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The influence of electrode structure on the adsorption and electro-oxidation of ethylene on platinum

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The adsorption and electro-oxidation of ethylene in acid electrolyte were studied on differently prepared platinum electrodes. A clear dependence of the apparent specific catalytic activity for ethylene electro-oxidation on platinum electrode structure was observed. Platinized platinum electrodes exhibit a low apparent specific catalytic activity which decreases on increasing the roughness factor due to additional overpotential contributions within the pores. The specific adsorptive characteristics and catalytic activity of non-porous platinum electrodes prepared by electroreduction of thick platinum oxide layers are independent of roughness factor and similar to those of smooth platinum electrodes.

1. Introduction

The adsorption and electro-oxidation of low molecular weight hydrocarbons and related organic compounds have been extensively studied on differently prepared platinum electrodes [1–14]. It appears that the specific catalytic activity of platinized platinum electrodes decreases as the roughness factor of the electrode increases [1–4, 7, 8]. The effect was attributed to surface structural factors [4, 7, 10, 11] and also to concentration and ohmic overpotentials arising within the pores and cracks existing in the platinum electrodeposit [2, 3, 8].

Thus, it is commonly accepted that the loss of efficiency of the electro-oxidation process on increasing the roughness factor is an unavoidable consequence of using highly porous electrodes which provide a high real to geometric area ratio. However, the recent development of a new platinizing technique offers the possibility of obtaining platinum electrocatalysts with a large and controlled surface roughness free of pores [15]. The electrochemical response of the resulting surface is very reproducible and corresponds to that of a uniformly polarized electrode surface. Hence, different electrocatalytic reactions can be studied disregarding undesirable overpotential contributions originated within the porous electrode structure.

The present work refers to the adsorption and electro-oxidation of ethylene in acid electrolyte on differently prepared platinum electrodes. In this case, kinetic data allow a critical comparison of the specific catalytic activity exhibited by different platinum electrocatalysts. The influence of the electrode structure on the ethylene adsorption and electro-oxidation characteristics is considered.

2. Experimental details

Runs were carried out in a conventional three-electrode compartment, Pyrex glass cell. Two types of platinum working electrode were used: platinum electrodes obtained by electroreduction of thick platinum oxide layers [15] and platinized platinum electrodes. In both cases, electropolished platinum wire electrodes (0.5 mm in diameter) of geometric area between 0.08 and 0.30 cm^2 were employed as starting material. The counterelectrode was a large-

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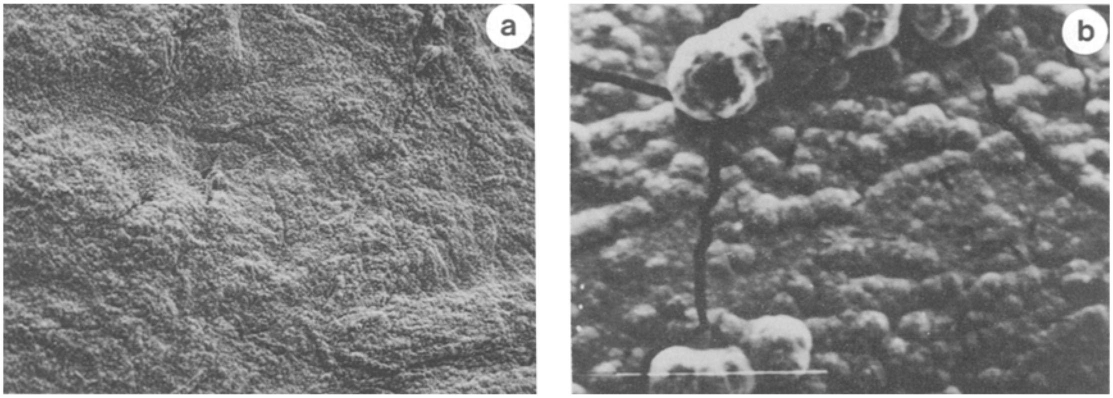

Fig. 1. SEM patterns of the surfaces of stabilized platinum electrodes.(a) Platinum electrode (procedure I); f = 460. (b) Platinum electrode (procedure II); f = 420. × 750.

area platinum sheet. The potential of the working electrode was measured against a RHE immersed in the ethylene-free electrolyte (1 M H_2SO_4), prepared from Analar H_2SO_4 (Merck) and triply distilled water. CP-grade ethylene (Matheson) was employed. Experiments were run either in the absence of ethylene (blanks) or under ethylene saturation at 1 atm, at 40, 60 and 80° C.

The first type of platinum electrode was made by applying a repetitive square wave potential signal to electropolished platinum in 1 M H_2SO_4 at 30° C, followed by a slow electroreduction scan [15] (procedure I). The repetitive square wave potential signal characteristics were $E_l = 0$ V, $E_u = 2.4$ V, $f = 2.5$ kHz and $t = 3$–10 min.

The second type of platinum electrode was prepared by platinum plating on electropolished platinum from a 2% H_2PtCl_6 solution in 1 M HCl at room temperature, either galvanostatically (1–2 mA cm^{-2}) or potentiostatically (0.12 V vs SHE) (procedure II). The degree of platinization, w, was between 7.5 and 67.0 mg of electrodeposited platinum per cm^2 of initial real electrode area [16].

Freshly prepared platinum electrodes of both types were stabilized by means of a triangular potential cycling at a potential sweep rate, v, of 0.3 V s^{-1} between 0.05 and 1.40 V in 1 M H_2SO_4 at 30° C. The time required to attain a stable voltammogram with electrodes prepared by procedure I became less than 1 h, whereas those made through procedure II required ~10 h. The real surface area was voltammetrically determined through the H-adatom monolayer charge [17, 18]. Thus, the roughness factor, f, corresponds to the ratio between the real and geometric electrode area.The stabilized platinum electrode surfaces were examined by scanning electron microscopy (SEM).

Prior to both ethylene adsorption and steady-state electro-oxidation measurements, the working platinum electrode was subjected to the potential step pretreatment already described in previous publications [19, 20]. After the electrode pretreatment the potential was held at a preset value, E_{ad}, to adsorb ethylene during a certain time, t_{ad}. Likewise, for the steady-state ethylene electro-oxidation, the stationary current was read after 1 h holding at each preset potential.

3. Results

3.1. *SEM patterns of differently prepared platinum electrodes*

The SEM pattern of the surface of a stabilized platinum electrode with a large roughness factor obtained by electroreduction of a thick oxide platinum layer shows a uniform, fine-grained, rough structure practically free of large pores, with only small cracks (Fig. 1a). On the other hand, the SEM pattern of the surface of a stabilized, highly platinized platinum electrode with a roughness factor comparable to that of Fig. 1a, presents globular deposits with cracks

Fig. 2. SEM pattern of the cross-section of a stabilized platinum electrode (procedure II); $f = 420$. × 7000.

and fissures produced by internal stresses (Fig. 1b). The SEM pattern of a cross-section of the highly platinized platinum electrode reveals clearly the porous structure of the electrode (Fig. 2).

3.2. *Voltammograms run in the 0.05–1.40 V range in ethylene-free 1 M H_2SO_4*

The stabilized voltammograms run in the 0.05–1.40 V range depend strongly on the type of platinum electrode used. Thus, electrodes of large roughness factor obtained by electroreduction of the thick platinum oxide layer exhibit a voltammetric behaviour, at any value of v, similar to that of both smooth and low platinized platinum electrodes, that is, clearly defined current peaks related to the H- and O-electroadsorption–electrodesorption are observed [16] (Fig. 3). On the other hand, the voltamograms run at 0.03 V s^{-1} with highly platinized platinum electrodes of relatively large roughness factor show remarkable differences as compared to conventional voltammograms for low platinized platinum electrodes, particularly an anomalous large voltammetric charge in the H-adatom potential range (Fig. 4a). This behaviour, as explained in a previous work [16], is due to the absorption of hydrogen into the porous electrode structure. In this case, the absorption of hydrogen influences the different steps involved in the hydrogen electrode reaction. As was previously found [16] the anomalous effect decreases as v increases (Fig. 4b). However, for highly platinized platinum electrodes with roughness factors comparable to that of Fig. 3, the voltammetric response, even at 0.3 V s^{-1}, is appreciably distorted with respect to the conventional voltammogram for smooth platinum, probably due to ohmic overpotential contributions arising from the porous structure.

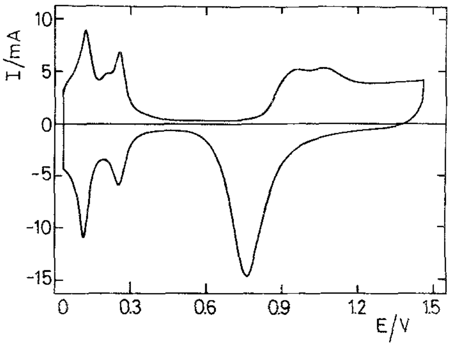

Fig. 3. Voltammogram run at 0.1 V s^{-1} in 1 M H_2SO_4, 30° C, for a stabilized platinum electrode (procedure I). Real electrode area = 55 cm^2; $f = 460$.

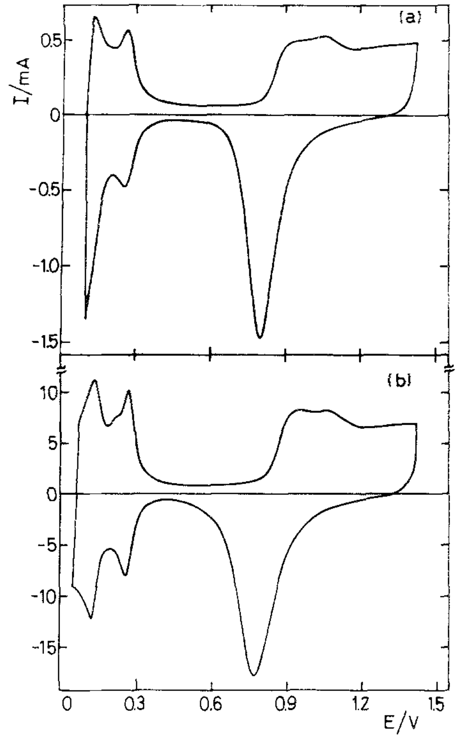

Fig. 4. Voltammograms run at different v in 1 M H_2SO_4, 30° C, for stabilized platinum electrodes (procedure II). (a) v = 0.03 V s^{-1}; real electrode area = 18 cm^2; $f = 120$. (b) v = 0.3 V s^{-1}; real electrode area = 27 cm^2; $f = 250$.

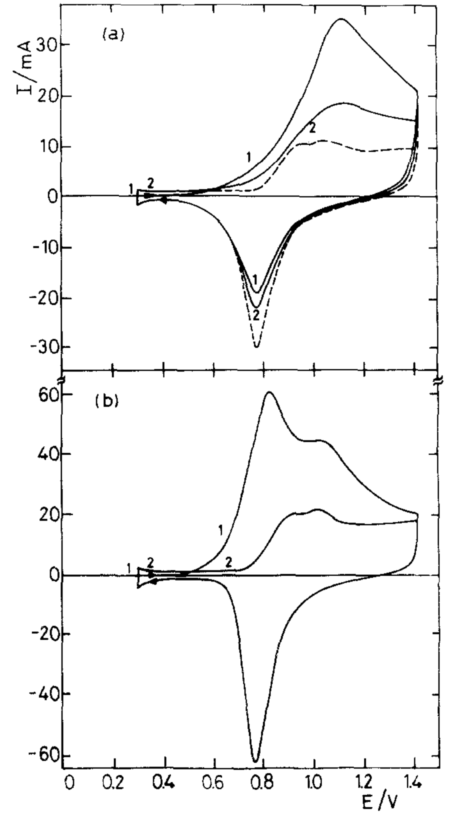

Fig. 5. Voltammograms runs at $0.4\,V\,s^{-1}$ in 1 M H_2SO_4 for stabilized platinum electrodes (procedure I). $E_{ad} = 0.30$ V; $t_{ad} = 5$ min. (a) $T = 40°C$; real electrode area = $30\,cm^2$; $f = 260$. (b) $T = 80°C$; real electrode area = $46\,cm^2$; $f = 380$. The blank corresponds to the dashed line. Full lines correspond to the 1st and 2nd potential scans in the ethylene-saturated electrolyte.

3.3. *Voltammograms run in ethylene-saturated 1 M H_2SO_4 without hydrocarbon readsorption*

These runs were carried out at $0.4\,V\,s^{-1}$ between 0.30 and 1.40 V, immediately after holding the potential at $E_{ad} = 0.30$ V for $t_{ad} = 5$ min, with differently prepared platinum electrodes in 1 M H_2SO_4 under ethylene saturation. At 80° C the first potential scan run with platinum electrodes of large roughness factor (obtained by electroreducing the thick platinum oxide layer) exhibits, as for low platinized platinum [19], the initiation of the adsorbed hydrocarbon electro-oxidation at ~0.40 V and the corresponding anodic current peak at ~0.80 V (Fig. 5b). The second potential scan approaches that of the blank (free-ethylene electrolyte). This indicates that practically no hydrocarbon readsorption takes place during the potential scan and also that the electro-oxidation of adsorbed ethylene has been already completed. Furthermore, the voltammetric charges related to the electroreduction of the O-containing layer, both in the presence and in the absence of ethylene, are practically equal. The charge related to the adsorbed ethylene electro-oxidation, Q_E, can be calculated by subtracting from the total anodic charge (previously corrected for the double layer effect) the charge corresponding to the electroreduction of the O-containing layer formed during the anodic potential scan [19].

On decreasing the temperature to 40° C the anodic current peak (corresponding to the hydrocarbon electro-oxidation) and that of the O-containing layer overlap, yielding a broad anodic current peak at ~1.10 V (Fig. 5a). Furthermore, as a result of the anodic switching potential required at 40° C to minimize any OER contribution, a small fraction of adsorbed ethylene still remains on the surface without oxidizing after the first electro-oxidation cycle. In this case, considering that the difference between the amount of O-containing layer formed in the absence and in the presence of ethylene is equal to the amount of adsorbed ethylene remaining without oxidizing, the true charge related to the adsorbed ethylene electro-oxidation, Q_E, can be obtained by the method described elsewhere [19].

The voltammograms, run at $0.4\,V\,s^{-1}$ under the same conditions as above with porous, highly platinized platinum electrodes of relatively large roughness factor, show a considerable contribution of hydrocarbon readsorption. To avoid this interference, larger potential sweep rates should be used (Fig. 6).

3.4. *Dependence of Q_E on the potential sweep rate*

For preset values of E_{ad} and t_{ad}, the charge related to ethylene electro-oxidation on differently prepared platinum electrodes depends on v (Fig. 7). At any temperature the Q_E versus v plot exhibits a region where Q_E remains practically constant and another region where Q_E increases as v decreases. This effect is caused by

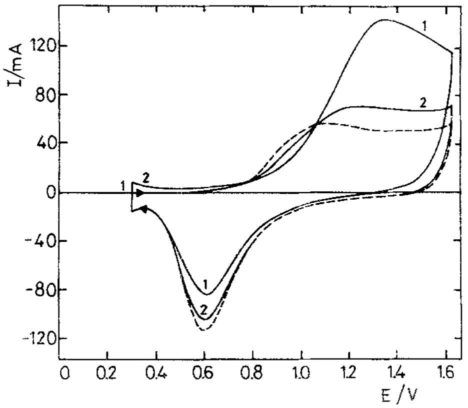

Fig. 6. Voltammograms run at 10 V s^{-1} in 1 M H_2SO_4, 40° C, for a stabilized platinum electrode (procedure II); real electrode area = 7 cm^2; $f = 90$; $E_{ad} = 0.30$ V; $t_{ad} = 5$ min. The blank corresponds to the dashed line. Full lines correspond to the 1st and 2nd potential scans in the ethylene-saturated electrolyte.

the difference in the rates of the simultaneous ethylene readsorption and adsorbed ethylene electro-oxidation [19]. The hydrocarbon readsorption during the potentiodynamic scan is negligible in the v range where Q_E remains constant. The suitable range of v for the electro-oxidation of adsorbed ethylene under hydrocarbon readsorption free conditions is markedly dependent on the preparation procedure of the platinum electrode, Thus, for electrodes of large roughness factor prepared by electroreduction of the thick platinum oxide layer there is practically no interference of ethylene readsorption at $v \geqslant 0.4$ V s^{-1} (Fig. 7), as was previously observed for low platinized platinum [19]. On the other hand, for porous, highly platinized platinum electrodes of relatively large roughness factor, v should be either equal or larger than 10 V s^{-1} to attain the hydrocarbon readsorption free condition (Fig. 7).

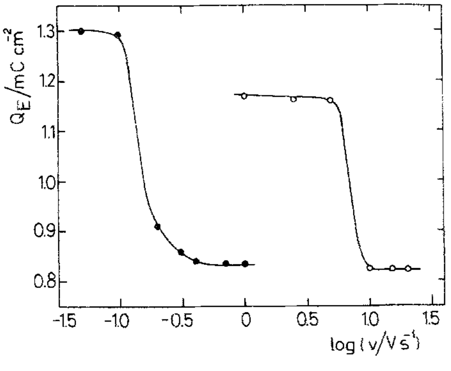

Fig. 7. Dependence of Q_E on v at $E_{ad} = 0.30$ V, $t_{ad} = 5$ min and $T = 40$° C. (●) Platinum electrode (procedure I); $f = 260$. (○) Platinum electrode (procedure II); $f = 170$.

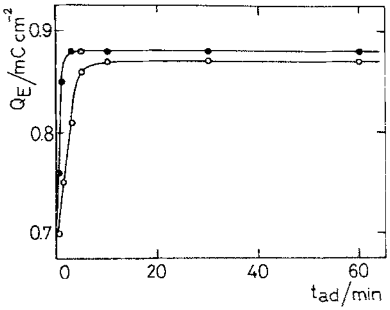

Fig. 8. Dependence of Q_E on t_{ad} at $E_{ad} = 0.25$ V and $T = 40$° C. (●) Platinum electrode (procedure I); $f = 320$. (○) Platinum electrode (procedure II); $f = 170$.

3.5. *Dependence of Q_E on the adsorption time*

The time required to reach the stationary ethylene surface coverage at the potential of maximum ethylene adsorption is also dependent on the preparation procedure of the platinum electrode (Fig. 8). Thus, with electrodes of large roughness factor prepared by electroreduction of thick platinum oxide layers, Q_E attains a limiting value after 2–5 min, in agreement with the data for low platinized platinum [19]. Under the same conditions, with porous, highly platinized platinum electrodes of relatively large roughness factor, the minimum time required to reach the stationary surface coverage by the adsorbed ethylene is ~10 min.

3.6. *Dependence of Q_E on the adsorption potential*

The influence of E_{ad} on Q_E was determined in the ethylene-saturated solution after attaining the stationary coverage for differently prepared platinum electrodes. The maximum charge ($Q_{E,M} = 0.88$ mC cm^{-2} real electrode area, $E_{ad} = 0.25$ V) related to the electro-oxidation of adsorbed ethylene, becomes practically independent of both the temperature (40–80° C range) and the preparation procedure of the platinum

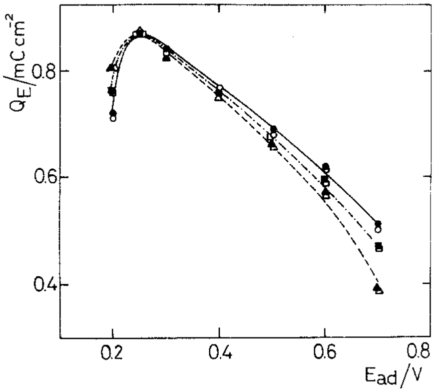

Fig. 9. Dependence of Q_E on E_{ad} at different temperatures. (a) Platinum electrode (procedure I); $f = 320$. (●) $T = 40°$ C; (■) $T = 60°$ C; (▲) $T = 80°$ C. (b) Platinum electrode (procedure II); $f = 170$. (○) $T = 40°$ C; (□) $T = 60°$ C; (△) $T = 80°$ C.

electrode (Fig. 9). The value of $Q_{E,M}$ is in a good agreement with that already reported for ethylene adsorption on both smooth [21] and low platinized platinum [19]. For E_{ad} lower than 0.20 V electrochemical hydrogenation of ethylene takes place, whereas for E_{ad} greater than 0.30 V the decrease of Q_E with E_{ad} is due to the proper hydrocarbon electro-oxidation. The contribution of the latter process becomes more remarkable as the temperature is raised.

3.7. *Stationary current–potential curves for ethylene electro-oxidation*

The conventional stationary current–potential curves for the electro-oxidation of ethylene on differently prepared platinum electrodes in 1 M H_2SO_4 at 80° C were determined under potentiostatic conditions in the 0.40–0.70 V range. The stationary current was read after 1 h holding at each preset potential. As the stationary ethylene surface coverage changes with the applied potential, the stationary current has been corrected for the ethylene degree of surface coverage at the preset potential to obtain the proper E/log i relationship [19]. For electrodes prepared by electroreduction of thick platinum oxide layers, Tafel lines with slope equal to the 2.303 $(2RT/F)$ ratio are obtained independently of the roughness factor value (Fig. 10). On the other hand, for porous highly platinized platinum electrodes, Tafel lines with slopes larger than the 2.303 $(2RT/F)$ ratio are obtained (Fig. 10). In this case, the deviation from the 2.303 $(2RT/F)$ ratio is larger as the roughness factor increases.

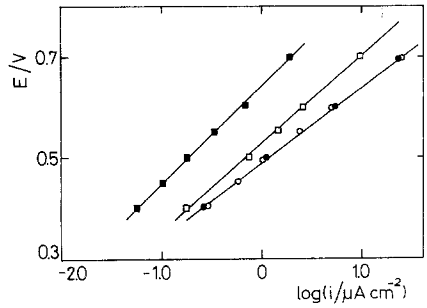

Fig. 10. Stationary E/log i plots for ethylene electro-oxidation in 1 M H_2SO_4; 80° C. (a) Platinum electrodes (procedure I): (○) $f = 280$; (●) $f = 440$. (b) Platinum electrodes (procedure II): (□) $f = 250$; (■) $f = 420$. Current densities corrected by the ethylene surface coverage.

3.8. *Electrode structure and specific catalytic activity for ethylene electro-oxidation*

The specific catalytic activity of differently prepared platinum electrodes for ethylene electro-oxidation in 1 M H_2SO_4 at 80° C can be evaluated through the stationary current density read after 1 h at 0.5 V. This current density value is denoted as the apparent specific catalytic activity and it is expressed in μA cm^{-2} real electrode area. Otherwise, the true specific catalytic activity should correspond to that of the uniformly polarized electrode.

The dependence of the apparent specific catalytic activity on the roughness factor for smooth platinum, platinum obtained by electroreducing a thick platinum oxide layer and platinized platinum is shown in Fig. 11. For those electrodes obtained through electroreduction of thick platinum oxide layers the apparent specific catalytic activity is practically independent of the roughness factor, and the average value of the apparent specific catalytic activity is equal to that resulting for smooth platinum. For the sake of comparison,the stationary ethylene electro-oxidation current per unit of real electrode area for smooth platinum is taken as a measure of the true specific catalytic activity. Conversely, platinized platinum electrodes exhibit a marked

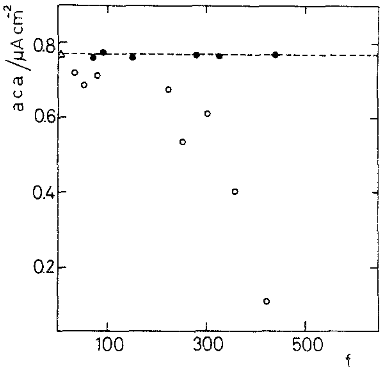

Fig. 11. Dependence of the apparent specific catalytic activity (aca) on the roughness factor for differently prepared platinum electrodes, 1 M H_2SO_4; 80° C. (△) Smooth platinum; (●) platinum electrodes (procedure I); (○) platinum electrodes (procedure II).

decrease in the apparent specific catalytic activity on increasing the roughness factor, i.e. as the electrode structure is made increasingly porous. Porous electrodes involve non-uniformly polarized surfaces. Consequently, a loss efficiency for ethylene electro-oxidation on these electrodes is observed.

4. Discussion

4.1. *General considerations*

The present results show that both the specific adsorptive characteristics and the specific catalytic activity of platinum electrodes prepared by electroreduction of thick platinum oxide layers are independent of the roughness factor and similar to those of smooth platinum electrodes. These electrodes exhibit a normal voltammetric behaviour at any value of v in the H- and O-electroadsorption–electrodesorption potential range. Furthermore, their apparent specific catalytic activity for the steady-state ethylene electro-oxidation corresponds to the true specific catalytic activity of platinum, namely that of a uniformly polarized electrode. In this respect, SEM patterns of electroreduced platinum electrodes show highly rough surfaces which are uniformly accessible due to the almost complete absence of pores.

On the other hand, the non-stationary and steady-state electrochemical behaviour of platinized platinum electrodes basically depends on the degree of porosity and pore size distribution. Thus, porous platinized platinum electrodes usually operate under diffusive and ohmic limitations and, consequently, the electrode surface works non-uniformly. In addition, changes in the properties of the solution in the small pores during the occurrence of electrochemical processes may also significantly affect the electrochemical response of platinized platinum electrodes [16, 22].

On the basis of the preceding discussion, the influence of the structure of differently prepared platinum electrodes on both the voltammetric response in the H- and O-electroadsorption–electrodesorption potential range and in ethylene-saturated solutions and on the specific catalytic activity for the steady-state electro-oxidation of ethylene will be considered.

4.2. *Influence of the platinum electrode structure on the voltammetric response in the ethylene-free electrolyte*

As has been pointed out previously [22], platinized platinum electrodes usually contain a large fraction of micropores, depending on the preparation procedure. Furthermore, the absorption of hydrogen occurs either during the platinizing and/or during the potentiodynamic stabilization at low values of v for freshly porous platinized electrodes. Thus, when a stabilized porous platinized platinum electrode is subjected to a slow anodic potential scan from 0.40 to 1.40 V, as occluded hydrogen is oxidized,the local concentration of hydrogen ions within the small pores is increased and the reversible hydrogen electrode potential shifts towards potential values more positive than that of the SHE. Therefore, during the cathodic potential scan, hydrogen ion discharge occurs earlier. In this case a fraction of discharged hydrogen penetrates into the pores restoring in part the amount of occluded hydrogen [16]. Hence, under potentiodynamic cycling the total current drained through porous platinized platinum electrodes depends on the local polarization distribution and, therefore, the corresponding voltammograms will be appreciably distorted. On the other hand, as the platinum electrodes prepared by electroreduction of thick platinum oxide layers are practically free of pores and/or large cracks, they show a normal electrochemical behaviour on potentiodynamic cycling.

4.3. *Influence of the platinum electrode structure on the ethylene electroadsorption characteristics*

In an earlier paper it was reported that the amount of chemisorbed ethylene per unit of real electrode area in 1 M H_2SO_4 at 90° C decreased on increasing the roughness factor of platinized platinum electrodes [3]. The phenomenon was attributed to micropores and cracks at the platinum surface which become inaccessible to ethylene molecules. Conversely, present results show that the maximum ethylene surface coverage is practically independent of both roughness factor and electrode structure. However, to attain the stationary ethylene surface coverage, the adsorption times for porous highly platinized platinum electrodes are significantly larger than those for electroreduced platinum electrodes of similar or larger roughness factor. This difference in the adsorption time arises from the kinetic hindrances caused by the porous electrode structure. In this respect, the disagreement between data reported earlier and the present results can be attributed either to the fact that the adsorption times reported in [3] were not sufficiently large to attain the ethylene stationary coverage or to anomalous hydrogen adsorption which was not taken into account in the determination of the real surface area from galvanostatic charging curves. The latter would lead to exceedingly large values for the real surface area.

Steric factors related to the different accessibility of adsorption sites for ethylene molecules or hydrogen atoms have, in principle, a minor effect, as ethylene surface coverage involves the blocking of about 90% of the sites available to hydrogen [23].

4.4. *Influence of the platinum electrode structure on the ethylene steady-state electro-oxidation*

For flooded porous electrodes operating under conditions controlled by ohmic–activation or activation–concentration overpotential, the theoretical analysis according to various models [24–26] predicts a non-uniform current density distribution, and values of Tafel slope which are twice the values observed for planar electrodes.

The experimental E/log i relationships corresponding to the steady-state electro-oxidation of ethylene on porous, highly platinized platinum electrodes show, in fact, Tafel lines with slopes significantly larger than the 2.303 $(2RT/F)$ ratio corresponding to low platinized platinum electrodes [19]. The deviation from the 2.303 $(2RT/F)$ ratio increases according to the roughness factor (Fig. 10). This fact evidences undesirable overpotential contributions that originate within the porous structure. On the other hand, the steady-state electro-oxidation of ethylene on the uniformly accessible surfaces of platinum electrodes prepared by electroreduction of thick platinum oxide layers leads to a roughness factor-independent Tafel slope equal to the 2.303 $(2RT/F)$ ratio.

4.5. *Platinum electrode structure and specific catalytic activity for ethylene electro-oxidation*

It was previously found that the increase in roughness factor for ethylene electro-oxidation on porous platinized platinum electrodes at a constant potential leads to a decrease in the current per unit of real electrode area [3]. This was related to a reduced rate of penetration of ethylene molecules into micropores and cracks [3]. A similar dependence of the rate of ethylene electro-oxidation at a constant potential on the roughness factor of porous platinized platinum electrodes was observed in the present work. However, on using non-porous platinum electrodes prepared by electroreduction of thick platinum oxide layers, the specific catalytic activity for ethylene electro-oxidation becomes independent of the roughness factor and equal to that of a smooth platinum electrode, since the electrode surface is uniformly polarized. Then, although the conclusion about the influence of transport limitations on the decrease of the ethylene electro-oxidation rate on platinized platinum electrodes remains valid, the actual effect arises from the proper porous nature of the platinized platinum electrodes; however, this is not a consequence of the concomitant increase in roughness factor. Thus, the electrochemical behaviour of platinized platinum electrodes is mainly determined by the pore size distribution and the thickness of the porous electrodeposits.

In conclusion, the true specific catalytic activity of platinum electrodes for ethylene electro-oxidation is independent of roughness factor, and the decrease of the apparent specific catalytic activity observed on platinized platinum electrodes should be related to the variation of the corresponding porosity parameters. Furthermore, as the character and number of structural defects must be different at smooth platinum and non-porous electroreduced platinum electrodes, the surface structural factors have a minor influence on the true specific catalytic activity of platinum, in agreement with previous work [27].

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