

# Surface metal modifiers for methanol electrooxidation on platinum; silver and mercury

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**Abstract** The catalytic activity of platinum surfaces towards methanol electrooxidation can be modified by the deposition of a second metal using different methodologies. There is little information about the catalytic performance of polycrystalline platinum modified by silver and mercury adatoms using spontaneous and electrochemical deposition methods. Cyclic voltammetrics have been performed to compare the current vs potential profiles of modified platinum surfaces in acid solution at room temperature. The inhibition of the hydrogen adatom voltammetric profile by foreign metal adatoms on platinum was used to calculate the degree of surface coverage by the metal. Poisoning effects were checked by anodic stripping experiments of methanol residues on the modified platinum surfaces at adsorption potentials in the hydrogen electrosorption region using a micro flux cell. Methanol solution oxidation was also evaluated at slow scan rates of up to 0.8 vs reversible hydrogen electrode (RHE) on the platinum-modified surfaces. The comparison between the amounts of carbon-monoxide-type residues and the solution oxidation of methanol was analysed to check for their utility as catalytic surfaces for direct methanol fuel cells.

**Keywords** Methanol · Platinum · Electrocatalysis · Silver · Mercury

## Introduction

Many efforts have been encouraged to enhance the electrocatalytic performance of methanol oxidation, attending to its application in direct methanol fuel cells. Because the reaction occurs by a self-poisoning mechanism, it is clear that catalysts properties must be overchanged to impede the formation of carbon-monoxide-type species. The oxidation of these adsorbed residues is accomplished by the co-adsorption of oxygen-containing species arising from water discharge on noble metals [1, 2]. Platinum appears to be the most efficient catalysts for the sequential deprotonation reaction in acid medium; however, water discharge occurs at potentials larger than 0.5 V [1, 3]. Therefore, the research guides have been oriented towards the surface modification of polycrystalline (pc) and single crystal platinum surfaces by metal deposits at sub- or monolayer levels. These new electrocatalysts are able to oxidize methanol at lower potentials than bare platinum. The better performance of binary catalysts such as, Pt/Sn, Pt/Re, Pt/Mo, Pt/Ru, and Pt/Os can be explained by two different effects: by the low onset potentials for water adsorption on the foreign metal and by the new electronic surface configuration of platinum atoms, which weakens the chemical bonds between platinum and the adsorbed residue [4, 5].

Reaction modifiers: silver and mercury deposition on noble metals

The deposition of foreign metals on noble surfaces can be performed by different methods: alloy formation [6–9], under-

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Dedicated to Professor Dr. Algirdas Vaskelis on the occasion of his 70th birthday.

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potential deposition (upd) [10, 11], overpotential depositions (opd), codepositions [12, 13], and metal adsorptions [14]. In all of them, the application of a potentiostatic or galvanostatic pulse is required [15]; however, good results (especially at low coverages) have been obtained using the spontaneous deposition process [16–20]. It is a very simple process that does not require any sophisticated electrochemical equipment and does not obey ohmic drops at low concentration depositions. Large values of coverage can be reached by multiple spontaneous depositions, as it has been demonstrated for ruthenium on Au(111) and for tin on pc platinum [21, 22] (Gualtieri et al., in preparation). Besides ruthenium and osmium, there is lack of information about the physicochemical properties of spontaneous deposition [23, 24]. Thus, one of the scopes of this paper is the study of silver and mercury deposition on pc platinum in sulfuric acid media.

Silver deposition has been studied by a large number of techniques [25–32], being most of them on gold and platinum in sulfate or perchlorate electrolytes [32–43]. Aging potentiostatic effects were also studied [41, 42] for silver electrochemical deposition on Pt(111) and pc platinum. Two different stages for silver deposition on platinum were observed: one at 1.1 V responding to silver–platinum alloy electrodisolution (overlapped with the oxygen electroadsorption at free platinum sites) and the other at 0.65 V due to the silver oxidation (from the onset of the bulk deposition process) deposited on the former surface alloy [40–43]. The former process splits into two peaks when potentiostatic aging is conducted. Spectroscopic techniques such as, X-ray photoelectron spectroscopy (XPS) and angle resolved X-ray photoelectron spectroscopy (ARXPS) were used to determine the chemical composition of silver films on platinum in acid solution [44]. The technique was not able to discern between the presence of silver oxides or sulfates; only an energy shift of the clean silver  $3d_{5/2}$  band at upd level of  $-0.5$  eV was detected.

A silver monolayer on Pt(100) was detected using Auger electron spectroscopy and cyclic voltammetry, which tends to form a three-dimensional structure [45]. Besides, using *on-line* cyclic voltammetry with scanning tunneling microscopy (STM) images [46], a double voltammetric contribution was found on an unreconstructed Pt(100) just before the bulk deposition process; that is, the two silver layers form by two distinct and independent processes with characteristic charge densities. Similar results on Pt(111) were found by Herrero et al. [47], where the first deposition consists of a 1.25 monolayer between 0.85 and 0.69 V (vs Ag/AgCl), the second deposition (0.2 monolayer) occurs between 0.69 and 0.45 V, and the third peak of 0.75 monolayer between 0.45 and 0.36 V. On the Pt(110) surface, the adsorption/desorption of silver and oxygen are not distinguishable in the more positive region of the voltammogram.

Mercury deposition on highly oriented carbon at low overpotentials takes place as a progressive nucleation and a diffusion-controlled three-dimensional growth [48]. It has to be noted that mercury upd on pc platinum exhibits similar features as silver even at different surface roughness [40]. In the case of smooth platinum, mercury deposition from a 0.1 mM mercurous salt in perchloric acid shows two anodic peaks at  $0.10 \text{ V s}^{-1}$ , one at ca. 0.66 V (due to bulk oxidation) and the other at 1.07 V (assigned to mercury upd). However, only a single cathodic peak at 0.75 V, including a shoulder assigned to the simultaneous oxygen electrodesorption and initiation of mercury upd, is observed. On the other hand, on columnar surfaces, four anodic peaks are seen at low scan rates ( $0.005 \text{ V s}^{-1}$ ): the first, due to bulk anodic stripping; the other, assigned to oxygen adsorption; the third, due to mercury upd; and the last, presumably due to mercury dealloying. For increasing scan rates, columnar electrodes show only one anodic peak due to the overlapping of the oxygen electroadsorption and the stripping of mercury upd [43, 49]. It was also found that the surface and subsurface diffusion processes in the bulk of the metal occur in the case of mercury.

Mercury deposition on Au(111) from mercuric ions is an interesting process, as its interaction covers a wider potential range than on platinum [50–53]. The multiple voltammetric peaks reported in the literature were associated with the influence of crystallographic orientation, which in the case of single crystal gold electrodes, are strongly shifted by the presence of absorbable anions, such as (bi)sulfate or halides [54]. A detailed study on the mercury coadsorption with anions is given in [55]. It was found as an ordered mercurous sulfate bilayer structure formed by a partial charge transfer. At more negative potentials where mercury is almost totally discharged, two additional ordered hexagonal mercury ad-layers are formed.

Platinum substrates modified by mercury- or silver-deposited layers have been checked for electrocatalysis applications; however, there is no accordance with respect to its effect upon the anodic oxidation of small alcohols [15, 40]. Therefore, a study of the potential uses of silver-(mercury-) modified platinum toward the oxidation of small alcohols is a topic that deserves special attention.

## Experimental

Electrochemical runs were conducted at room temperature in a micro-flux three-electrode cell using different pc platinum wires (0.5-mm diameter, 99.999% purity from Goodfellow) as working electrodes. The electrochemical set-up was completed using a large-area-platinum counter electrode and a reversible hydrogen reference electrode (RHE). The 1-M sulphuric-acid-supporting electrolyte was

prepared from J.T. Baker reagent with MilliQ®–Millipore-treated water (18.2 MΩ cm of resistivity). All potentials in the text are referred to the RHE scale.

Smooth platinum working electrodes were immersed, first, in hot concentrated sulfuric acid/nitric acid solution for half an hour, then, repeatedly rinsed in Milli-Q® water, and finally, placed in the supporting electrolyte. Platinum working electrodes were electrochemically activated, firstly, by a 20-min potential holding at 2.0 V in 1-M sulfuric acid solution; secondly and after the solution was replaced by fresh supporting electrolyte, repetitive 2.5-V s<sup>-1</sup> scans were run for 20 min; and finally, stabilized by 15 min of potential cycling at 0.10 Vs<sup>-1</sup> between 0.035 and 1.50 V. The real surface area of the pc platinum electrodes was 0.30 cm<sup>2</sup>, which was calculated from the integration of the hydrogen-adsorption voltammetric profile after double layer correction.

The 0.1-mM silver-containing solution was prepared from silver sulfate (Merck), and the 0.1-mM mercury-containing solution was prepared from mercuric sulfate in 1-M sulfuric acid solutions.

In the case of spontaneous deposition, the immersion time (considered as the time in contact with the metal-containing solution) varied from  $t_{\text{dep}}=15$  to 120 s. Stabilization of the spontaneous deposition on platinum was performed after washing the electrode with the supporting electrolyte by several potential cycles in the hydrogen adatom region at 0.10 V s<sup>-1</sup> until repetitive scans are reached. On the other hand, electrochemical opd was performed by potentiostatic holding at  $E_{\text{dep}}=0.10$  V for  $t_{\text{dep}}=5$  min. All deposition processes were followed by cyclic voltammetry either in the 0.035 to 1.50 V or 0.035 to 0.60 V range at 0.010 or 0.10 V s<sup>-1</sup> sweep rates in oxygen-free 1-M sulfuric acid solution.

The calculation of the degree of surface coverage by silver and mercury ( $\theta_{\text{Me}}$ ) on pc platinum was conducted by the integration of the voltammetric profile of the interface in the hydrogen adsorption region after double-layer correction.

$$\theta_{\text{Me}} = \frac{Q_{\text{H}}^{\circ} - Q_{\text{H}}}{Q_{\text{H}}^{\circ}}, \quad (1)$$

$Q_{\text{H}}^{\circ}$  and  $Q_{\text{H}}$  being the hydrogen adatom charged density before and after metal deposition, respectively.

Methanol solution oxidation was studied by linear sweep voltammetry, scanning the potential from 0 to 0.80 V at 0.01 Vs<sup>-1</sup> in oxygen-free 0.1 M methanol+1 M sulfuric acid. The electrocatalytic activity of the new composite 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 platinum surfaces as follows. First, a potential holding at  $E_{\text{ad}}=0.25$  V during  $t_{\text{ad}}=10$  min was applied to adsorb methanol from 0.1-M methanol+1 M sulfuric acid. Afterwards, and holding the potential at the

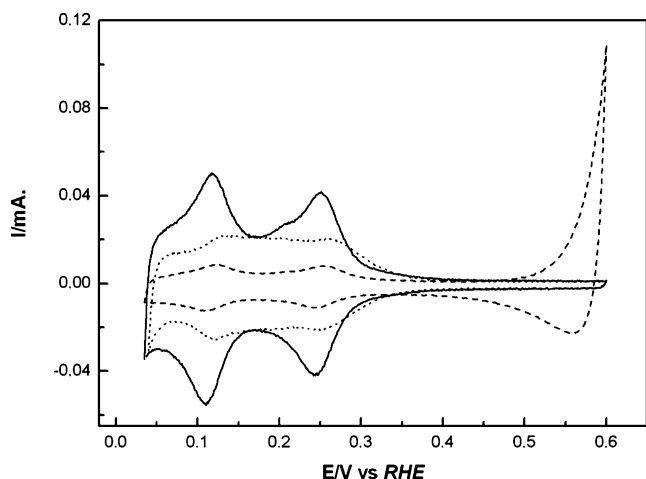
same value, the methanol-containing solution was replaced with the supporting electrolyte with a double flask micro-flux system to eliminate any diffusion contribution from the alcohol. Immediately after, the potential was scanned from  $E_{\text{ad}}$  to 0.035 V and subsequently toward positive values up to 1.50 V at 0.10 V s<sup>-1</sup> to obtain the whole stripping voltammogram of methanol residues in the supporting electrolyte.

## Results and discussion

Independent of the deposition method (spontaneous or electrochemical), the changes in the potentiodynamic profiles of pc platinum by silver and mercury at opd levels at 0.1 V s<sup>-1</sup> in acid media (free from dissolved metals) can be grouped into those metals interacting with platinum within the double layer and with the oxygen adsorption region.

The interaction of silver and mercury on pc platinum in acid media

The spontaneous ( $t_{\text{dep}}=60$  s) deposition (open-circuit potential of platinum in 0.1-mM silver sulfate+1 M sulfuric acid=1 V and constant) and electrochemical deposition ( $E_{\text{dep}}=0.10$  V,  $t_{\text{dep}}=5$  min) of silver from 0.1-mM silver sulfate+1 M sulfuric acid solution on pc platinum were performed at room temperature. The electrochemical contours of both depositions can be observed in Fig. 1 from 0.05 to 0.60 V at 0.10 V s<sup>-1</sup> in oxygen-free 1-M sulfuric acid solution. The comparison with the blank cyclic voltammogram of pc platinum is achieved by the superimposed curve in the same figure. Both deposition methods produce a decrease of the hydrogen adsorption region as expected. However, different features are observed for the two types of depositions; in the case of the spontaneous process, less surface coverage values are achieved ( $\theta_{\text{Ag}}=0.30$ ), comparing to those observed for the electrochemical deposition ( $\theta_{\text{Ag}}=0.80$ ). Moreover, the voltammetric contour of the electrochemical deposition of silver is nearly the same as in the case of bare platinum between 0.035 and 0.40 V, but with lower current densities for the strong and the weakly adsorbed hydrogen peaks. It has to be noted that the so-called third anodic hydrogen peak is not observed at all, which indicates that silver deposition involves basically (110) sites. On the other hand, in the case of silver spontaneous deposition, the weakly adsorbed hydrogen peak is positively shifted from 0.12 V in 0.02 V, whereas the “third anodic peak” (at 0.195 V) and the strong hydrogen adsorbate are similarly populated by hydrogen adatoms. Besides, the cathodic contribution observed in the cyclic voltammetric profile shows another “third cathodic peak” at 0.188 V. The main difference arising from silver



**Fig. 1** Cyclic voltammetric profiles of stabilized silver spontaneous deposition (*dotted line*) and electrochemical deposition (*dashed line*) on pc platinum run from 0.05 to 0.60 V at  $0.10 \text{ V s}^{-1}$  in oxygen-free 1-M sulfuric acid solution at room temperature. The *continuous line* represents the cyclic voltammetric profile of bare pc platinum. The spontaneous ( $t_{\text{dep}}=60 \text{ s}$ ) and electrochemical deposition ( $E_{\text{dep}}=0.10 \text{ V}$ ,  $t_{\text{dep}}=5 \text{ min}$ ) of silver were performed in oxygen-free 0.1-mM silver sulfate+1-M sulfuric acid solution at room temperature

electrochemical deposition is the appearance of a sharp peak beginning at 0.5 V. On the other hand, when the potential cycling started at 0.40 V, the charge consumed in the negative sweep through the hydrogen upd region exceeds (about 10%) the charge consumed in the oxidation of the adsorbed hydrogen, indicating that silver impedes hydrogen adatoms to desorb from the surface in the positive going scan—the same features found by Vaskevich and Gileadi [42].

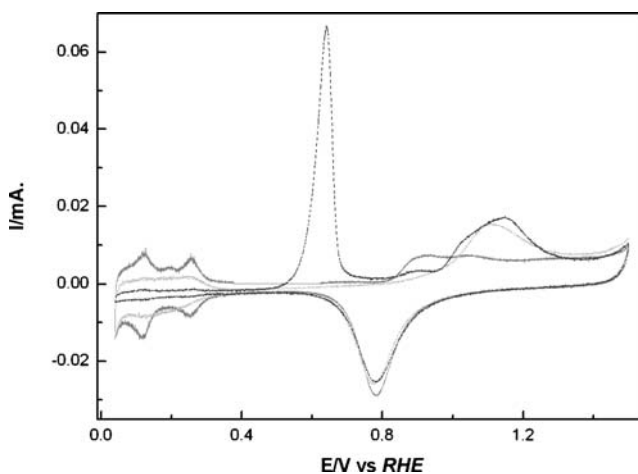
In Fig. 2, the voltammetric contour of silver electrochemical deposition at  $E_{\text{dep}}=0.10 \text{ V}$  for  $t_{\text{dep}}=5 \text{ min}$  is shown together with the spontaneous deposition of silver for  $t_{\text{dep}}=60 \text{ s}$  up to 1.50 V and run at  $0.010 \text{ V s}^{-1}$  in oxygen-free sulfuric acid solution. Besides the silver electrodisolution sharp peak from silver–silver domains at 0.65 V, three distinct voltammetric peaks can be seen that corresponds to upd processes, one at 0.89 V and two very near 1.04 and 1.15 V. According to Vaskevich et al. [41] and Martins et al. [40], the latter two peaks are associated to the splitting of the 1.1-V peak due to the first stages of silver–platinum alloy formation. The positively shifted peak corresponds to the oxidation of silver from the inner platinum lattice (from the alloy), and the one at 1.04 V is probably a silver oxidation process from outer silver–platinum interaction. This analysis based on our voltammetric results coincides with the interpretation of potentiostatic aging as responsible of the early stages of silver–platinum alloy formation by Vaskevich et al. [41]. The peak at 0.89 V probably corresponds to the early stages of platinum oxide formation in the presence of silver adatoms.

On the other hand, silver spontaneous deposition at low scan rates shows similar voltammetric features than those obtained at  $0.10 \text{ V s}^{-1}$ , that is, only one peak at 1.1 V. The inhibition of the platinum oxide formation is clear in the cyclic voltammetric response, that is, within the 0.85 to 1.05 V range; an important suppression of the early stages of platinum oxide is observed, caused by the presence of silver adatoms. The voltammetric profile of the hydrogen upd region is slowly restored, while the peak associated with the oxidation of silver upd adatoms decreases. Four cycles are needed to obtain the repetitive voltammetric profile of bare platinum in sulfuric acid.

In the cathodic voltammetric scan, there is no difference between the platinum oxide reduction peak (at 0.78 V) of the silver deposited and bare platinum surfaces for both deposition processes; that is, silver adatoms are located at active sites not required for initial water discharge, being the precursors of platinum oxide. Thus, it is likely that the upd peak at 1.1 V involves two electrochemical processes, one of the silver adatom oxidation itself and the other a retard platinum oxide formation. An isopotential point is observed for this transition at 1.0 V.

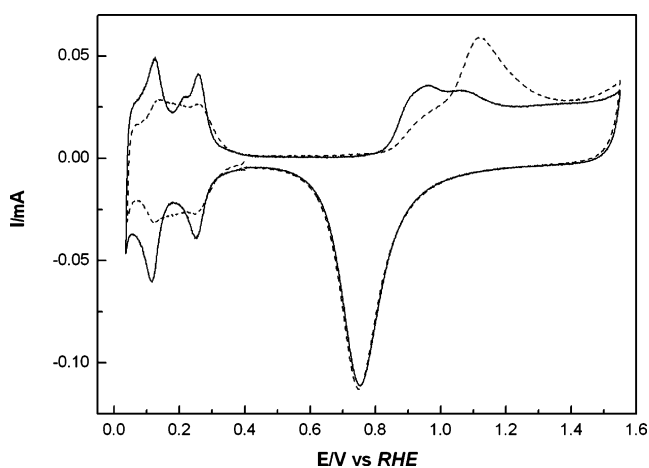
At medium–large potential scans, silver electrochemical deposition exhibits similar voltammetric profiles to that of spontaneous deposition at any sweep rate. The open circuit potential for the latter process was always 1 V during the entire deposition; thus, the 0.65-V peak (due to bulk silver oxidation) is not observed.

Similarities in the electrochemical response of mercury spontaneous deposition to silver on pc platinum were found



**Fig. 2** Cyclic voltammetric profiles of stabilized silver spontaneous deposition (*light gray line*) and electrochemical deposition (*dashed gray line*) on pc platinum run from 0.05 to 1.50 V at  $0.010 \text{ V s}^{-1}$  in oxygen-free 1-M sulfuric acid solution at room temperature. The *continuous black line* represents the cyclic voltammetric profile of bare pc platinum. The spontaneous ( $t_{\text{dep}}=60 \text{ s}$ ) and electrochemical deposition ( $E_{\text{dep}}=0.10 \text{ V}$ ,  $t_{\text{dep}}=5 \text{ min}$ ) of silver were performed in oxygen-free 0.1-mM silver sulfate+1-M sulfuric acid solution at room temperature

in this work. Therefore, as a matter of comparison, we only show the spontaneous ( $t_{\text{dep}}=60$  s) deposition of mercury from 0.1-mM mercuric sulfate+1 M sulfuric acid solution on pc platinum. The electrochemical contour is depicted as superimposed with the voltammetric response of bare platinum (Fig. 3) from 0.05 to 1.50 V run at  $0.10 \text{ V s}^{-1}$  in oxygen-free 1-M sulfuric acid solution after spontaneous deposition. The calculation of  $\theta_{\text{Hg}}$  after stabilization by cycling in the hydrogen region reaches 0.40. According to the voltammetric results, mercury deposition takes place in all the crystallographic sites available for hydrogen adsorption, finally showing the same current contributions for the three anodic peaks. Extending the upper potential limit to 1.50 V, five cycles at  $0.10 \text{ V s}^{-1}$  are required to reach the voltammetric bare pc platinum profile in 1-M sulfuric acid. A single and large anodic peak at 1.20 V due to upd mercury oxidative desorption to solution can be observed. The inhibition of the platinum oxide formation is clear in the cyclic voltammetric response, that is, within the 0.85 to 1.10 V potential ranges; an important suppression of the early stages of platinum oxide is observed to be caused by the presence of mercury adatoms. The voltammetric profile of the hydrogen upd region is slowly restored, while the peak associated with mercury oxidation decreases. There is no alteration of the platinum oxide reduction peak and is exactly that of bare platinum; that is, again mercury adatoms occupy platinum active sites not required for water discharge. It is likely that the mercury upd peak at 1.2 V involves two processes, mercury adatom oxidation itself and the platinum oxide formation. An isopotential point is observed for this transition at 1.1 V.



**Fig. 3** Cyclic voltammetric profile of stabilized mercury spontaneous deposition (*dotted line*) on pc platinum run from 0.05 to 1.50 V at  $0.10 \text{ V s}^{-1}$  in oxygen-free 1-M sulfuric acid solution at room temperature. The *dashed line* depicts the stabilized voltammetric profile in the hydrogen adsorption region. The *continuous line* represents the cyclic voltammetric profile of bare pc platinum. The spontaneous ( $t_{\text{dep}}=60$  s) deposition of mercury was performed in oxygen-free 0.1-mM mercuric sulfate+1-M sulfuric acid solution at room temperature

Methanol catalytic oxidation on the different modified platinum surfaces

#### Generalities on methanol adsorption and oxidation

In spite of most electrocatalytic reactions occurring in water as solvent, the study of methanol adsorption on platinum under ultrahigh vacuum (UHV) conditions or at a gas/solid interface is also of interest. There are not so many papers dealing with methanol adsorption in an UHV chamber [56, 57]. It adsorbs without reaction on Pt(111) at low temperatures (100 K), and based on thermal desorption experiments, it was concluded that a monolayer of methanol adsorbate desorbs at 180 K. The estimation of the heat of adsorption of molecular methanol was  $46 \text{ kJ mol}^{-1}$  on unreconstructed Pt(111) [58]. Infrared spectroscopy has been applied for the study of methanol adsorption on Pt(111) [59], and it was shown that 0.36 monolayer of methanol corresponds to the saturation of the desorption peak found at 180 K. Methanol multilayer coverages were also found, but with different infrared frequencies associated to the methyl and C–O stretching modes.

In UHV conditions, methanol can be dissociatively desorbed as carbon monoxide and molecular hydrogen at temperatures between 200 and 300 K. A stable surface methoxy intermediate ( $\text{CH}_3\text{O}^-$ ) forms by the scission of the O–H bond [60]. The Pt(110)-( $1 \times 2$ ) reconstructed surface is only to show stable methoxy species co-adsorbed with oxygen, but on (111) and (100) platinum planes, the surface combination leading carbon dioxide is demonstrated [59].

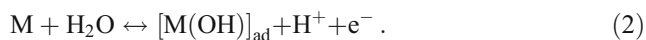
The first paper on methanol electrocatalysis under UHV conditions was carried out by Attard et al. [61] on the most active surface, Pt(110). Similar results to those on Pt(111) were found, that is, carbon monoxide and molecular hydrogen, but with a slightly larger methanol surface coverage, that is,  $\theta=0.10$ . It was the first time that methoxy species are proposed as intermediate, different to the carbon monoxide or formyl species earlier proposed by Bagotsky et al. [62]. However, traces of formyl species has also been detected on reconstructed Pt(110) using vibration spectroscopy, which was able to coadsorb with atomic oxygen [63].

The electrochemical oxidation of methanol has been extensively studied on pc platinum [64] and platinum single crystal surfaces [14, 65] in acid media at room temperature. Methanol electrooxidation occurs either as a direct six-electron pathway to carbon dioxide or by several adsorption steps, some of them leading to poisoning species, prior to carbon dioxide as final product. The most convincing evidence of carbon monoxide as a catalytic poison arises from in-situ IR fast Fourier spectroscopy. 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 modification of platinum surfaces by foreign metal atoms promotes the oxidation of methanol either in UHV conditions or in the electrochemical environment. This promotion model has been mainly discussed in electrochemistry using the “third body model” [65, 66], the “ligand effect” [15], or the “bifunctional effect” [15, 68]. A theoretical review on the inclusion of metal reaction promoters was performed by Anderson et al. [68] and later discussed in [5]. There are a lot of papers on the matter but not a real consensus on the effects of each metal over the platinum efficiency towards methanol electrooxidation. Therefore, a lot of questions need to be answered. There is accordance till now that, for platinum alloys, the two metals that are able to promote methanol oxidation are ruthenium and tin. The case of ruthenium is interesting because it was also studied under UHV conditions [69, 70]. The reaction of methanol on Pt/Ru alloys results in the production of carbon dioxide at lower potentials than on pure platinum. However, the presence of tin as Pt<sub>3</sub>Sn alloys only enhances methanol oxidation at low potentials, increasing carbon dioxide production (and diminishes that of carbon monoxide production) [70, 71]. The addition of tin (II) ions to previously adsorbed methanol produces a fast oxidation process demonstrated by differential electrochemical mass spectrometry (DEMS) experiments [72]. No experimental results were found for methanol oxidation on platinum surfaces promoted by mercury deposition, and very little using tungsten [73].

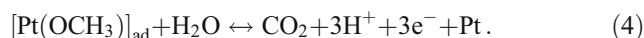
The adsorption of methanol takes place mostly on platinum-free sites at potentials lower than 0.6 V and higher than 0.10 V. The mechanism for spontaneous deposition on noble metals has not been clarified yet. Nevertheless, according to literature, the simultaneous deposition of platinum and ruthenium from PtCl<sub>6</sub><sup>2-</sup> and Ru(H<sub>2</sub>O)<sup>3+</sup> occurs by a first-hydrogen adatom reduction of the ruthenium complex to metallic ruthenium, which subsequently reduces the chloroplatinate anion to metallic platinum by the surface oxidation of ruthenium to RuOxHy species [74]. Moreover, Hubbard [75] proposed for the case of tin spontaneous deposition from tin(II) species the auto deprotonation to metallic tin and tin(IV) interface species and the subsequent surface oxidation of metallic tin to Sn(OH)<sub>2</sub>. Generally, in the presence of foreign metals, M, on platinum, the bifunctional mechanism proposes that M promotes the water discharge at lower potentials than pure platinum,



These species promote the oxidation of the adsorbate by either a direct re-combination (reaction 3) of the species through a Langmuir–Hinshelwood mechanism [15] (Scheme 1),



or indirectly by the reverse Eley–Rideal mechanism when the intermediate is a methoxy species as follows (reaction 4), where no other metal is really needed [76]:

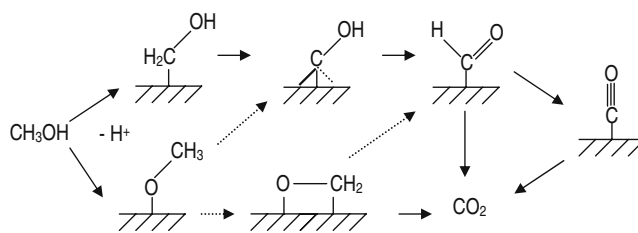


According to the ligand effect theory, the energy level of the modified substrate is changed to weaken the bond energy of the carbon monoxide adsorbate to facilitate its oxidation. The best choice of the alloying or codeposited elements depends on which step of the latter mechanism is the rate-determining step (normally reaction 3). Therefore, also the molar fraction has to be 1:1 if this is true. Different results were obtained, so the discussion is still opened.

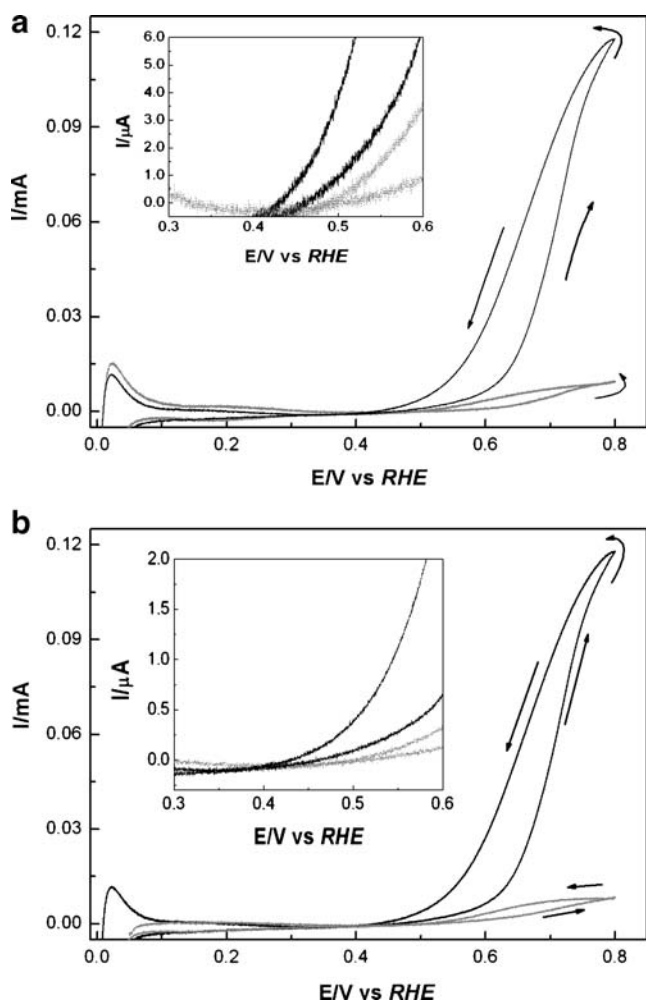
#### Methanol solution oxidation on platinum-modified surfaces

*Methanol solution oxidation on spontaneous deposited foreign metals on platinum* To test the poisoning effects of carbon monoxide residues in the kinetics of methanol oxidation, linear sweep voltammograms were recorded at rather low scan rates; i.e., 0.01 V s<sup>-1</sup>, in oxygen-free methanol acidic solution. Two different experiments were run depending on the method of metal deposition on platinum, but in all of them, the following potential sequence was performed starting at 0.05 V with a first positive going scan up to 0.80 V and then the negative potential sweep down to 0 V.

Figure 4 shows the linear voltammetry for methanol solution (0.1 M) oxidation studied in 1-M sulfuric acid at 0.01 V s<sup>-1</sup> on pc platinum. It is compared with the electrochemical response on Pt/Ag surfaces in Fig. 4a and in b with Pt/Hg. Some interesting features can be detailed here. In the case of Fig. 4a, methanol oxidation on bare platinum exhibit the higher oxidation currents during both



**Scheme 1** General scheme of methanol electrooxidation, considering series and parallel pathways to form carbon dioxide as product. *Solid and dashed arrow lines* are the demonstrated and possible reaction pathways, respectively



**Fig. 4** First positive and subsequent negative potential going scan for methanol oxidation in 0.1-M methanol+1-M sulfuric acid run at  $0.01 \text{ V s}^{-1}$  on **a** bare pc platinum (continuous line) and Pt/Ag surfaces (dash gray line), and **b** bare pc platinum (continuous line) and Pt/Hg (gray line). All spontaneous depositions were obtained at  $t_{\text{dep}}=60 \text{ s}$  in the prepared solutions. The starting potential=0.05 V, lower potential limit=0 V, and upper potential limit=0.80 V. Inset are the same figures (a and b) at a more resolved scale from 0.30 to 0.60 V and from 0 to 6.0  $\mu A$  and 0 to 2.0  $\mu A$ , respectively

potential incursions. The presence of more platinum active sites susceptible of methanol adsorption on bare platinum is enough to produce largest anodic methanol oxidation currents. This experiment is another evidence that foreign metals are not able to adsorb methanol as well as platinum, and the statistic distribution of those metal modifiers are not as isolated atoms but in large islands all along the electrode. Methanol oxidation currents for Pt/Ag surfaces, clearly denoting an inhibiting character towards the organic oxidation.

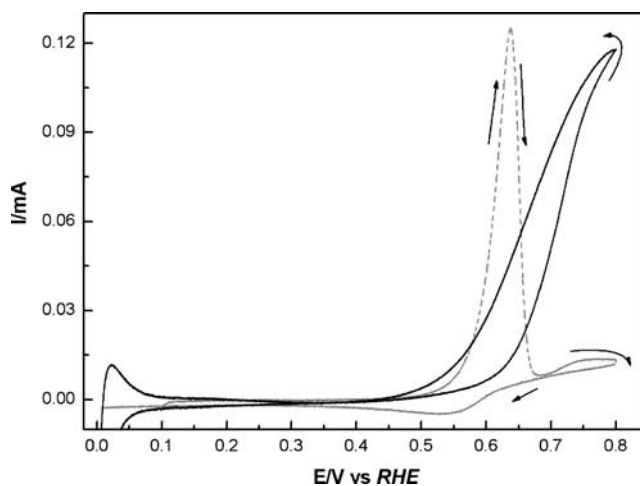
On the other hand, it is also important to show in the surfaces studied for methanol solution oxidation shown in Fig. 4a that the first anodic incursion exhibits lower current (at a fixed potential) than those observed during the

negative potential going scan (see arrows in the Fig. 4). This aspect has been observed in many experiments, and it is ascribed to the gradual lost of carbon monoxide adsorbates (as poisons and not as intermediates) that, in the negative potential scan from 0.8 V, leave free platinum active susceptible of methanol adsorption and oxidation. In the 0.02 to 0.10 V potential ranges, however, either on bare platinum or Pt/Ag, surfaces exhibit hydrogen oxidation currents.

Similar explanations can be given for the case of methanol oxidation on Pt/Hg in Fig. 4b. Methanol oxidation on Pt/Hg is similar to Pt/Ag, an inhibition effect is observed and also in the 0.05 to 0.20 V for hydrogen oxidation.

*Methanol solution oxidation on electrochemically deposited silver on platinum* Figure 5 shows the methanol solution oxidation current vs the potential profiles on the platinum surfaces modified by the electrodeposition of silver. The figure exhibits the potentiodynamic profile in deaerated solutions of 0.1-M methanol+1 M sulfuric acid at  $0.010 \text{ V s}^{-1}$  from 0.035 to 0.80 V and vice versa. Mercury-modified surfaces were not studied, as they do not exhibit interesting catalytic behaviour. As it has been presented in “Experimental”, all electrochemical opd depositions were performed by potentiostatic, holding at  $E_{\text{dep}}=0.10 \text{ V}$  for  $t_{\text{dep}}=5 \text{ min}$ , independent of the nature of the metal complex ion.

The case of the methanol oxidation on Pt/Ag ( $\theta=0.80$ ) is totally different because a large opd peak is observed at ca. 0.65 V, coinciding with the bulk silver oxidation (see Fig. 2). No net catalytic activity is observed for this surface towards methanol oxidation (the currents for methanol



**Fig. 5** First positive and subsequent negative potential going scan for methanol oxidation in 0.1-M methanol+1-M sulfuric acid run at  $0.01 \text{ V s}^{-1}$  on bare pc platinum (continuous line) and Pt/Ag (light gray dashed line). All electrochemical depositions produced at  $E_{\text{dep}}=0.10 \text{ V}$  for  $t_{\text{dep}}=5 \text{ min}$ . Starting potential=0.05 V, lower potential limit=0 V (shown only from 0.40 V), and upper potential limit=0.80 V

oxidation are ca. 10% of those on bare platinum). From 0.68 V, catalytic activity is observed at an anodic current of 8  $\mu\text{A}$ , reaching a maximum value of 0.75 V at of 14  $\mu\text{A}$ . After subsequent cycles, the silver bulk deposition rapidly decrease but methanol oxidation does not activate. It seems that, at these potentials, the platinum surface free from silver is occupied by water and hydroxyl species with no disposition towards methanol. In this sense, the negative going potential sweep shows the silver deposition process on platinum again, so the inhibition still occurs. This effect is not observable for silver spontaneous deposition on platinum, probably due to the lower coverage ( $\theta_{\text{Me}}=0.30$ ). The figure is a complex composition of two processes; during the first potential cycle, the oxidation of bulk silver at 0.64 V (probably to  $\text{Ag}^+$  and some  $\text{Ag}_2\text{O}$ ) is seen with a little current for methanol oxidation starting from 0.68 V. Nevertheless, the cathodic sweep exhibits a counter reduction peak with a maximum intensity of  $-4.5 \mu\text{A}$ . On the other hand, in the second cycle, an anodic contribution at 0.60 V can be observed with a current peak of 19.0  $\mu\text{A}$ , while no reduction peak is observed at all.

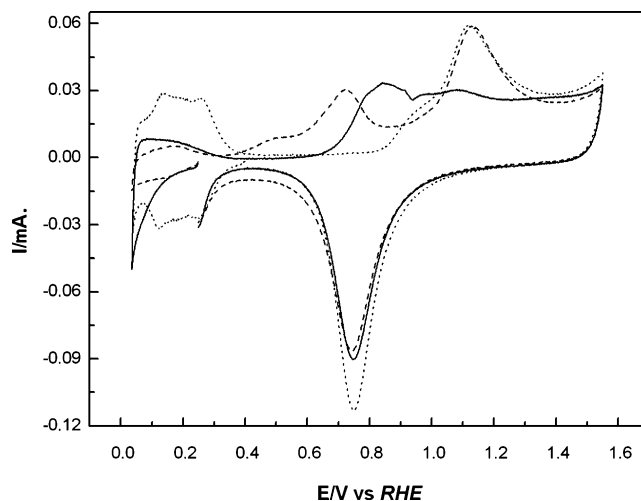
It is important to note that, for successive potential cycles, methanol oxidation currents decrease in the positive going potential scans but not for the negative ones. It seems that the presence of methanol in the bulk of the solution produces a constant supply of fuel for oxidation (practically not containing carbon monoxide adsorbates).

#### Anodic stripping profiles of methanol residues on platinum-modified surfaces

In some cases, we have performed stripping profiles to separate the adsorbate contribution from the methanol solution contribution to the current profiles. Thus, silver was selected for this purpose.

The potentiodynamic response of methanol residues produced at  $E_{\text{ad}}=0.25 \text{ V}$  for  $t_{\text{ad}}=10 \text{ min}$  run at  $0.10 \text{ V s}^{-1}$  on Pt/Ag spontaneous deposition ( $\theta_{\text{Ag}}=0.30$ ) in the supporting electrolyte is shown in Fig. 6. The experiment was performed according to the procedure explained in “Experimental”. It also shows the potentiodynamic response of the silver spontaneously deposited platinum surface,  $t_{\text{dep}}=60 \text{ s}$ , in the supporting electrolyte, together with that of bare platinum. Because, for mercury spontaneous deposition, almost the same features were found, we only present the results for methanol residue oxidation on silver spontaneous platinum.

As expected, the potentiodynamic profile of methanol residue oxidation shows a marked decrease in the hydrogen voltammetric region due to methanol adsorption. The further inhibition of hydrogen desorption caused by methanol adsorbed at  $E_{\text{ad}}=0.25 \text{ V}$  leaves the following hydrogen



**Fig. 6** Stripping voltammetric profiles of adsorbed methanol in oxygen-free 1-M sulfuric acid solution recorded at  $0.10 \text{ V s}^{-1}$  from 0.05 to 1.5 V on (continuous line) pc platinum and (dashed line) Pt/Ag electrodes. The latter were prepared from 0.1-mM silver sulfate+1 M sulfuric acid for  $t_{\text{dep}}=60 \text{ s}$  ( $\theta_{\text{Ag}}=0.30$ ). Methanol adsorbates were produced from a 0.10-M methanol+1-M sulfuric acid solution at  $E_{\text{ad}}=0.25 \text{ V}$  for  $t_{\text{ad}}=10 \text{ min}$ . The dotted gray lines show the potentiodynamic profile of the stabilized silver spontaneous deposition on pc platinum run from 0.05 to 1.50 V at  $0.10 \text{ V s}^{-1}$  in oxygen-free 1-M sulfuric acid solution

charge  $Q_{\text{H}_1} = 29 \mu\text{C cm}^{-2}$ , and the remaining area after silver spontaneous deposition is  $Q_{\text{H}_2} = 143 \mu\text{C cm}^{-2}$ . Therefore, considering that silver is not displaced by methanol residues, the real coverage by the organic species is

$$\vartheta_{\text{MeOH}} = \frac{Q_{\text{H}_2} - Q_{\text{H}_1}}{Q_{\text{H}}^0} \quad (5)$$

being the original hydrogen surface charge density,  $Q_{\text{H}}^0 = 210 \mu\text{C cm}^{-2}$ .

In this case, the value of  $\vartheta_{\text{MeOH}}$  is 0.54 lower to that obtained on a bare platinum surface. On pc platinum, the values  $Q_{\text{H}}^0 = 210 \mu\text{C cm}^{-2}$  and  $Q_{\text{H}_1} = 40 \mu\text{C cm}^{-2}$  have to be used, i.e.,  $\vartheta_{\text{MeOH}}$  is 0.81. However, the value of  $\vartheta_{\text{MeOH}}$ , considering the real surface to be occupied, is 0.80.

The complete stripping voltammogram for methanol residues oxidation on a Pt/Ag surface shows three peaks, one at 0.52 V, another at 0.72 V, and the last at 1.05 V. Because the superimposed voltammogram of the Pt/Ag response in the supporting electrolyte shows the same 1.1 V peak (assigned to silver oxidation from silver–platinum domains), the one at 0.72 V is likely to be the oxidation of methanol residues to carbon dioxide. The “pre-wave” (previously observed in other surfaces during methanol oxidation [77]) is ascribed to a dissociative methanol adsorption, probably leading to formyl or more reduced carbon monoxide species.

The anodic charge density for the stripping of methanol residues on Pt/Ag is  $Q_0 = 219 \mu\text{C cm}^{-2}$ , a value that is



higher than that obtained from the oxidation of methanol residues formed on a bare platinum surface ( $Q_{O_0} = 195 \mu\text{C cm}^{-2}$ ) in the same experimental conditions. The methanol residues stripping peak on bare platinum lies ca. 0.80 V, which can be clearly deconvoluted into two distinct peaks, one at 0.78 V (with  $Q_{O_1} = 173 \mu\text{C cm}^{-2}$ ) and the other at 0.84 V (with  $Q_{O_{II}} = 21 \mu\text{C cm}^{-2}$ ). The largest contribution attributed to the first peak may be the linearly bounded carbon monoxide adsorbates.

On the other hand, in the case of Pt/Ag, the deconvolution of the “pre-wave” and the anodic peak gives rise to two real peaks located at 0.52 V ( $Q_{O_1} = 59 \mu\text{C cm}^{-2}$ ) and 0.72 V ( $Q_{O_{II}} = 160 \mu\text{C cm}^{-2}$ ) with a relative surface charge ratio of 2.7. This means that the highest contribution to the total adsorbed species is the more oxidizable configuration, which may be the bridge configuration.

The observation of the entire voltammogram and the profiles of the two deconvoluted features show that methanol residues on Pt/Ag are not stripped in a single cycle. Thus, the anodic peak at 0.52 V is completely stripped in the first cycle, while two more potential cyclings are needed for the second anodic peak, involving 25.0 and 12.0  $\mu\text{C cm}^{-2}$  of charge densities. In this sense, the relative difference between the  $Q_{O_0}$  values of methanol residue oxidation on bare platinum and Pt/Ag is ca. 10 %. Therefore, at 0.25 V of adsorption potential, methanol residues are not able to displace silver from the platinum surface. Anyway, the important thing is that the oxidation of methanol on Pt/Ag starts at much lower potentials than that of 0.64 V on bare platinum; that is, it starts at ca. 0.4 V. It seems that the first methanol dissociation (deprotonation) produces a rather important oxidation on Pt/Ag surface, but leading carbon-monoxide-type adsorbates that are not stable over silver domains. In spite of the less methanol molecules adsorb on the surface, the influence of the foreign metal as a new catalyst produces similar hydrogen displacement. Again, we can say that methanol does not adsorb over silver nor displace silver atoms.

Based on our experiments (Fig. 6), we can say that the first “pre-wave” (0.52 V) of methanol residue oxidation on Pt/Ag is independent of the second anodic peak. Two different and independent compounds (oxidizing at 0.52 and 0.72 V, with  $Q_{O_1}$  and  $Q_{O_{II}}$ , respectively) are formed with a surface charge ratio of 2.7. It is also evident that no single adsorption configuration for the possible species involving  $Q_{O_1}$  and  $Q_{O_{II}}$  can be envisaged because the relation between each of them with the remaining  $Q_{H_0}$  after adsorption cannot be calculated. It has to be noted that, after the first single anodic sweep, the “pre-wave” peak has totally disappeared, and then, another possible configuration for this residue can be formyl species. The “lifetime” of formyl and pure carbon-monoxide-adsorbed species on

platinum and their possible detection by in-situ infrared techniques is a recurrent discussion. The first complete paper about the detection of formyl adsorbates was by Juanto et al. [78]. The shortest lifetime of these species and the hundred interferograms needed to measure infrared spectra at each potential value produces the surface conversion of formyl to carbon monoxide and more stable species on platinum. In our case, it is possible that formyl adsorbates firstly occur because the second peak at ca. 0.72 V requires three cycles to completely oxidize from the surface.

Contrary to the result for methanol oxidation in the solution, it was expected that Pt/Ag would shift the peak position towards positive potentials; however, the peak oxidation has a “pre-wave” of ca. 0.52 V, ca. 0.3 V more negative and less populated than on bare platinum. Moreover, the distance between each peak on Pt/Ag is 0.20 V, whereas between each deconvoluted peaks on pure platinum is 0.06 V. This difference explains the less interaction between each adsorbate on Pt/Ag, probably as a consequence of the very different configurations of adsorbed species.

This implies that methanol residue is absorbed less strongly on Pt/Ag than on clean platinum, or that the supply of oxygen-containing species needed for residues oxidation to carbon dioxide is limited on platinum. The decrease in the binding energy of methanol residues may, therefore, be due to the electronic alteration of surface platinum atoms by silver, diminishing carbon monoxide or formyl bonding to Pt/Ag, which will be verified independently. Thus, the surface that has the highest propensity to carbon monoxide chemisorption is less active than other surfaces toward methanol solution oxidation via the direct oxidation path. Apparently, methanol oxidative dissociation on Pt/Ag favors the direct formation of a more reduced carbon monoxide adsorbate and is not very much affected to produce carbon dioxide. The silver additive does not act as a third body promoter that can modify the platinum assemble by a selective site blocking. Instead of impeding carbon monoxide chemisorption, it favors this pathway.

## Conclusions

The scientific interest of metal spontaneous and electrochemical depositions on platinum deserves special attention in preparing novel anode electrocatalysts. In the case of methanol fuel cells, poison-resistant electrodes are also a matter of research to complete the design of the electrocatalyst. Inhibitory effects were found toward methanol oxidation for spontaneous, deposited, and modified platinum/silver and mercury surfaces. In the case of platinum/silver surfaces, a more reduced adsorbed residue is detected with one third of the relative charge between each

deconvoluted charge oxidation peak. In spite of this surface being the worst for methanol oxidation, it is of special academic interest and is being studied, showing that the type of deposition process strongly affects the catalytic properties of the resulting surfaces. Some in situ spectroscopic and microscopic techniques are advance.

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## References

- Iwasita T (2002) *Electrochim Acta* 47:3663
- Samant PV, Rangel CM, Romero MH, Fernandes JB, Figueiredo JL (2005) *J Power Sources* 151:79
- Ramershrishnan VBG, Todd L, Renxuan J, Kevin L, Smotkin E (1998) *J Phys Chem B* 102:9997
- Beden B, Leger JM, Lamy C (1992) In: Bockris JO'M, Conway BE, White RE (eds) *Modern aspects of electrochemistry*, vol. 22. Plenum, New York, pp 97–247
- Koper MT (2004) *Surf Sci* 548:1
- Iwasita T, Nart FC, Vielstich W (1990) *Ber Bunsen-Ges Phys Chem* 94:1030
- Gasteiger H, Markovic N, Ross PN, Cairns E (1993) *J Phys Chem* 97:12020
- Gasteiger H, Markovic N, Ross PN, Cairns E (1994) *J Electrochem Soc* 141:1795
- Markovic N, Gasteiger H, Ross PN, Villegas I, Weaver M (1995) *J Electrochim Acta* 40:91
- Friedrich K, Geyzers K, Linke U, Stimming U, Sumper J (1996) *J Electroanal Chem* 402:123
- Chrzanowski W, Wieckowski A (1998) *Langmuir* 14:1967
- Krausa M, Vielstich W (1994) *J Electroanal Chem* 379:307
- Hogarth M, Munk J, Shukla A, Hammnett A (1994) *J Appl Electrochem* 24:85
- Chrzanowski W, Kim H, Wieckowski A (1998) *Catal Letters* 50:69
- Coutanceau C, Ralotondrainibé A, Lima AI, Garnier E, Pronier S, Léger J, Lamy C (2004) *J Appl Electrochem* 34:61
- Janssen M, Moolhuysen J (1976) *Electrochim Acta* 21:861
- Spinacé E, Neto A, Linardi M (2004) *J Power Sources* 129:121
- Crown A, Johnston C, Wieckowski A (2002) *Surf Sci* 506:L268
- Strbac S, Johnston C, Lu G, Crown A, Wieckowski A (2004) *Surf Sci* 573:80
- Colle V, Giz M, Tremiliosi Filho G (2003) *J Braz Chem Soc* 14:601
- Strbac S, Behm RJ, Crown A, Wieckowski A (2002) *Surf Sci* 517:2078
- Thiel PA, Madey TE (1987) *Surf Sci Rep* 7:211
- Marković NM, Ross PN Jr (2002) *Surf Sci Rep* 45:117
- Kolb DM, Przasnyski M, Gerisher H (1974) *J Electroanal Chem* 54:25
- Ndieyira JW, Ramadan AR, Rayment T (2001) *J Electroanal Chem* 503:28
- Oyamatsu D, Kanemoto H, Kuwabata S, Yoneyama H (2001) *J Electroanal Chem* 497:97
- Santos MC, Mascaro LH, Machado SAS (1998) *Electrochim Acta* 43:2263
- Mrozek P, Sung Y-E, Wieckowski A (1995) *Surf Sci* 335:44
- Seo M, Aomi M, Yoshida K (1994) *Electrochim Acta* 39:1039
- Kolb DM (2002) *Surf Sci* 500:722
- Kolb DM (1978) In: Gerisher H, Tobias CW (eds) *Advances in electrochemistry and electrochemical engineering*, vol. 11. Wiley–Interscience, New York
- Ogaki K, Itaya K (1995) *Electrochim Acta* 40:1249
- Sugita S, Abe T, Itaya K (1993) *J Phys Chem* 97:8780
- Esplandiú MJ, Schneeweiss MA, Kolb DM (1999) *Phys Chem Chem Phys* 1:4847
- Garcia S, Salinas D, Mayer C, Schmidt E, Staikov G, Lorenz WJ (1998) *Electrochim Acta* 43:3007
- van Hove MA, Koestner RJ, Stair PC, Biberian JP, Kesmodel LL, Bartos I, Somorjai GA (1981) *Surf Sci* 103:189
- Ndieyira JW, Ramadan AR, Rayment T (2001) *J Electroanal Chem* 503:28
- Parajón Costa B, Canullo J, Vásquez Moll D, Salvarezza RC, Giordano MC, Arvia AJ (1988) *J Electroanal Chem* 244:261
- Salvarezza RC, Vásquez Moll DV, Giordano MC, Arvia AJ (1986) *J Electroanal Chem* 213:301
- Martins ME, Salvarezza RC, Arvia A (1996) *J Electrochim Acta* 41:2441
- Vaskevich A, Rosenblum M, Gileadi E (1995) *J Electroanal Chem* 383:167
- Vaskevich A, Gileadi E (1998) *J Electroanal Chem* 442:147
- Martins ME, Salvarezza RC, Arvia A (1991) *J Electrochim Acta* 36:1617
- Palacio C, Ocón P, Herrasti P, Díaz D, Arranz A (2003) *J Electroanal Chem* 545:53
- El Omar F, Durand R, Faure R (1984) *J Electroanal Chem* 160:385
- Bittner AM (1997) *J Electroanal Chem* 431:51
- Herrero E, Buller LJ, Abruña HD (2001) *Chem Rev* 101:1897
- Salinas DR, Cobo EO, García SG, Bessone JB (1999) *J Electroanal Chem* 470:120
- Martins ME, Salvarezza RC, Arvia AJ (1998) *Electrochim Acta* 43:549
- Li J, Herrero E, Abruña HD (1998) *Colloids Surf A* 134:113
- Herrero E, Abruña HD (1998) *J Phys Chem B* 102:444
- Herrero E, Abruña HD (1997) *Langmuir* 13:4446
- Inukai J, Sugita S, Itaya K (1996) *J Electroanal Chem* 403:159
- Abaci S, Zhang L, Shannon C (2004) *J Electroanal Chem* 571:169
- Abruña HD, Feliú JM, Brock JD, Buller LJ, Herrero E, Li J, Gómez R, Finnefrock A (1998) *Electrochim Acta* 43:2899
- Kizhakevariam N, Stuve EM (1993) *Surf Sci* 286:246
- Villegas I, Weaver MJ (1995) *J Chem Phys* 103:2295
- Sexton BA, Rendulic KD, Hughes AE (1982) *Surf Sci* 121:181
- Wang J, Masel RI (1991) *Surf Sci* 235:199
- Bagotskii VS, Iofa ZA, Frumkin AN (1947) *Zh Fiz Khim* 21:241
- Attard GA, Chibane K, Ebert HD, Parsons R (1989) *Surf Sci* 224:311
- Bagotsky VS, Vassiliev YuB, Khazova OA (1977) *J Electroanal Chem* 81:229
- Franaszczuk K, Herrero E, Zelenay P, Wieckowski A, Wang J, Masel RI (1992) *J Phys Chem* 96:8509
- Hogarth M, Munk J, Shukla A, Hammnett A (1994) *J Appl Electrochem* 24:85
- Beden B, Hahn F, Lamy C, Leger JM, Tacconi N, Lezna R, Arvia AJ (1987) *J Electroanal Chem* 261:215
- Bockris JO'M, Wroblowa H (1964) *J Electroanal Chem* 7:428
- Watanabe M, Motoo S (1975) *J Electroanal Chem* 60:275
- Anderson AB, Grantscharova E, Seung S (1996) *J Electrochem Soc* 143:2075
- Gasteiger HA, Markovic NM, Ross PN, Cairns EJ (1994) *J Electrochem Soc* 141:1795
- Gasteiger HA, Markovic NM, Ross PN, Cairns EJ (1993) *J Phys Chem* 97:12020
- Haner A, Ross PN (1991) *J Phys Chem* 95:3740

72. Bittins-Cattaneo B, Iwasita T (1987) *J Electroanal Chem* 238:151
73. Shen PK, Tseung ACC (1994) *J Electrochem Soc* 141:3082
74. Brankovic SR, McBreen J, Adzic RR (2001) *J Electroanal Chem* 503:99
75. Hubbard AT (1988) *Chem Rev* 88:633
76. Spinacé EV, Neto AO, Linardi M (2004) *J Power Sources* 129:121
77. Batista EA, Malpass G, Motheo AJ, Iwasita T (2004) *J Electroanal Chem* 571:273
78. Juanto S, Beden B, Hahn F, Leger JM, Lamy C (1987) *J Electroanal Chem* 237:119