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Article

Amorphous Palladium-Silicon Alloys for the Oxidation of Formic Acid and Formaldehyde. A Voltammetric Investigation

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A oxidação eletrocatalítica de ácido fórmico e formaldeído foi estudada por voltametria cíclica sobre eletrodos de Pd e da liga amorfa de Pd(Si), com os resultados obtidos sendo comparados com aqueles similares disponíveis na literatura. A oxidação do HCOOH ocorre sobre Pd por meio de desidrogenação catalítica direta via $(:C(OH)_2)_{ads}$, enquanto que sobre Pd(Si) não existem evidências da formação deste intermediário. Este fenômeno é uma conseqüência da presença de sítios inertes de Si na superfície, que diminui a probabilidade da ocorrência de sítios ativos adjacentes disponíveis para esta adsorção. Em altas concentrações de HCOOH, este intermediário sofre desidratação sobre a superfície de Pd e um pico de oxidação associado ao CO_{ads} pode ser observado. Para o HCHO, o mecanismo de oxidação sobre os dois eletrodos é similar àqueles já discutidos na literatura para a Pt. Entretanto, os óxidos formados sobre a liga amorfa Pd(Si) são mais reativos que aqueles sobre Pd, afetando, assim, a cinética total do processo para ambas as moléculas orgânicas, o que é evidenciado pelo aumento nas correntes anódicas observado nos voltamogramas.

The electrocatalytic oxidation of formic acid and formaldehyde on Pd and on amorphous Pd(Si) was studied by cyclic voltammetry and the results compared with the literature for similar systems. The oxidation of HCOOH on Pd occurs through direct catalytic dehydrogenation via $(:C(OH)_2)_{ads}$ while on Pd(Si) this intermediate does not appear to be formed. This is a consequence of the presence of inert Si on the surface that diminishes the probability of adjacent free sites. At high HCOOH concentrations, that intermediate undergoes dehydration on the Pd surface and CO_{ads} oxidation peak is observed. For HCHO, the oxidation mechanism on both electrode materials appears similar to that previously proposed for Pt. However, the oxides formed on the amorphous Pd(Si) alloy are more reactive than those on Pd thus affecting the overall kinetics of the process for both organic molecules, a fact revealed by the increase in anodic currents observed in the voltammograms.

Keywords: *formic acid, formaldehyde, palladium, amorphous metallic alloys, electrocatalytic oxidation*

Introduction

The electrochemical oxidation of small organic molecules has been widely studied due to their potential utilization as fuels in energy conversion systems[1,2]. The reasons for that are related to their low toxicity, facility of storage and handling and mainly their high energy density. Moreover, due to their simple molecular structure they should undergo a more straightforward reaction mechanism than other possible organic fuels. On the other hand, they present some limitations that hinder their use and justify the large number of studies periodically published on the subject. Such limitations are: (a) the low exchange current density on several transition metals makes it necessary to use noble metals, *e.g.*, Pt, Pd or its alloys, as electrocatalysts[3] and (b) the oxidation pathways generate some intermediate species that strongly adsorb on the surface thus blocking the active sites and inhibiting the reaction.

Capon and Parsons[4] studied the oxidation of formic acid on Pt, Rh, Pd, Ir and Au. The specific catalytic efficiency of those surfaces was discussed. The authors showed[4] that on Pd the oxidation undergoes a special route because the total dehydrogenation of the molecule by the catalyst surface avoids the formation of strongly adsorbed CO. However, the authors identified a poisoning species that was proposed to be (**:**$C(OH)_2$) adsorbed onto two adjacent sites of the surface. Such reaction scheme was also used by Pavese *et al.*[5] in their study of the effect of Pd(II) ions on the oxidation of formic acid on Pd. On the other hand, the oxidation of formaldehyde proceeds by a route that includes the formation of adsorbed CO as the main reaction intermediate and shows the well-known voltammetric anodic peak in the cathodic sweep[6].

In order to minimize the poisoning effect of adsorbed intermediates, the oxidation of organic molecules has also been investigated on substrates modified by the presence of foreign metals ad-atoms such as Pb or Sn[7]. These modified surfaces were found to be very effective in inhibiting the strong adsorption of catalytic poisons as they almost eliminate the required multiple neighboring adsorption sites. However, such submonolayers of ad-atoms are frequently unstable and difficult to obtain. An alternative methodology is the use of amorphous metallic alloys. Metallic glasses are single phase alloys without long range order, although they present local order over small domains[1]. The modification of the surface by the inclusion of an inert component can often be comparable to that obtained by underpotentially deposited metal atoms. Moreover, amorphous metallic alloys usually provide stable and easy-to-handle surfaces.

Sun *et al.*[8] investigated the oxidation of formic acid and methanol on amorphous $Pt_{66}Sb_{34}$ electrodes. They found that the rates of oxidation of such molecules on that substrate were 5 to 20 times higher than on pure Pt electrodes. Machida *et al.*[9] studied the oxidation of formaldehyde on a series of amorphous Cu-Pd-Zr ternary alloys. The surfaces were previously etched with aqueous HF to promote the dissolution of Zr. An exchange current density as high as 1.2×10^{-4} A cm^{-2} (real area) at 0.30 V (RHE) was found for an electrode with a 1:3 ratio for Cu:Pd. Archer *et al.*[10] reported a surface-activated $PdNi_5P_{19}$ alloy that was found to be more active for methanol oxidation than platinized Pt.

The purpose of this work is to study the electrocatalytic oxidation of formic acid and formaldehyde on polycrystalline Pd and amorphous Pd(Si) alloy by steady-state cyclic voltammetry.

Experimental

The working electrodes used in this work were a Pd foil with an electroactive area of 6.9×10^{-3} cm^2 and a $Pd_{80}Si_{20}$ amorphous ribbon prepared by rolling quenching with an electroactive area of 3.2×10^{-3} cm^2. The method of calculation of electroactive areas and other experimental details are given elsewhere[11].

The electrolytes were prepared with H_2SO_4 (suprapur Merck, Darmstadt) and Milli-Q water (Millipore, USA) as 0.5 M solutions. To these blank solutions, formic acid (PA Merck, Darmstadt) or formaldehyde (PA Merck, Darmstadt) were added in proper amounts. The experiments were carried out using a Mod. 174A Polarographic Analyser EG&G PARC linked to a PC 386 microcomputer.

Results and Discussion

Formic acid oxidation

The stabilized voltammetric behavior (obtained after the 4th cycle) at 50 mV s^{-1} of a deaerated 0.5 M HCOOH + 0.5 M H_2SO_4 solution and for different anodic inversion potentials is presented in Fig. 1 for polycrystalline Pd and for amorphous Pd(Si).

The results for Pd (Fig. 1) are in close agreement with those reported before[4,5] and can be interpreted by the mechanism proposed by Capon and Parsons[4], *i.e.*,

$$Pd + HCOOH \longrightarrow Pd(COOH)_{ads} + H^+_{aq} + e^- \quad (1)$$

$$HCOOH + Pd(COOH)_{ads} \longrightarrow Pd(C(OH)_2)_{ads} + CO_2 + H^+_{aq} + e^- \quad (2)$$

$$Pd(C(OH)_2)_{ads} \longrightarrow Pd + CO_2 + 2H^+_{aq} + 2e^- \quad (3)$$

where neither $(CO)_{ads}$ nor $(CHO)_{ads}$ are included as intermediates. Therefore, the only adsorbable poison produced is (**:**$C(OH)_2)_{ads}$ and this is responsible for the slow inhibition detected in the anodic sweep. The anodic currents observed between 0.9 and 0.2 V in the cathodic sweep are also related to the oxidation processes (1-3). These processes are initially superimposed to the reduction of the PdO layer that is formed at potentials more anodic than 0.9 V where the initial oxidation of formic acid practically ceases. From these equations it can be observed that the final products are CO_2 and H^+.

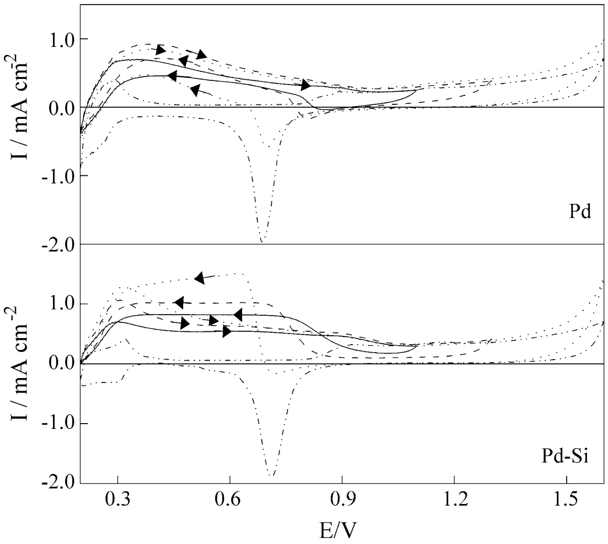

Figure 1. Cyclic voltammograms on Pd and Pd-Si alloy for the oxidation of formic acid from a 0.5 M HCOOH + 0.5 M H_2SO_4 solution at 50 mV s^{-1} for different inversion potentials. Dash-dot-dot line corresponds to the blank solution.

On the other hand, the results for amorphous Pd(Si) (Fig. 1), although similar to those for Pd, reveal that under these experimental conditions the reduction of the oxide layer is not detected. Therefore, the limiting anodic currents observed from 0.9 to 0.2 V are much better defined and appear earlier in the voltammogram. This indicates that either the poisoning species ($\mathbf{:}C(OH)_2)_{ads}$ is interacting very weakly with the surface or it is not formed at all since it requires two adjacent sites. In the later case, the oxidation of HCOOH should be completed by a process such as,

$$Pd(Si)(COOH)_{ads} \longrightarrow Pd(Si) + CO_2 + H^+_{aq} + e^- \quad (4)$$

The absence of an oxide layer of the type Pd(Si)O revealed by these results needs to be further investigated but some previous evidence is already available. In fact, studies on the oxide formation on amorphous Pd(Si) alloys[11] showed that the first (hydroxide) layer is not well defined on these surfaces while the second (oxide) layer is more easily reduced than on pure polycrystalline Pd. Therefore, this Pd(Si)O could be sufficiently reactive to undergo a chemical reaction with formic acid present in solution, *i.e.*,

$$Pd(Si)O + HCOOH \longrightarrow Pd(Si) + CO_2 + H_2O \quad (5)$$

thus releasing a clean surface at much less cathodic potentials.

In order to increment the participation of adsorbed intermediates on the reaction pathway, voltammetric experiments at 50 mV s^{-1} were carried out on Pd and Pd(Si) in 0.5 M H_2SO_4 solutions containing 5 M HCOOH. Fig. 2 shows the results obtained when the 4th cycle was recorded for three different inversion potentials, *i.e.*, 1.1, 1.3 and 1.5 V. After the initial coincidence of the currents associated to the hydrogen oxidation on a surface free from adsorbed intermediates, the oxidation of HCOOH yields much larger currents on Pd than on Pd(Si). This fact could be explained in terms of a change in the nature of adsorbed intermediate, from that represented by $Pd(C(OH)_2)_{ads}$ in (3) to $Pd(Si)(COOH)_{ads}$ as in reaction (4). As the first intermediate requires two adjacent surface sites to adsorb while only one site is necessary for the second one, the overall result is an increase of approximately two times in the current values, as observed in Fig. 2.

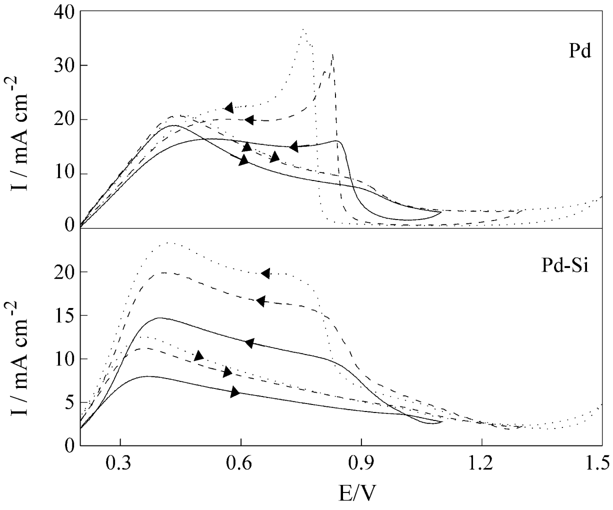

Figure 2. Cyclic voltammograms on Pd and Pd-Si alloy for the oxidation of formic acid from 5 M HCOOH + 0.5 M H_2SO_4 at 50 mV s^{-1} with three different inversion potentials: 1.1 (full line), 1.3 (dashed line) and 1.5 V (dotted line).

On the other hand, on Pd the presence of a large anodic peak is observed at the onset of the oxide layer reduction in the cathodic sweep, a behavior similar to that observed for formaldehyde solutions (see later). Such an anodic peak has been associated to the oxidation of CO adsorbed on a freshly reduced electrode surface. Therefore, the mechanism for formic acid oxidation must include a step where this intermediate is formed. As the electrode surface must be fully covered by a hydroxide layer, the onset of the reduction process should produce a small number of free sites where the species ($\mathbf{:}C(OH)_2$) could be accommodated. Meanwhile, it is difficult to imagine that a single site could stabilize this gem-diol intermediate and dehydration must occur, quickly followed by oxidation to CO_2, *i.e.*,

$$Pd(C(OH)_2)_{ads} \longrightarrow Pd(CO)_{ads} + H_2O \quad (6)$$

$$Pd(CO)_{ads} + Pd(OH)_{ads} \longrightarrow 2Pd + CO_2 + H^+_{aq} + e^- \quad (7)$$

A different situation is observed on the Pd(Si) response at high HCOOH concentration (Fig. 2). In this case, the cathodic sweep does not show an anodic peak but a plateau. This is probably related to the nature of the intermediates formed during the anodic sweep. As the Pd(Si) surface possesses less active neighboring sites than the Pd surface, the CO_{ads} blocking layer observed on Pd - requiring two or three active sites for each CO molecule stabilized on the surface - is unlikely to occur.

Formaldehyde oxidation

Figure 3 shows the 4th cycle of the voltammetric response at 50 mV s^{-1} of a deaerated 0.5 M HCHO + 0.5 M H_2SO_4 solution for different inversion potentials on polycrystalline Pd and on amorphous Pd(Si) alloy. These results are very similar to those previously reported for polycrystalline Pd[12] and reveal the presence of strongly adsorbed catalytic poisons. These species are responsible for the surface blockage that inhibits the oxidation of formaldehyde at potentials less anodic than 0.9 V in the direct sweep.

Although formaldehyde presents a somewhat simpler structure than formic acid, the number of publications reporting studies of its electro-oxidation is considerable smaller than those of formic acid. Even the mechanism of such a reaction on Pd surfaces in acid medium is not

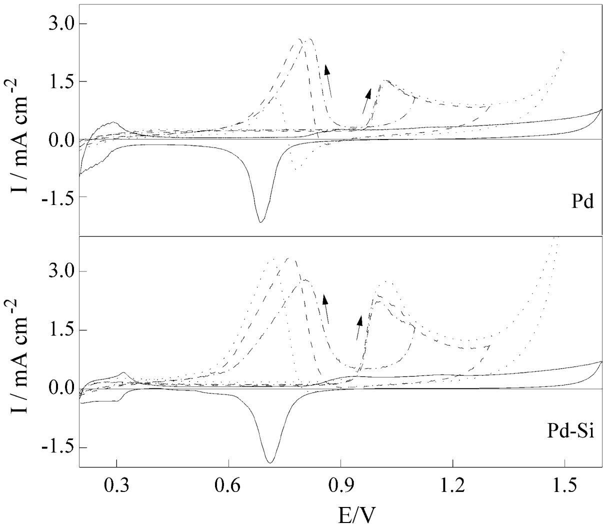

Figure 3. Cyclic voltammograms on Pd and Pd-Si alloy for the oxidation of formaldehyde from 0.5 M HCHO + 0.5 M H_2SO_4 at 50 mV s^{-1} for different inversion potentials. Full line corresponds to the blank solution.

promptly available. Meanwhile, the close similarity between the voltammetric responses on Pd and on Pt[2] suggests the possibility of using an analogous mechanism for both metals.

Therefore, the reaction on Pd should proceed following the steps:

$$Pd + (HCHO)_{sol} \longrightarrow Pd(HCHO)_{ads} \quad (8)$$

$$Pd(HCHO)_{ads} \longrightarrow Pd(CHO)_{ads} + H^+_{aq} + e^- \quad (9)$$

$$Pd(CHO)_{ads} \longrightarrow Pd(CO)_{ads} + H^+_{aq} + e^- \quad (10)$$

$$Pd + H_2O \longrightarrow Pd(OH)_{ads} + H^+_{aq} + e^- \quad (11)$$

$$Pd(CHO)_{ads} + Pd(OH)_{ads} \longrightarrow 2Pd + CO_2 + 2H^+_{aq} + 2e^- \quad (12a)$$

$$Pd(CHO)_{ads} + Pd(OH)_{ads} \longrightarrow Pd + Pd(COOH)_{ads} + H^+_{aq} + e^- \quad (12b)$$

$$Pd(CO)_{ads} + Pd(OH)_{ads} \longrightarrow 2Pd + CO_2 + H^+_{aq} + e^- \quad (12c)$$

$$Pd(CO)_{ads} + Pd(OH)_{ads} \longrightarrow Pd + Pd(COOH)_{ads} \quad (12d)$$

$$Pd(COOH)_{ads} \longrightarrow Pd + CO_2 + H^+_{aq} + e^- \quad (13)$$

It can be observed that, differently from the mechanism previously described for formic acid, several adsorbed intermediates are postulated. The presence of these species on Pd has been detected by electrochemically modulated infrared spectroscopy[13], a fact that supports the assumption made for the use of the above mechanism. Such species constitute catalytic poisons, which are responsible for surface blockage and consequent inhibition of reaction rates. This explains the fact that the anodic currents are very small in the initial part of the voltammogram since only reactions (8-10) are slowly occurring and blocking the surface. When the potential reaches *ca.* 1.0 V, the oxidation of the Pd surface starts (11) and, consequently, the following reactions in the mechanism that are responsible for the peak at this potential. Provided the inversion potential is not sufficiently positive, the surface remains free from poisons and/or $(OH)_{ads}$ and reactions (11-13) slow down. On such a free surface, reactions (8-10) occur at a high rate but, as the surface becomes again covered by intermediates, the peak at *ca.* 0.8 V develops.

For the amorphous Pd(Si) electrode (Fig. 3) the voltammetric response is very similar to that of polycrystalline Pd. The only difference is that the lower reactivity of the Pd(Si) oxide layer, due to the existence in the vicinity, of a small number of active sites than on the Pd surfaces, diminishes the contribution of Eqs. (11) – (12c) thus stabilizing the adsorbed intermediates. As a consequence, the peak height in the reverse sweep is almost independent of the inversion potential and the rate of CO_2 generation is enhanced on the amorphous surface. A set of reactions that can describe those oxidation processes is:

$$Pd(Si) + (HCHO)_{sol} \longrightarrow Pd(Si)(HCHO)_{ads} \quad (14)$$

$$Pd(Si)(HCHO)_{ads} \longrightarrow Pd(Si)(CHO)_{ads} + H^+_{aq} + e^- \quad (15)$$

$$Pd(Si)(CHO)_{ads} \longrightarrow Pd(Si)(CO)_{ads} + H^+_{aq} + e^- \quad (16)$$

$$Pd(Si)(CO)_{ads} + H_2O \longrightarrow Pd(Si) + CO_2 + 2H^+ + 2e^- \quad (17)$$

The oxidation of formaldehyde was also carried out on Pd and Pd(Si) electrodes in 0.5 M H_2SO_4 solutions contain-

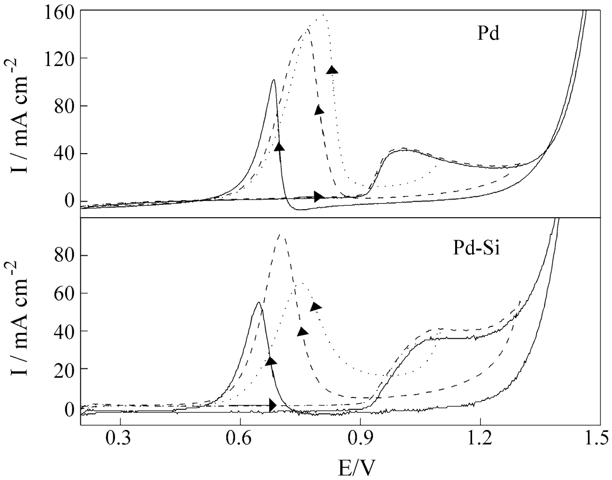

Figure 4. Cyclic voltammograms on Pd and Pd-Si alloy for the oxidation of formaldehyde from 5 M HCHO + 0.5 M H_2SO_4 at 50 mV s^{-1} with three different inversion potentials: 1.1 (full line), 1.3 (dashed line) and 1.5 V (dotted line).

ing 5 M HCHO. The resulting voltammograms (4th cycle) are shown in Fig. 4 for different inversion potentials. The enhanced electrocatalytic activity of the Pd(Si) surface towards the direct oxidation of HCHO to CO_2 becomes more evident at high concentration of the reagent. As can be seen in Fig. 4, the anodic sweep presents one peak at approximately 1.0 V, similar on both electrodes, which corresponds to the oxidation of HCHO to CO_{ads} or CHO_{ads} in accordance with reactions (11-13). After this peak, the next electrochemical process of interest is the generation of CO_2, indicated by the sharp increase in anodic currents. This reaction on Pd is observed only at potentials more positive than 1.2 V while on Pd(Si) it begins at approximately 1.0 V overlapping the CO_{ads} oxidation peak. Such an enhanced activity is probably related to the higher reactivity of the surface oxides formed on this amorphous structure.

Conclusions

The oxidation of formic acid on polycrystalline Pd proceeds in a way that involves the formation of $(\mathbf{:}C(OH)_2)_{ads}$ on the surface while on the amorphous Pd(Si) alloy the presence of this poisoning intermediate is not evident. At high concentrations of the organic substrate, the initial oxidation steps are much faster on Pd since this material shows a higher H-absorption than Pd(Si). In addition, a large peak is observed on Pd due to the oxidation of CO that must result from dehydration of the $(\mathbf{:}C(OH)_2)_{ads}$ intermediate. The oxides formed on amorphous Pd(Si) are very reactive and their reduction peak does not appear in the cathodic branch of the voltammograms.

For formaldehyde oxidation, the results of this work indicate that the prevailing mechanism on Pd and Pd(Si) is very similar to that reported for Pt surfaces. The main difference noticed here is the higher reactivity of the surface oxides in the case of the amorphous alloy. This effect is clearly shown at high concentrations of formaldehyde by the increased catalytic activity towards CO_2 formation at high positive potentials.

The enhanced catalytic activity detected in this work for the oxidation of small organic molecules on amorphous surfaces should be further explored. This might help in the investigations aiming to use such compounds as fuels in energy systems.

Acknowledgments

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