 to 0.80 V at 0.01 $V\,s^{-1}$ both in 0.5 M methanol + 1 M sulfuric acid.

The electrocatalytic activity of the new composed platinum surfaces was also checked in the case of methanol surface oxidation by stripping experiments. The stripping voltammetric oxidation of methanol residues was performed on the different surfaces. In each case, a potential holding at $0.10 \leqslant E_{ad} \leqslant 0.35$ V during 10 min was applied to adsorb methanol. Afterward, and holding the potential at the same value, the methanol containing solution was replaced with the supporting electrolyte to eliminate any diffusion contribution from methanol. Immediately after, the potential was scanned from E_{ad} to 0.05 V and subsequently toward positive values up to 1.50 V at 0.10 $V\,s^{-1}$ to obtain the whole stripping voltammogram of methanol residues in the supporting electrolyte. The pictures in the paper are only shown for $E_{ad} = 0.25$ V because they exhibit the highest oxidation extent of methanol residues on free pc platinum surfaces during preliminary tests.

3. Results and discussion

3.1. On the spontaneous deposition of ruthenium and osmium on pc platinum

Platinum surfaces were modified by osmium and ruthenium spontaneous deposition in order to reach only θ values lower than 0.25. After the surface was modified by immersion in a fixed salt solution, the new electrodes were subjected to three voltammetric cycles between 0.05 and 0.80 V in the supporting solution to stabilize the surface.

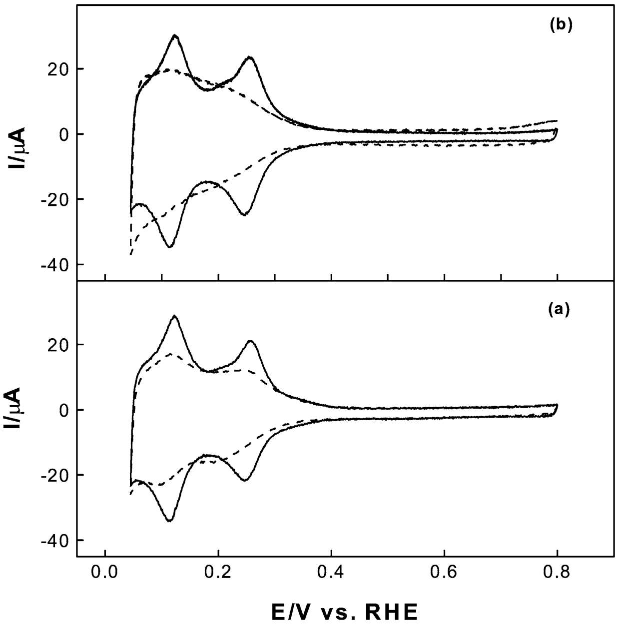

Fig. 1. Cyclic voltammetric profiles of (a) ruthenium and (b) osmium adlayers (dashed lines) on pc platinum (solid lines) in 1 M sulfuric acid between 0.05 and 0.80 V at 0.10 $V\,s^{-1}$. The foreign metal adlayers were prepared according to the experimental section.

The changes in the voltammetric profile of pc platinum performed at 0.1 $V\,s^{-1}$ caused by ruthenium adatoms are depicted in Fig. 1a. In this case potential values higher than 0.80 V were avoided to impede ruthenium oxidative desorption from the surface. The comparison of this new profile with that of pc platinum evidences partial inhibition of the hydrogen adsorption peaks by ruthenium species. Furthermore, it is likely that ruthenium species adsorb on the same surface sites as hydrogen adatoms, since the voltammetric features of the latter are not potential shifted.

In the case of a freshly prepared solution, the adsorption of ruthenium on platinum from $Ru(H_2O)_6^{3+}$ occurs through the specific adsorption of chloride [25]. Thus, by simply taking the depletion of the hydrogen adatom voltammetric profile and assuming that one Ru^{3+} species adsorbs onto three platinum atoms, the formation of metal ruthenium adsorbates involves three electrons. Values of θ calculated in this way show results comparable with the ones estimated by Auger spectroscopy for a single crystal [25] under similar conditions of immersion time and concentration of the metal solutions. After 120 s of immersion in 0.5 mM $RuCl_3$ + 0.2 M sulfuric acid for an open circuit the values of θ ranges from 0.22 to 0.25 after cycling only up to 0.80 V. In the case of a ruthenium-containing solution aged 2–3 days, it has been demonstrated [37] by spectrophotometric and ion-exchange resin experiments that the hydrolysis of ruthenium-containing species in acid media leads to $RuO(H_2O)_4^{2+}$ (ruthenyl species). The kinetics of adsorption on pc platinum is similar, but not the mechanism. However, after the three voltammetric incursions up to 0.80 V the degree of surface coverage by ruthenium on platinum yields the same results. It has been observed that traces of chloride in the $RuO(H_2O)_4^{2+}$ diluted acidic solution increases solubility. However, as in the case of osmium-containing solutions, polymerization can be also observed only when large local concentrations of Os^{3+} during the solution preparation occur.

The chemical state of ruthenium on platinum, especially during methanol oxidation, was also investigated by a number of surface techniques [38–40], providing evidence of the formation of metal ruthenium and oxides such as RuO_2, RuO_3, RuO_4, and Ru_2O_3, depending on the cycling potential.

On the other hand, ruthenium-containing solutions aged for more than 1 month were also studied. According to the literature [37,41], the oxidation of ruthenyl species can easily produce perruthenate ions, RuO_4^-, which are stable in acid and alkaline solutions. The spontaneous deposition of ruthenium on platinum from perruthenate ions is also possible. In fact, after three cycles from 0.05 to 0.80 V at 0.10 $V\,s^{-1}$, ruthenium adlayers with $\theta = 0.22$ can be obtained.

Fig. 1b evidences the voltammetric changes of the pc platinum/sulfuric interface at 0.10 $V\,s^{-1}$ produced by osmium adlayers. As a difference from deposited ruthenium, it seems that there are no preferred platinum surface sites for osmium deposition, since the hydrogen adatom contour exhibits a smooth current distribution with larger currents near the hydrogen evolution reaction and no preferred adsorption potentials. There are, however, some discrepancies because of the extreme sensitivity to solution composition and surface platinum topography, as explained in the Introduction. In the case of using a freshly prepared $Os(H_2O)_6^{3+}$ solution, values of $\theta = 0.20$ were obtained after 60 s of immersion time. This solution is rapidly oxidized to an electrolyte composed of H_2OsCl_6 species, which is able to adsorb on platinum, yielding, after three cycles in the range 0.05 to 0.80 V, the same value of θ. In contrast to the case of ruthenium, further solution oxidations of osmium salts are not observed in acid media.

Moreover, and as a difference from the case of spontaneous ruthenium deposition on platinum, anodic and cathodic contributions can be observed ca. 0.7 V. According to the literature, they may be the components of a redox couple related to the surface oxidation of osmium to OsO_2, confirmed through spectroscopic data [6]. Therefore, the voltammetric contour up to 1.50 V is obviously needed in the case of pc platinum, as shown below.

The total recovery of the pc platinum surface is an important factor to consider in electrocatalysis. According to Janssen and Moolhuysen [21], cyclic voltammetric profiles of foreign rare metals on platinum can be used to distinguish between relatively stable or unstable modified electrode systems for catalysis. An electrochemical interface was considered to be unstable when metal adatoms were completely removed after one cycle up to 1.6 V. The complete removal of ruthenium and osmium from the platinum surface is only quantitative after several cycles between 0.6 and 1.5 V. Thus, in our experience, the hydrogen region must be avoided, since either hydrogen adsorbates or molecular hydrogen can reduce metal ions on platinum [25,42].

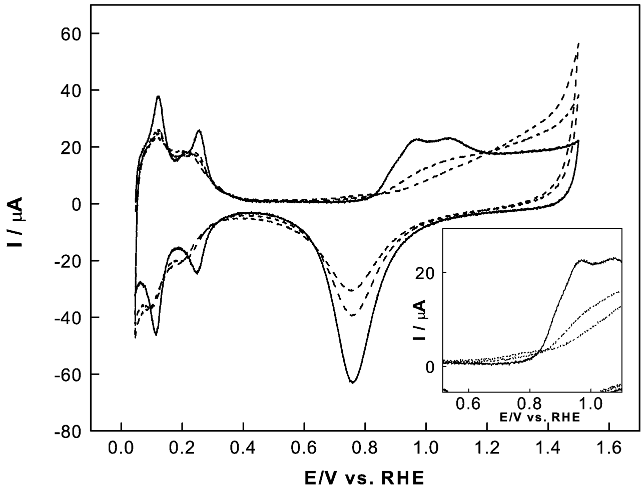

Fig. 2. Cyclic voltammetric profile of spontaneous deposition of ruthenium (dashed line) performed from 0.05 to 1.50 V at 0.1 $V\,s^{-1}$ (first and sixth cycles) compared to pc platinum (continuous line) in 1 M sulfuric acid. In the inset the details of the region 0.55–1.1 V are depicted.

To check for the voltammetric features of foreign metal oxidation on platinum, voltammetric runs were performed with upper potentials larger than 0.80 V. Fig. 2 shows the cyclic voltammetric profile of spontaneous ruthenium deposition on pc platinum when the upper potential limit is extended up to 1.50 V. As found before, when immersion times of 120 s are used, ruthenium species inhibit the hydrogen-adatom region. Otherwise, it has to be noticed that the use of aged instead of freshly prepared ruthenium-containing solutions did not show differences in the voltammetric curves or in the catalytic activity toward methanol oxidation (see below).

Fig. 2 shows the slow increase of the oxidation current near 0.6 V (in the inset of the figure), probably due to the formation of RuO_2 and RuO_3 surface species detected by XPS measurements [9,39,43,44]. According to these measurements metallic ruthenium is no longer seen for potentials larger than 0.80 V, but the increase in the amount of surface oxides is evident. After the potential is extended toward more positive values, the partial inhibition of platinum oxides is clear, as a lower reduction charge density is observed in the reverse scan. Moreover, a sudden increase in the current previous to the oxygen evolution reaction is also depicted in the same figure. In the case of a freshly prepared solution, Iwasita et al. [25] (see also [42]) proposed that chloride can be specifically adsorbed on Pt(111), and Ru^{3+} acts only as the counterion. Fig. 2 shows the oxidative desorption of chloride as a breakpoint from 1.4 V. However, in that paper it is also stated that at low potentials (below the potential of zero charge of Pt(111) in diluted sulfuric acid) and after metallic ruthenium is deposited, the desorption of chloride occurs. This is not totally true, since during sub-

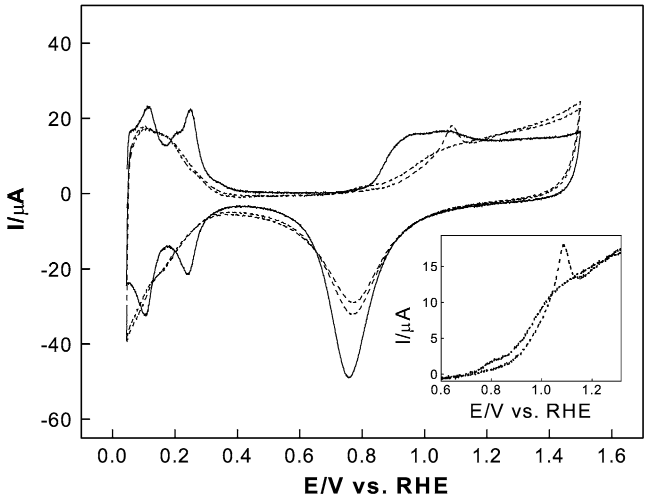

Fig. 3. Cyclic voltammetric profile of spontaneous deposition of osmium (dashed line) performed from 0.05 to 1.50 V at 0.1 V s^{-1} (two first cycles) compared to pc platinum (continuous line) in 1 M sulfuric acid. In the inset the details of the region 0.6–1.2 V are depicted.

sequent anodic scans the breakpoint at 1.4 V can be also observed.

Fig. 3 shows the adsorption of osmium-containing species on pc platinum when the potential limit is extended up to 1.5 V at 0.10 V s^{-1}. In the first anodic scan, the inhibition of platinum oxide formation is also evidenced, due to the presence of metallic osmium and oxygen-containing species at a submonolayer level. According to results found by XPS core-level spectra [9] and in contrast to the case of ruthenium, metallic osmium can be found in the whole potential range, i.e., also up to 1.4 V. The nature of the oxidized species of osmium is OsO_2 in the entire potential region from 0.05 to 1.50 V, but with only 25% of a metallic osmium monolayer [9].

As in the case of Pt(111) surfaces [6], our results on pc platinum confirm the voltammetric features found for osmium surface species. An anodic/cathodic current contribution (see inset in Fig. 3) can be seen from 0.7 to 0.9 V, assigned to the Os/OsO_2 redox couple, which seems to be a quasi-reversible system. This can be better observed when the potential is scanned only up to 0.9 V (not shown in this paper). When the potential is extended up to 1.5 V, the osmium submonolayer is oxidatively transformed as a new species at 1.1 V. This peak was observed before by Wieckowski and co-workers [6] on Pt(111) and was assigned to an intermediate state between Os^{4+} and Os^{8+} species according to the binding energies from XPS measurements. Moreover, it is also seen in Fig. 3 that the oxidation peak of osmium species is only seen in the first positive incursion, probably due to the dissolution of Os^{8+} adatoms at 1.50 V. During the second cycle (see inset in Fig. 3), the shoulder just prior to platinum oxide formation, located between 0.70 and 0.85, is better observed. This fact makes us think that the total dissolution of osmium oxygen-containing species is not possible in a single cycle.

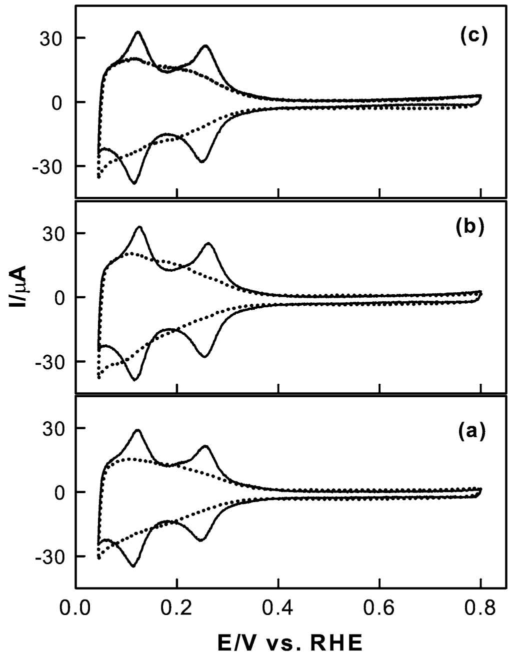

Fig. 4. Cyclic voltammetric profiles of metal adlayers (short dotted lines) obtained by (a) Method 1, (b) Method 2, and (c) Method 3 (60 s immersion time) on pc platinum compared with bare platinum (continuous line) at 0.10 V s^{-1} in 1 M sulfuric acid.

3.2. On the spontaneous deposition of binary combinations on pc platinum

The electrochemical response of ternary Pt/Ru/Os systems in the hydrogen adatom potential region was studied previous to methanol oxidation. The comparison of voltammetric profiles run from 0.05 to 0.80 V at 0.10 V s^{-1} for the different surfaces (obtained as explained in Section 2) is shown in Fig. 4.

From the observations of Fig. 4, some conclusions can be extracted. First of all, the similarities between voltammetric profiles of surfaces covered by osmium-containing species and those of ternary systems are clear. The broad pattern of the hydrogen potential region and the lack of well-defined peaks for the three curves resemble those of a solely osmium deposition. It seems that osmium species governed the deposition process when it was deposited before or after ruthenium. On the other hand, a detailed analysis of the voltammetric profile showed a slight enhancement of the so-called third anodic peak of the hydrogen region in the case of osmium first adsorbed and ruthenium and osmium co-adsorbed on platinum (Figs. 4b and 4c). This observation makes us think that the osmium species adsorbs in a nonuniform layer, making possible the adsorption of hydrogen as the third anodic peak. This has been also verified by STM images and XPS measurements on Pt(111) by Crown and Wieckowski [7]. The authors found that osmium deposition on a platinum single crystal occurs in a nonuniform mode with preferential deposition on edges of terraces and defects. These data were also found on Pt(110) and Pt(100) based on other STM images.

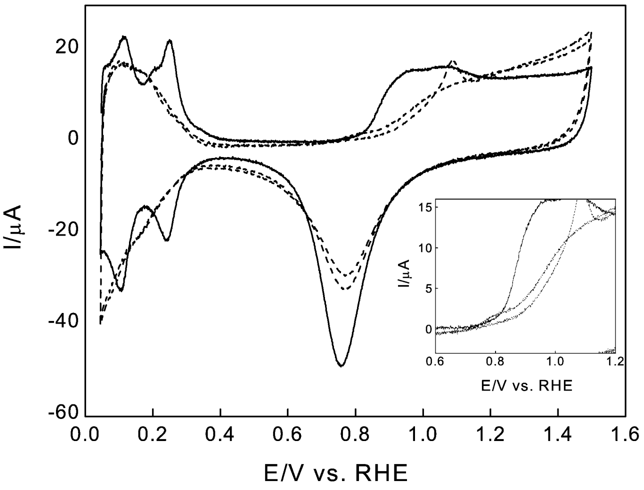

Fig. 5. Cyclic voltammetric profiles of pc platinum after simultaneous Os + Ru deposition (Method 3 in the text) by immersion in 0.5 mM Os^{3+} + 0.5 mM Ru^{3+} + 0.2 M sulfuric acid at 0.10 $V\,s^{-1}$ in 1 M sulfuric acid. Immersion times: 0 s (solid line), 60 s (dashed line), and 600 s (dotted line).

The values of θ resulting from the calculations of the voltammetric hydrogen adatom region in curves (a), (b), and (c) of Fig. 4 were 0.25, 0.22, and 0.23, respectively.

In the case of Method 3 deposition, the increase of the immersion time produces depletion of platinum oxide formation (Fig. 5). The characteristic osmium oxidative peak located at 1.1 V is now shifted toward more positive potentials; i.e., when ruthenium adatoms are present, osmium species are more stable on pc platinum. The anodic shoulder just before platinum oxide formation, typical of Pt/Ru or Pt/Os binary systems, only appears for immersion times longer than 600 s. The degree of inhibition of platinum oxide formation is proportional to the immersion time as well as to the extent of chloride oxidative desorption. In this case, increasing times of spontaneous deposition require several potential cycles to desorb the metal from platinum.

3.3. *Methanol oxidation on bare Pt, Pt/Ru, Pt/Os, and ternary combinations*

One of the factors limiting the practical development of methanol fuel cells is the poisoning of platinum anodes during their operation. Although this reaction is fast on bare platinum, carbon monoxide appears as an intermediate in the reaction and poisons the surface. The better performance of binary catalysts compared to bare platinum due to the bifunctional model for the fuel oxidation mechanism is well known [45–48]. Thus, cyclic voltammetry and chronoamperometric plots of methanol in solution and residues adsorbate oxidation on the different platinum-modified surfaces were studied in this work.

On one hand, methanol oxidation in solution was studied in 0.5 M methanol + 1 M sulfuric acid by linear sweep voltammetry on different platinum substrates. Fig. 6 shows a comparison between four linear positive-going voltammetric runs within the range 0.05–0.80 V performed at 0.01 $V\,s^{-1}$ on pc Pt, Pt/Ru, Pt/Os, and Pt/Ru–Os (obtained according to Method 3).

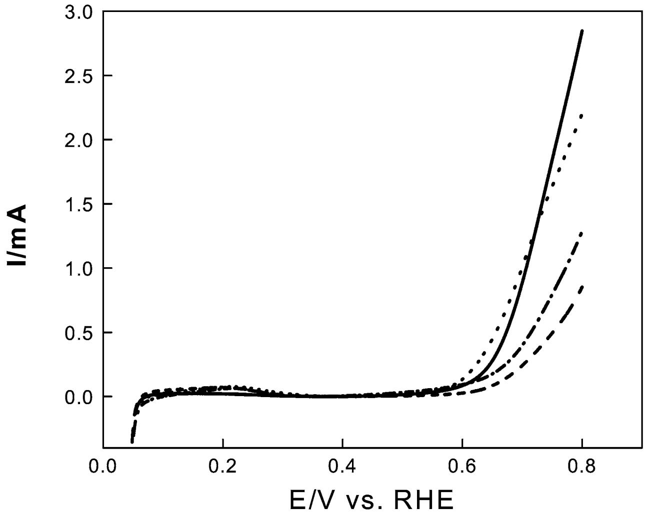

Fig. 6. Positive-potential-going scans of methanol oxidation on different prepared surfaces in 0.5 M methanol + 1 M sulfuric acid at 0.01 $V\,s^{-1}$: (continuous line) bare pc platinum; (dotted line) Pt/Ru; (dash-dotted line) Pt/Os; (dashed line) Pt/Ru–Os (obtained after 60 s of immersion).

Some interesting features can be detailed here. In the case of Pt/Ru and bare platinum we can state that the onset of methanol solution oxidation on Pt/Ru at potentials applicable in the case of fuel cells (ca. 0.6 V) is slightly lower than that obtained in the case of bare platinum, i.e., 30 mV. On the other hand, the currents observed at higher potentials (ca. 0.7 V) are almost similar on both electrodes but with different slopes. A cross point at 0.72 V is observed, from which methanol oxidation on bare platinum exhibits larger currents.

On the other hand, the onset potential for methanol oxidation of the Pt/Os presents the lowest value of all the explored surfaces, i.e., 0.40 V. Also, at 0.60 V, the current value is comparable to that of bare platinum. The surface prepared by Method 3 curves shows the lowest current values of all the studied surfaces. This means that the surface is not able to exhibit active platinum sites for methanol oxidation because they are compromised for ruthenium and osmium interactions with platinum.

The reverse scan (not shown in the figure) presents higher current values at 0.01 $V\,s^{-1}$ for all of the studied surfaces. The literature about methanol solution oxidation reports lower currents in the reverse scans when higher potential sweep rates are used (0.05–0.10 $V\,s^{-1}$) [25,29].

These results were also attractive for ethanol oxidation studies on Pt(100)/Ru surfaces [27]. It has been found that in 0.1 M ethanol the currents for the oxidation occur on Pt(100)/Ru at ca. 0.2 V before than that on bare Pt(100). Also the reverse cathodic sweep occurs with larger currents because the potentiodynamic scan was performed at low scan rates (0.02 $V\,s^{-1}$).

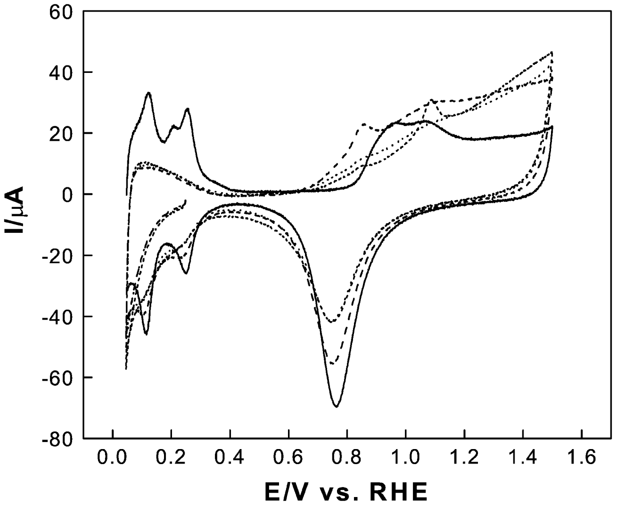

Fig. 7. First cathodic and subsequent anodic voltammetric profiles of methanol oxidation residues produced at $E_{ad} = 0.25$ V in 1 M sulfuric acid at 0.10 V s^{-1} on (dashed line) bare pc platinum; (dotted line) Pt/Ru; (short dashed line) Pt/Os superimposed on the repetitive voltammogram of pc platinum in 1 M sulfuric acid (continuous line).

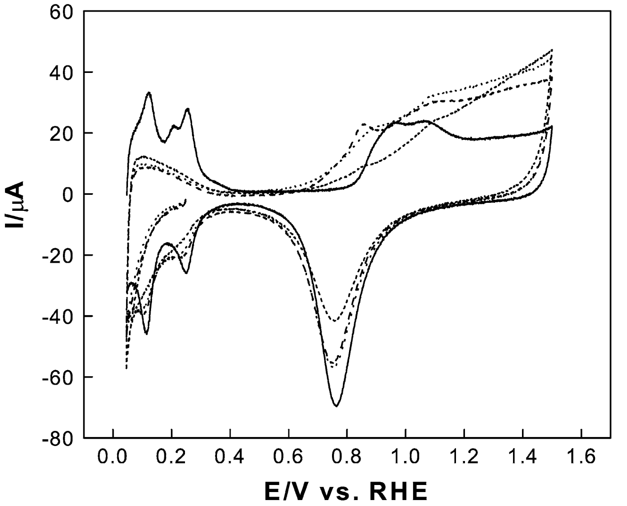

Fig. 8. First cathodic and subsequent anodic voltammetric profiles of methanol oxidation residues produced at $E_{ad} = 0.25$ V in 1 M sulfuric acid at 0.10 V s^{-1} on (dashed line) bare pc platinum; (dotted line) Pt/Ru/Os produced by Method 1; (dash-dotted line) Pt/Os/Ru produced by Method 2; (short dashed line) Pt/Ru–Os produced by Method 3 with an immersion time of 60 s superimposed on the repetitive voltammogram of pc platinum in 1 M sulfuric acid (continuous line).

Since the electrooxidation of methanol on platinum is an electrocatalytic process, the formation of methanol residues on the different surfaces has to be analyzed. The selected adsorption potentials for the organic molecule were $0.10 \leqslant E_{ad} \leqslant 0.35$ V in 0.5 M methanol + 1 M sulfuric acid solution. Figs. 7 and 8 exhibit the first cathodic and subsequent anodic voltammetric stripping profiles of methanol oxidation residues produced on pc Pt, Pt/Ru, Pt/Os, and Pt/Ru/Os (prepared by Method 1), Pt/Os/Ru (prepared by Method 2), and Pt/Ru–Os (prepared by Method 3 using an immersion time of 60 s). The curves were compared with each voltammogram of modified platinum in the supporting electrolyte (1 M sulfuric acid) to consider the foreign metal dissolution during potential cycling (not shown in this case). It is important to note that the residual charge density attained within the hydrogen region is the same for all the curves. This means that even in the presence of ruthenium and osmium adatoms, the final coverage by hydrogen adatoms is the same independently of the explored surface. The same behavior is observed for the ternary systems.

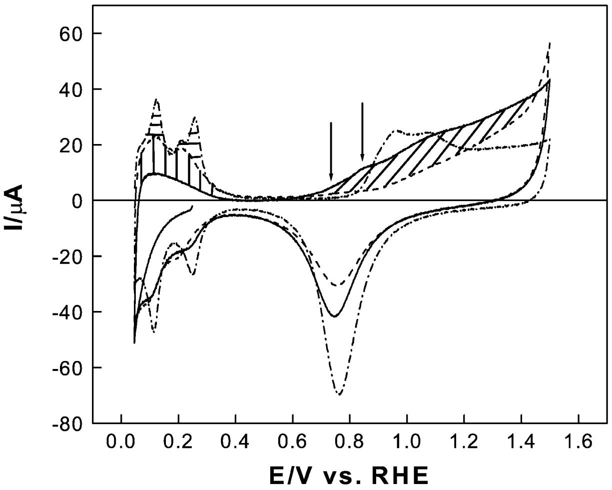

Fig. 9. First cathodic and subsequent anodic voltammetric profiles of (dashed line) Pt/Ru; (continuous line) Pt/Ru with methanol adsorbed at $E_{ad} = 0.25$ V; (dash-dotted line) pc platinum at 0.10 V s^{-1} in 1 M sulfuric acid. The vertical arrows show the double current contribution for methanol residues oxidation.

Both figures show that the charge density involved in the oxidation of methanol residues is lower in the case of the modified surfaces than on bare pc platinum within the 0.7–0.9 region. It seems that the oxidation potential range for methanol on the modified platinum surfaces extends up to 1.5 V. As was found before [49–51] for carbon monoxide adsorption and electrooxidation on Pt(110) and nanodispersed platinum modified by ruthenium adsorption, a new form of adsorbate was detected, assigned to carbon monoxide chemisorbed on ruthenium islands. Therefore, a double current contribution for methanol residues oxidation was found in this paper, as is shown in Fig. 9. This has also been observed by Iwasita and co-workers [16] using RHEED patterns to study carbon monoxide electrooxidation. The island structure of ruthenium changed after surface oxidation of the molecule, reflecting the mobility of this metal on platinum.

The oxidation charge density of methanol residues found typically for the case of pc platinum is decreased because of the presence of oxidation of the foreign admetal. However, to really conclude about the efficiency of the modified platinum surface toward methanol oxidation, a comparison between methanol adsorption (in the hydrogen adatom region) and oxidation (in the region from 0.40–0.65 up to 1.50 V according to the case) must be considered. In this way, the rationalized quotient between the charge of methanol adsorbate oxidation ($Q_{O,M}$) and the real amount of hydrogen dis-

Table 1

Electrode surface	$Q_{H,M}$ (μC/cm^2)	$Q_{O,M}$ (μC/cm^2)	$Q_{O,M}/2Q_{H,M}$
Pt	157.4	295.9	0.94
Pt/Ru	94.4	198.2	1.05
Pt/Os	81.2	242.9	1.50
Pt/Ru/Os	60.9	105.1	0.86
Pt/Os/Ru	60.0	103.0	0.85
Pt/Ru–Os	85.8	335.2	1.95

placed only by methanol ($Q_{H,M}$) was considered to evaluate the "oxidation efficiency" of each modified surface. For this purpose, the involved charges were calculated from graphics; $Q_{H,M}$ (with area shown with vertical grids) and $Q_{O,M}$ (denoted as transversal grids). In order to improve the visualization, hydrogen atoms displaced by ruthenium are also shown as horizontal grids. Table 1 shows the values of the stated charge densities and their ratio for the different platinum surfaces.

According to the data in Table 1, Pt/Os and Pt/Ru surfaces show a higher efficiency toward methanol oxidation than pc platinum. Therefore, in spite of methanol having fewer platinum sites to adsorb on than on bare platinum, the influence of the foreign metal as a new catalyst is evidenced through the larger values of oxidation charges. Besides, in the case of simultaneous deposition of ruthenium and osmium on platinum, the efficiency of methanol oxidation is higher than on Pt/Os and Pt/Ru surfaces. On the other hand, this effect is not traduced for the subsequent deposition of ruthenium and osmium (and vice versa). In this case, the ratio between $Q_{O,M}$ and $Q_{H,M}$ is lower than one. Two situations account for this behavior: either the occupation of the foreign admetals inhibits the adsorption of methanol in the hydrogen adsorption region or the catalytic activity of the ternary system is lower than expected. This can be evaluated by subtracting the hydrogen charge density left by the foreign metals and that left by methanol. Considering the data of Table 1, we can see that the real factor that is affecting the efficiency toward methanol oxidation is the real catalytic effect of the surface, since the surface concentrations of hydrogen adatoms are nearly the same.

It has to be said that for the simultaneous adsorption of ruthenium and osmium, the value of the ratio between the oxidation charge for methanol and the hydrogen atoms replaced by the alcohol is the largest of all. It seems that there is a synergetic effect of both adatoms toward methanol oxidation (per the same amount of adsorbed hydrogen). This kind of results have been found previously by other authors [3,46] for ternary (Pt–Ru–Os) and quaternary (Pt–Ru–Os–Ir) alloys at different temperatures. The improved performance of these catalysts can be explained by the bifunctional mechanism for methanol oxidation and the primary role of both metals is the decrease of the onset potential for the water decomposition. However, the interaction between foreign metals on platinum as a contribution to explain this kind of behavior can not be discarded.

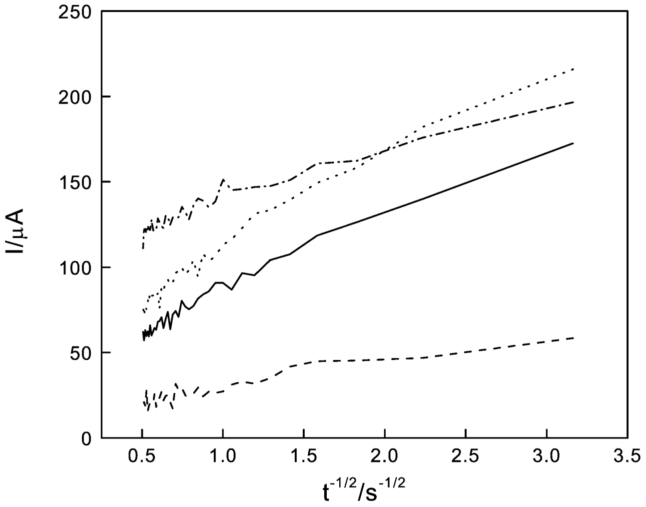

Fig. 10. Current transients for 0.5 M methanol solution oxidation + 1 M sulfuric acid performed at 0.70 V onto (continuous line) bare pc platinum; (dashed line) Pt/Os, (dotted line) Pt/Ru–Os, and (dash-dotted line) Pt/Ru electrode surfaces.

Methanol oxidation current transients at a constant potential provide more detailed information about the oxidation kinetics on the different substrates. We have performed the chronoamperometric curves in 0.5 M methanol + 1 M sulfuric acid solutions on bare platinum, Pt/Ru, Pt/Os, and Pt/Ru–Os surfaces. The selected potential was 0.70 V, where oxygen-containing species are present in all the study surfaces. A background experiment was also performed in the absence of methanol (only with supporting electrolyte) to check for the double layer charging component at each potential. When this current contribution is subtracted, we can calculate the early stages of the methanol oxidation rate at 0.70 V. Each plot shows a typical diffusion-control mechanism for a dissolved molecule oxidation process. This assumption was based on the linear behavior found for the current transient vs the reciprocal of square root of time (Fig. 10). Data taken from the linear regression of the current transients (within the domain 1.7–3.2 $s^{-1/2}$) were used to calculate the rate of methanol oxidation. These values for the different surfaces were estimated from the ratio between the slope of the current transient curve at zero time and the observed maxima current. The Pt/Ru–Os surfaces exhibit the highest methanol oxidation rates (2.3 s^{-1}), followed by Pt/Ru (1.8 s^{-1}). The rate for methanol oxidation on Pt/Os is 1.7 s^{-1}, similar to that of Pt/Ru, whereas for bare platinum the lowest value was found (1.1 s^{-1}). Again, a "synergetic effect" between ruthenium and osmium is evidenced in these experimental conditions.

4. Summary

The promotion of surface modifications of pc platinum by the spontaneous deposition of ruthenium, osmium, or their combinations results in new active surfaces with specific activities toward the oxidation of methanol. Despite a lot of research on ruthenium-modified platinum single-crystal surfaces, there is still a need to solve the complex mechanism of metallic chemisorption and especially the understanding of the nature of active surface sites able to oxidize methanol residues. Therefore, this work will be continued on the three basal platinum single-crystal surfaces to analyze the problem of methanol adsorption on binary and ternary platinum systems with active foreign metals such as ruthenium, osmium, tungsten, and molybdenum.

5. Conclusions

Ruthenium and osmium surface coverages on pc platinum did not show significant variation in their values for different-aged solutions after cycling three times between 0.05 and 0.80 V in 1 M sulfuric acid. The average values found also for the ternary systems are ca. 0.25 ML.

The formation of surface-oxidized species of ruthenium and osmium on pc platinum found in 1 M sulfuric acid, already corroborated using surface spectroscopic techniques, seems to be responsible for the electrocatalytic activity of the modified platinum toward methanol oxidation.

Using a microflux cell it was possible to study the influence of ruthenium and osmium (and their combinations) on the formation and oxidation of methanol residues. It was clearly seen that the peak of methanol residue oxidation previous to platinum oxide formation is minimized in the case of a modified platinum surface. Even so, when the methanol adsorbate oxidation is normalized with respect to the relative amount of hydrogen displaced by methanol, the modified platinum surfaces (platinum/ruthenium, platinum/osmium, and platinum/ruthenium–osmium) show higher oxidation efficiencies.

Current transients for methanol oxidation and methanol stripping oxidation charges showed that platinum/ruthenium and platinum/osmium surfaces exhibit nearly the same electrocatalytic activity. On the other hand, the surface prepared by the co-adsorption of ruthenium and osmium on platinum exhibits the best performance under these experimental conditions.

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