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# Electrochemical oxidation of ethanol on Pt(hkl) basal surfaces in NaOH and Na<sub>2</sub>CO<sub>3</sub> media

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## Abstract

The electrooxidation of ethanol as well as its irreversible adsorption on platinum single crystal electrodes have been studied in NaOH and Na<sub>2</sub>CO<sub>3</sub> media. Pt(110) and Pt(100) electrodes show deactivation for oxidation of bulk ethanol in both media, caused mainly by a structural surface modification of the electrode surface. However, in NaOH solution Pt(111) exhibits the best behaviour on ethanol oxidation showing the highest current density and the most stable surface. From the SNIFT-IR spectra adsorbed CO is the main poisoning species in the irreversible adsorption of ethanol on Pt(110) and Pt(100); on Pt(111) only a very weak band of adsorbed CO is observed. From the FT-IR spectra obtained during the oxidation of ethanol on Pt(110), Pt(100) and Pt(111) electrodes, acetate anions have been identified as the main soluble oxidation product.

**Keywords** Ethanol; Platinum; Alkaline media, Electrodes

## 1. Introduction

The direct alcohol/air fuel cell is attractive for transportation as well as bulk power generation, since the alcohol is a convenient alternative to gaseous fuels. Together with methanol, ethanol is an alternative fuel with significant environmental benefits because it can be generated by renewable energy sources such as biomass.

For this reason, the investigation of electrocatalytic processes involved in the electrooxidation of small organic compounds has been subject of special interest during years [1,2].

The surface species and particularly the adsorbed species in electrocatalytic reactions play an important role in the electrode activity (as reactive intermediates, poisoning species, etc.) and in the selectivity of the reaction. The role of the poisoning intermediates has been recognized for a long time.

The structure of an electrocatalyst, such as platinum, also greatly influences the reaction rate as it is clearly observed using electrodes of well-defined and controlled surface structure. It has been shown that the electrocatalytic oxidation reactions of small organic compounds are structure-sensitive [1,2].

The nature of the adsorbed species formed during bulk ethanol oxidation and dissociative adsorption of ethanol has been studied by voltammetry [3–5], in situ infrared spectroscopy [6–11], differential electrochemical mass spectrometry (DEMS) [12,13] and Auger spectroscopy [14] on platinum electrodes.

The electrolyte also plays a role in the mechanism of electrocatalytic reactions. The use of alkaline solution in a fuel cell and particularly carbonate solutions has been proposed [1,15,16] due to its advantages with respect to acidic media: (i) the electrocatalytic activity on the oxidation reaction of organic fuels is larger than in acid solution, and (ii) the performance on the cathodic oxygen reduction is significantly enhanced.

In this work the influence of the surface structure of the platinum electrode on the ethanol oxidation reaction and its dissociative adsorption in NaOH and Na<sub>2</sub>CO<sub>3</sub> media has been studied.

## 2. Experimental

The test solutions were 0.1 M Na<sub>2</sub>CO<sub>3</sub> and 0.1 M NaOH (both Merck suprapur or p.a.) and the organic solution was from Merck (p.a.).

The water used for the preparation of the solutions was from a Millipore-Milli Q system. All potentials are referred to the reversible hydrogen electrode (RHE) immersed in the same solution.

The technique used for the isolation of the adsorbed species coming from the irreversible adsorption of the organic compound has been described in Refs. [3,4]. The electrode covered with a droplet of organic solution is introduced into the test solution and maintained at a potential,  $E_{\text{ads}}$ , during a time,  $t_{\text{ads}}$ , indicated in each figure. Just before starting the polarization programme, the excess of the organic compound is removed from the vicinity of the electrode by stirring.

In-situ Fourier-transform infrared (FT-IR) spectroelectrochemical data were collected using a Nicolet 5PC FT-IR system equipped with a liquid nitrogen-cooled MCT detector. The sample compartment was purged throughout the experiment using a 75–50 Balston clean air package. The cell was made of glass with a  $\text{CaF}_2$  window. The incidence angle at the electrode surface was approximately  $60^\circ$  with respect to the surface normal. All spectra were recorded with a resolution of  $8 \text{ cm}^{-1}$ .

### 3. Results and discussion

#### 3.1. Oxidation of irreversibly adsorbed species coming from ethanol

Fig. 1 shows the voltammetric response during the oxidation of irreversibly adsorbed species on a Pt(100) electrode in carbonate medium. It can be observed that during the polarization programme 'a' (cycling between 0.06 and 0.39 V) the hydrogen adsorption sites are partially blocked. Programme 'b' is immediately started after programme 'a'. During the first positive sweep, several oxidation peaks appear between 0.5 and

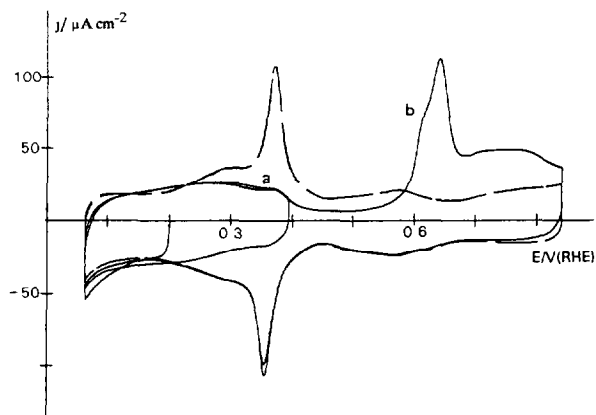


Fig. 1 Voltammogram of adsorbed species coming from the irreversible adsorption of ethanol on a Pt(100) electrode in  $0.1 \text{ M Na}_2\text{CO}_3$ ,  $\nu = 50 \text{ mV s}^{-1}$ ,  $E_{\text{ads}} = 0.2 \text{ V}$ , and  $t_{\text{ads}} = 2 \text{ min}$ . Polarization programme (a)  $0.2 \text{ V} \rightarrow 0.06 \text{ V} \rightarrow 0.39 \text{ V} \rightarrow 0.06 \text{ V}$ , (b)  $0.06 \text{ V} \rightarrow 0.85 \text{ V} \rightarrow 0.06 \text{ V}$  (two sweeps); (—) first and (---) second sweeps

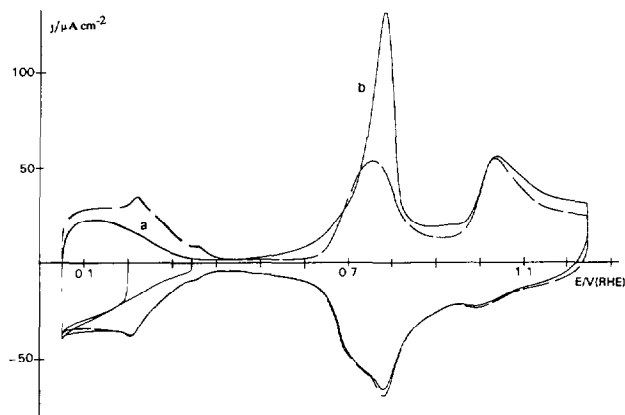


Fig. 2 Voltammogram of adsorbed species coming from the irreversible adsorption of ethanol on a Pt(111) electrode in  $0.1 \text{ M Na}_2\text{CO}_3$ ,  $\nu = 50 \text{ mV s}^{-1}$ ,  $E_{\text{ads}} = 0.2 \text{ V}$ , and  $t_{\text{ads}} = 2 \text{ min}$ . Polarization programme (a)  $0.2 \text{ V} \rightarrow 0.04 \text{ V} \rightarrow 0.34 \text{ V} \rightarrow 0.04 \text{ V}$ ; (b)  $0.04 \text{ V} \rightarrow 1.25 \text{ V} \rightarrow 0.04 \text{ V}$  (two sweeps); (—) first and (---) second sweeps

0.85 V. During the second sweep the profile of the voltammogram changes to the characteristic voltammogram of a Pt(100) electrode in the test solution [17]. However, the hydrogen adsorption/desorption process is still blocked indicating that not all the adsorbed species are removed from the surface of the electrode during these two sweeps up to 0.85 V.

The potential and the profile corresponding to the oxidation of the adsorbed species coming from dissociative adsorption of ethanol on a Pt(100) electrode (Fig. 1) are very similar to those obtained with the oxidation of adsorbed CO at approximately the same coverage degree in the same medium [17]. From this comparison, it is possible to assign the adsorbed species formed from ethanol on Pt(100) mainly to adsorbed CO.

Fig. 2 shows the voltammetric curve obtained during the oxidation of the irreversibly adsorbed species resulting from the dissociative adsorption of ethanol on a Pt(111) electrode. The weakly bonded hydrogen appears to be partially blocked (Fig. 2 (curve a)). The oxidation of the adsorbed species starts at 0.47 V giving a single peak at 0.78 V. This peak coincides in shape and potential with that obtained in the electrochemical oxidation of adsorbed CO on a Pt(111) electrode in the same medium [18]. Moreover, a small oxidation current can be observed between 0.85 and 1.25 V. This current can be associated with the oxidation of other adsorbed species as it does not appear in the subsequent cycles. From the second cycle up to 1.25 V, the characteristic voltammetric profile of Pt(111) in this medium [19] is practically obtained.

The behaviour obtained for a Pt(110) electrode is presented in Fig. 3 (the same behaviour was observed in perchloric medium [3]). Fig. 3 (inset), shows the voltammogram obtained for the polarization programme:  $0.3 \text{ V} \rightarrow 0.06 \text{ V} \rightarrow 0.34 \text{ V} \rightarrow 0.06 \text{ V}$ . A reduction

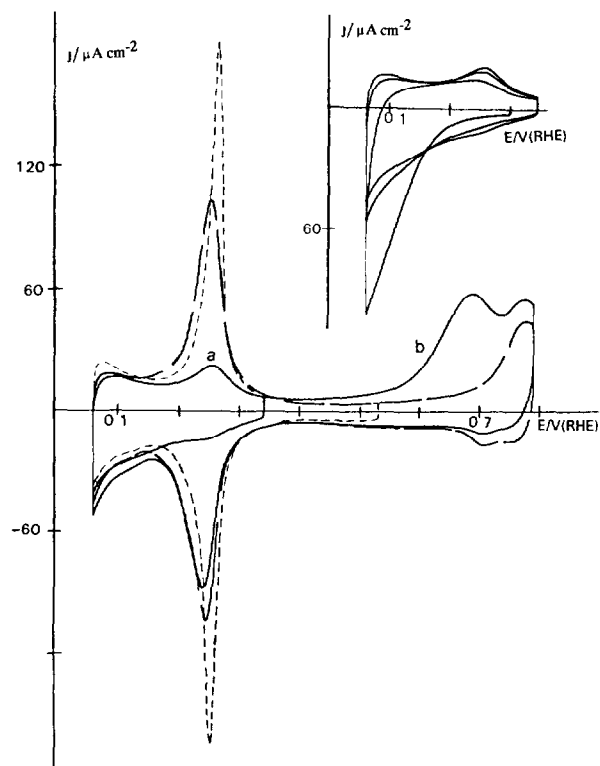


Fig. 3. Voltammogram of adsorbed species coming from the irreversible adsorption of ethanol on a Pt(110) electrode in 0.1 M  $\text{Na}_2\text{CO}_3$ ,  $\nu = 50 \text{ mV s}^{-1}$ ,  $E_{\text{ads}} = 0.3 \text{ V}$ , and  $t_{\text{ads}} = 2 \text{ min}$ . Polarization programme: (a)  $0.06 \text{ V} \rightarrow 0.34 \text{ V} \rightarrow 0.06 \text{ V}$ , (b)  $0.06 \text{ V} \rightarrow 0.79 \text{ V} \rightarrow 0.06 \text{ V}$  (two sweeps), (—) first, (---) second sweeps, and (----) test solution. Inset: first sweeps of polarization programme.  $0.3 \text{ V} \rightarrow 0.06 \text{ V} \rightarrow 0.34 \text{ V} \rightarrow 0.06 \text{ V}$ .

current appears during the first sweep and disappears in the next cycles. Fig. 3 (curve a) shows the stationary profile obtained in Fig. 3 (inset), the hydrogen adsorption/desorption process is partially blocked. During the first sweep up to 0.79 V (Fig. 3 (curve b)) a well-defined anodic peak is obtained at 0.69 V. This peak can be assigned to the electrochemical oxidation of adsorbed CO by comparing with the behaviour obtained with irreversibly adsorbed CO on Pt(110) in the same medium [20]. The oxidation peak at 0.77 V corresponds to the electrochemical oxygen adsorption. During the subsequent negative-going sweep from 0.79 to 0.06 V the hydrogen adsorption/desorption profile (between 0.06 and 0.4 V) appears to be still blocked. This result shows that not all the adsorbed residues have been removed from the surface of the electrode during the first sweeps up to 0.79 V.

Another important aspect observed in Fig. 3 is that the hydrogen adsorption/desorption profile (between 0.06 and 0.5 V) after oxidation of adsorbed species up to 0.79 V has been changed with respect to that obtained in test solution (Fig. 3 (curve ----)) at the same potential limit. This result has been associated with a structural surface modification induced by the adsorption of CO

Table 1

Electric charge ( $Q_{\text{ox}}$ ) starting oxidation potential, ( $E_i$ ) and oxidation peak potential, ( $E_{\text{peak}}$ ) of irreversibly adsorbed species on platinum single crystal electrodes in alkaline solutions

	$\text{Na}_2\text{CO}_3$			NaOH		
	Pt(100)	Pt(110)	Pt(111)	Pt(100)	Pt(110)	Pt(111)
$Q_{\text{ox}}$ ( $\mu\text{C}/\text{cm}^2$ )	191.6	113.3	170.0	265.4	109.3	152.4
$E_i$ (V)	0.50	0.46	0.47	0.47	0.43	0.47
$E_{\text{peak}}$ (V)	0.64	0.69	0.78	0.62	0.67	0.80
	0.74			0.79		

on a Pt(110) electrode in carbonate solution [20]. The study of the structural surface modification of a Pt(110) electrode in carbonate solution has shown that to obtain the same surface modification, without CO adsorption, more than 20 cycles of adsorption/desorption of oxygen up to 0.79 V are necessary [20,21]. This result eliminates the possibility that the surface modification, in this case, was only produced by surface oxidation.

In 0.1 M NaOH a similar behaviour has been observed for Pt(100), Pt(111) and Pt(110) electrodes, using the same polarization programmes described above.

Table 1 shows the electric charge and the potential corresponding to the oxidation of adsorbed species on Pt(hkl) basal planes in alkaline media. Only electric charge values of these peaks have significant differences between NaOH and  $\text{Na}_2\text{CO}_3$  media.

### 3.2. FT-IR study of the adsorbed species

In situ FT-IR spectroscopy has been used to identify the nature of the adsorbed species formed in the adsorption of ethanol on platinum single crystal electrodes.

SNIFT-IR spectra were obtained by recording reference and sample spectra at two different potentials, 0.05 and 0.35 V, respectively. Typically, 920 interferograms (approximately two scan per second,  $8 \text{ cm}^{-1}$  resolution) were recorded at each potential. The potential was switched from one potential to another every 92 scans to compensate for baseline changes during the collection of spectra.

Fig. 4 shows the SNIFT-IR spectra of adsorbed species on Pt(110), Pt(100) and Pt(111) electrodes in 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$  in the  $1700\text{--}2200 \text{ cm}^{-1}$  region. The existence of bands corresponding to adsorbed CO can be observed; however, the intensity and the shape of these bands depend strongly on the surface structure of the electrode. Thus, in the case of Pt(110) only a monopolar band is observed at  $2015 \text{ cm}^{-1}$  corresponding to linearly adsorbed CO. The shape of this band is a consequence of the overlapping of the absolute bands at each potential as occurs with the adsorption of CO on polycrystalline [22] and plat-

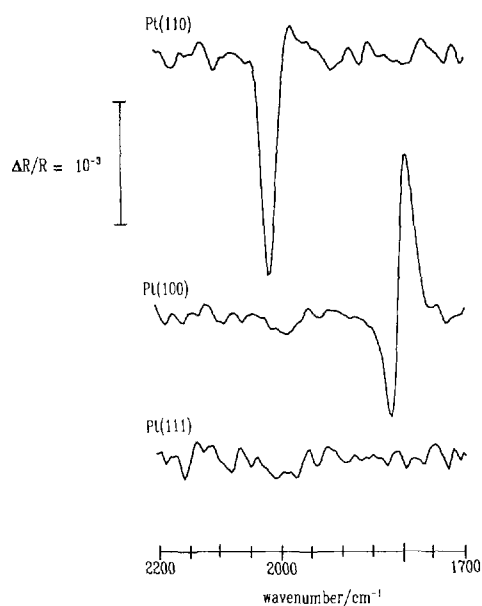


Fig. 4. SNIFT-IR spectra of the adsorbed species resulting from the adsorption of ethanol on Pt(110), Pt(100) and Pt(111) electrodes in 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1$  M  $\text{CH}_3\text{CH}_2\text{OH}$  solution. Reference potential = 0.05 V and sample potential = 0.35 V.

inum single crystal [23] electrodes. For Pt(100), a bipolar band center and approximately at  $1806\text{ cm}^{-1}$  and a small monopolar one approximately at  $1990\text{ cm}^{-1}$  appeared corresponding to multi-bonded and linearly adsorbed CO, respectively. In contrast, for a Pt(111) electrode, only the small monopolar band approximately at  $1990\text{ cm}^{-1}$  appears corresponding to linearly bonded CO.

Analogous spectroscopic results were obtained for the three platinum single crystal electrodes when NaOH solution is used instead of  $\text{Na}_2\text{CO}_3$ .

### 3.3. Ethanol oxidation

Fig. 5 shows the voltammogram for the oxidation of ethanol on Pt(100) electrode in carbonate medium. This figure shows the first two cycles and the seventh cycle up to 1 V. No bulk ethanol oxidation is observed until the adsorbed species coming from ethanol adsorption starts to oxidize (0.45–0.5 V).

During the positive going sweeps a single peak appears. In the negative-going sweep, two oxidation currents are observed at potentials less positive than the one monitored in the positive sweep. The current density decreases with the number of sweeps (about 36% between the first and the seventh sweep). This deactivation may be due to the following facts: (i) poisoning of the electrode surface; (ii) structural surface modification when the potential reaches values into the surface oxidation region (values greater than 0.85 V), and (iii) structural surface modification induced by the adsorbed species. In the region between 0.06 and

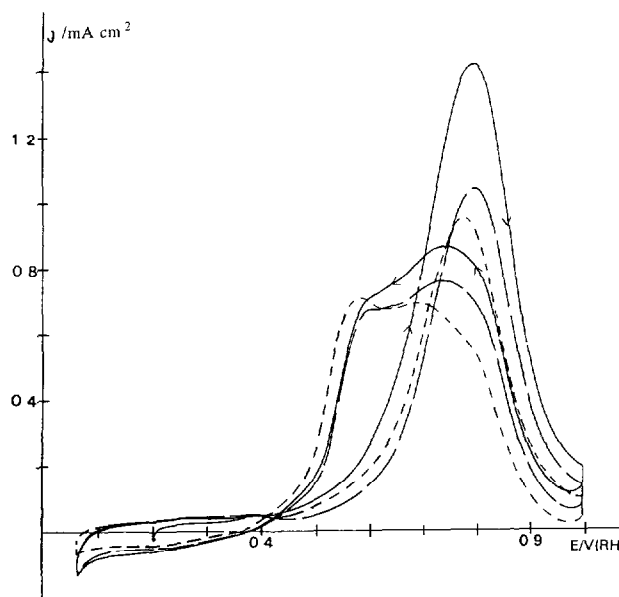


Fig. 5. Cyclic voltammograms of 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1$  M  $\text{CH}_3\text{CH}_2\text{OH}$  solution on a Pt(100) electrode, showing the (—) first, the (---) second and the (-·-·-) seventh cycles of ethanol oxidation up to 1 V;  $\nu = 50\text{ mV s}^{-1}$ .

0.4 V, practically no change in the amount of adsorbed hydrogen can be observed with the number of cycles. For this reason, the decrease of the activity of a Pt(100) electrode could mainly be associated to the (ii) and (iii) processes (although repetitive oxygen adsorption/desorption process does not cause a drastic change in the adsorption/desorption hydrogen process [24]).

If the upper potential limit is smaller than 0.85 V the behaviour is similar, showing the deactivation of the electrode.

In 0.1 M NaOH medium a similar behaviour is obtained. However, two significant differences can be observed (Table 2): (i) the current density of the first oxidation peak is greater in NaOH medium, and (ii) the decrease in the current density with the number of sweeps is more drastic in NaOH medium (about 54% between the first and the seventh sweep, instead of 36% in 0.1 M  $\text{Na}_2\text{CO}_3$  medium).

Fig. 6 shows the oxidation of ethanol on a Pt(111) electrode in 0.1 M  $\text{Na}_2\text{CO}_3$  medium. This behaviour appears less complex than the one obtained for a Pt(100) electrode. In the positive- and negative-going sweeps, a single peak approximately at the same range of potential is observed, and the voltammogram reaches a stationary state in the seventh cycle (Fig. 6). During the positive and negative sweeps of this seventh cycle the same current density has been obtained ( $1.9\text{ mA cm}^{-2}$ ). The small decrease in activity of a Pt(111) electrode (about 9%, Table 2), must be associated with the poisoning of the electrode, because no structural surface modification occurs up to 1.3 V in a solution free of ethanol [19,24].

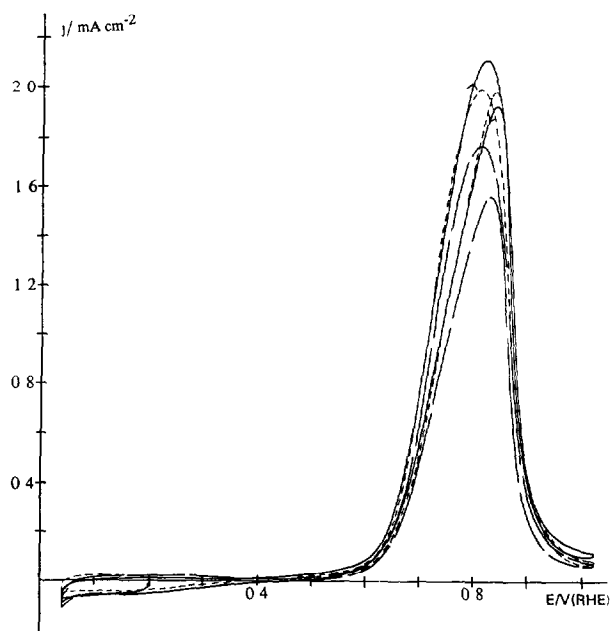


Fig. 6. Cyclic voltammograms of 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$  solution on a Pt(111) electrode, showing the (—) first, the (---) second and the (.....) seventh cycles of ethanol oxidation up to 1 V,  $\nu = 50 \text{ mV s}^{-1}$ .

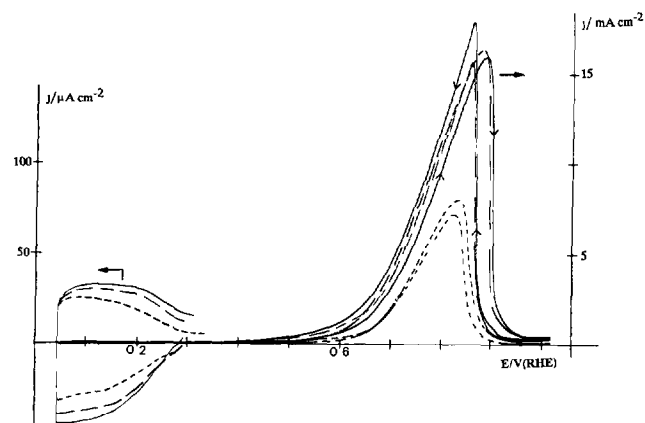


Fig. 7. Cyclic voltammograms of 0.1 M  $\text{NaOH} + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$  solution on a Pt(111) electrode, showing the (—) first, the (.....) second and the (---) seventh cycles of ethanol oxidation up to 1.02 V,  $\nu = 50 \text{ mV s}^{-1}$ .

Fig. 7 shows the electrooxidation of ethanol on a Pt(111) electrode in 0.1 M NaOH medium for the first, second and seventh cycle. The value of the current density in the first positive cycle ( $15.6 \text{ mA cm}^{-2}$ ) is about seven times greater than in carbonate medium ( $2.1 \text{ mA cm}^{-2}$ ) but a drastic loss of activity can be observed from the first to the seventh cycle (about 50% in contrast with the results in carbonate medium, 5%, see Fig. 6 and Table 2). The shape and potential value of the oxidation peak in the positive-going sweep and the negative one are different. These differences disappear in the subsequent sweeps. In the region between

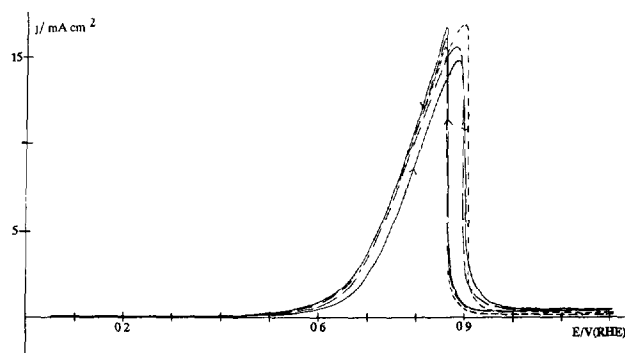


Fig. 8. Cyclic voltammograms of 0.1 M  $\text{NaOH} + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$  solution on a Pt(111) electrode, showing the (—) first, the (---) second and the (.....) seventh cycles of ethanol oxidation up to 1.2 V,  $\nu = 50 \text{ mV s}^{-1}$ .

Table 2

Starting oxidation potential ( $E_s$ ), peak potential ( $E_{\text{peak}}$ ) and current density ( $j$ ) of bulk ethanol oxidation on platinum single crystal electrodes in alkaline solutions

	$\text{Na}_2\text{CO}_3$			$\text{NaOH}$		
	Pt(100)	Pt(110)	Pt(111)	Pt(100)	Pt(110)	Pt(111)
$E_s$ (V)	0.45	0.48	0.45	0.45	0.45	0.45
$E_{\text{peak}}$ (V)	0.79	0.91	0.82	0.78	0.81	0.83
$j$ ( $\text{mA cm}^{-2}$ ) (first sweep)	1.4	4.5	2.1	2.2	5.7	15.6 <sup>a</sup> 14.9 <sup>b</sup>
$j$ ( $\text{mA cm}^{-2}$ ) (seventh sweep)	0.9	2.2	2	1.0	1.0	7.8 <sup>a</sup> 16.6 <sup>b</sup>
Deactivation percentage <sup>c</sup> (%)	36	51	5	54	82	50 <sup>a</sup> -11 <sup>b</sup>

<sup>a</sup>Upper potential limit 1.02 V.

<sup>b</sup>Upper potential limit 1.2 V.

<sup>c</sup>Calculated as:  $(j_{(1\text{st sweep})} - j_{(7\text{nd sweep})})/j_{(1\text{st sweep})}$

0.06 and 0.40 V (Fig. 7), the amount of adsorbed hydrogen decreases with the number of sweeps. This behaviour must be associated with the poisoning of the electrode, because no structural surface modification occurs at this upper potential limit (1.02 V).

Fig. 8 shows the voltammogram obtained for a Pt(111) electrode in NaOH medium when the upper potential limit is 1.2 V. In these conditions the shape, potential and current density value of the oxidation peaks remain practically unchanged in the first, second and subsequent sweeps (Table 2). Moreover, in the region between 0.06 and 0.40 V, practically no change in the amount of adsorbed hydrogen can be observed with the number of cycles.

In order to clarify the nature of the species responsible for the loss of activity of the Pt(111) electrode observed in Fig. 7, the following experiments were carried out:

(i) Using the same conditions as in Fig. 7 and after the seventh cycle, the potential was stopped at 1.0 V and the solution was stirred. The loss of electrode

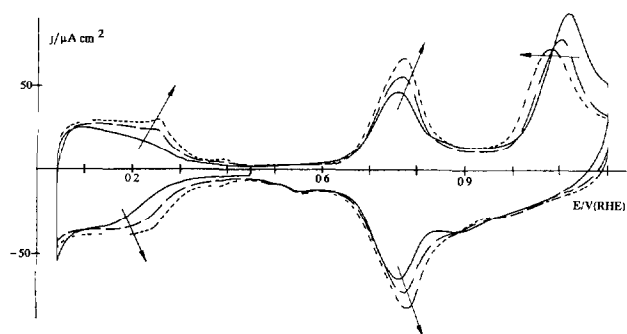


Fig. 9. Voltammograms of a Pt(111) electrode obtained after the seventh cycle of Fig. 7 and recorded in 0.1 M NaOH solution free of ethanol,  $\nu=50 \text{ mV s}^{-1}$ .

activity was still observed. The species responsible for the electrode poisoning must be adsorbed on the electrode.

(ii) Using the same conditions as in Fig. 7 and after the seventh cycle, when a great decrease in electrode activity has been observed, the upper potential limit increased until 1.2 V. Then, the peak of ethanol oxidation progressively increases with the number of cycles and the amount of adsorbed hydrogen in the 0.06 and 0.4 V region has been restored.

(iii) Using the same conditions as in Fig. 7 and after the seventh cycle, the potential was stopped at 1.0 V and the electrode was removed from the electrochemical cell. After being washed with ultrapure water, the electrode was introduced in 0.1 M NaOH free of ethanol at 0.45 V. The voltammogram (Fig. 9) shows an oxidation peak at 1.11 V, overlapped with the surface oxidation peak, that appears to be shifted to more positive potentials than in the test solution. Fig. 9 shows also the increase of the hydrogen adsorption/desorption process with the number of cycles up to 1.2 V.

From all these results it can be deduced that on a Pt(111) electrode in 0.1 M NaOH + 0.1 M  $\text{CH}_3\text{CH}_2\text{OH}$  solution, the decrease in activity, when the upper potential limit is 1.02 V, is mainly due to the poisoning of the electrode by the adsorbed ethanolic residues originating during the bulk ethanol oxidation. These adsorbed species are probably associated with the methyl group or with the two carbon atom species because these results are not observed in the oxidation of methanol in the same medium [18]. These adsorbed species are oxidized at potentials higher than 1.02 V giving a peak at 1.11 V (Fig. 9). As this behaviour was observed only in NaOH medium it could be related with the large quantity of ethanol that is oxidized in this medium in contrast with the carbonate medium (see the current density values in Table 2).

Fig. 10 shows the electrooxidation of ethanol on a Pt(110) electrode in 0.1 M  $\text{Na}_2\text{CO}_3$  for the first, second and seventh cycles. During the first positive sweep no direct oxidation of ethanol is observed approximately

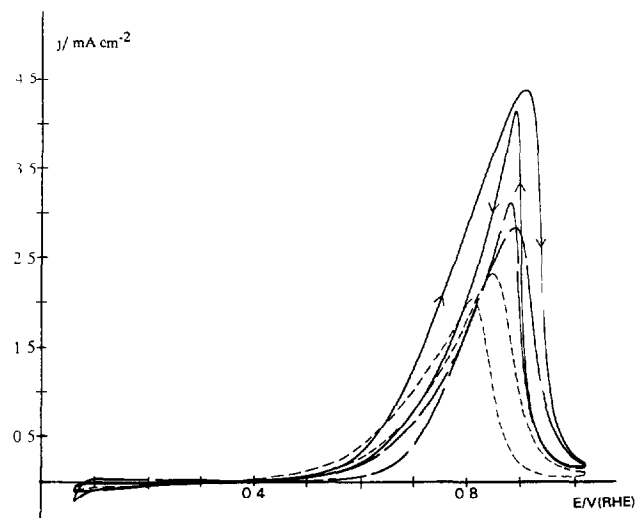


Fig. 10. Cyclic voltammograms of 0.1 M  $\text{Na}_2\text{CO}_3 + \text{CH}_3\text{CH}_2\text{OH}$  solution on a Pt(110) electrode, showing the (—) first, the (---) second and the (.....) seventh cycles of ethanol oxidation up to 1 V,  $\nu=50 \text{ mV s}^{-1}$

until a potential of 0.5 V is reached. At this potential the adsorbed species coming from dissociative adsorption of ethanol can be oxidized. The maximum current density ( $4.5 \text{ mA cm}^{-2}$ ) appears at 0.91 V. During the negative-going sweep, an oxidation peak appears at 0.88 V with a maximum current density of  $4.2 \text{ mA cm}^{-2}$ . The current densities decrease continuously during the second and subsequent cycles to reach a value of  $2.2 \text{ mA cm}^{-2}$  during the seventh positive cycle (about 51% between first and seventh cycles). As in the case of a Pt(100) electrode, the deactivation can be due not only to the electrode poisoning but also to structural surface modification caused either by surface oxidation at this upper potential limit or by the adsorbed species.

Fig. 11 shows the voltammetric profile for a Pt(110) electrode immersed in a 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$  solution. In the region between 0.06 and 0.4 V, the hydrogen adsorption/desorption process is monitored before the bulk ethanol oxidation. In the second positive sweep (Fig. 11 (curve ---)), the amount of desorbed hydrogen increases in comparison with the first positive sweep (Fig. 11 (solid line)). This increase is more pronounced in the tenth cycle (Fig. 11 (curve ----)). So, the surface of the Pt(110) electrode seems to be less blocked upon cycling. However, a drastic decrease in the oxidation current is observed in the positive sweep for the ethanol oxidation with the number of cycles (see 0.5–1 V region in Fig. 11).

Fig. 12 shows the voltammogram obtained with the electrode removed from the 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$  solution at 0.35 V, during the second positive sweep before the ethanol oxidation (Fig. 11 (curve ---)). After this, the electrode is introduced into another electrochemical cell in 0.1 M  $\text{Na}_2\text{CO}_3$  solution free of ethanol at 0.3 V. After elimination of

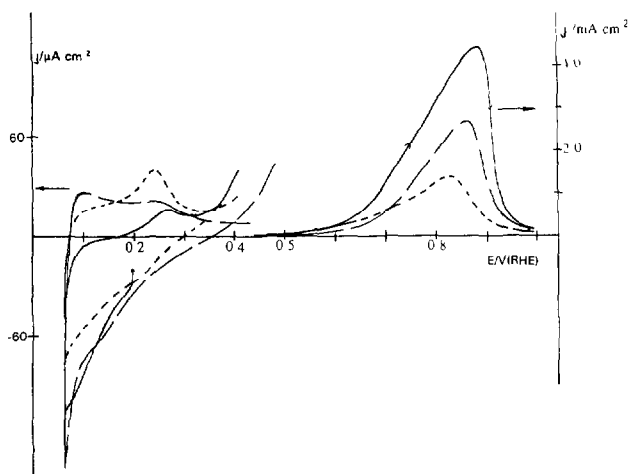


Fig. 11. Cyclic voltammograms of 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$  solution on a Pt(110) electrode, showing the (—) first, the (---) second and the (-·-·-) tenth cycles of ethanol oxidation up to 1 V,  $\nu = 50 \text{ mV s}^{-1}$ .

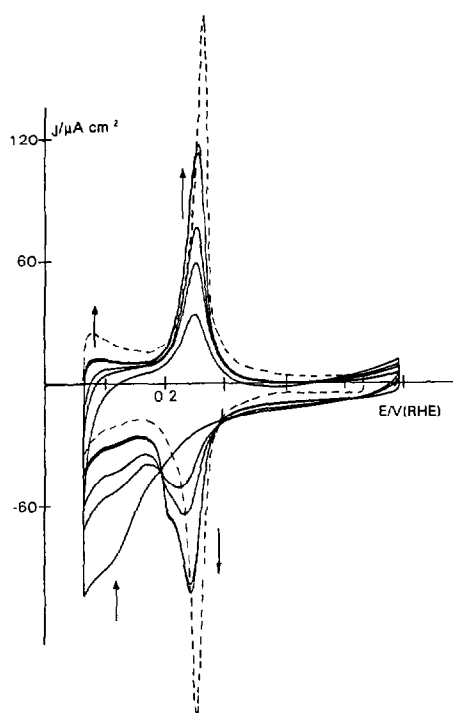


Fig. 12 Voltammograms of Pt(110) electrode removed from a 0.1 M  $\text{Na}_2\text{CO}_3 + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$  solution during the second positive sweep before the ethanol oxidation up to 1 V and introduced in a 0.1 M  $\text{Na}_2\text{CO}_3$  solution at 0.3 V,  $\nu = 50 \text{ mV s}^{-1}$ .

the adsorbed species, the hydrogen profile is very different to that obtained for a flame cleaned Pt(110) electrode in the same solution (Fig. 12 (dashed line)). This change in the hydrogen profile has been assigned to a structural surface modification [20,21].

From these results it can be suggested that the deactivation of the Pt(110) electrode, is produced mainly by the modification of the surface structure. This structural surface modification is induced by the adsorbed

species together with the surface oxidation up to 1.0 V.

Using 0.1 M  $\text{NaOH} + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$  solution instead of carbonate, a similar behaviour is observed for a Pt(110) electrode, although the maximum current density of the positive-going sweep decreases about 82% between the first and the seventh cycle (51% in the carbonate case, see Table 2).

#### 3.4. FT-IR study of ethanol oxidation

In situ FT-IR spectroscopy can be used to monitor the different reactions occurring in the presence of ethanol in the solution as a function of potential. In this way, Fig. 13 shows the sequences of different spectra in the  $1000\text{--}3000 \text{ cm}^{-1}$  region corresponding to Pt(110), Pt(100) and Pt(111) electrodes obtained in a 0.1 M  $\text{CH}_3\text{CH}_2\text{OH} + 0.1 \text{ M NaOH}$  solution during a single potential sweep from 0.05 to 1 V at  $1 \text{ mV s}^{-1}$ . The reference spectrum was recorded just starting the sweep (0.07 V). A set of 99 interferograms was acquired per 50 mV interval, corresponding to a single spectrum, which is referred to the average potential of the interval. The spectra presented here are in NaOH solution because in  $\text{Na}_2\text{CO}_3$  solution the strong band between  $1400$  and  $1450 \text{ cm}^{-1}$  corresponding to the carbonate anion masks with other bands in this spectral region.

For the three platinum single crystal electrodes two negative bands approximately at  $1550$  and  $1415 \text{ cm}^{-1}$  are clearly observed when the potential increases. These bands can be assigned to the asymmetrical and symmetrical stretching ( $\nu_2(\text{CO}_2^-)$ ,  $\nu_3(\text{CO}_2^-)$ ) of acetate produced in the oxidation of ethanol. The appearance of adsorbed CO on Pt(110) and Pt(100) can also be discerned from the bands at  $1990$  and  $1790 \text{ cm}^{-1}$  respectively (Fig. 13 (insets)). These bands assigned to adsorbed CO decrease with the increase in the potential. The bands that appear below  $1100 \text{ cm}^{-1}$  for the three platinum single crystal electrodes can be assigned to the C-C and C-O stretching of the ethanol in the solution. The band approximately  $1350 \text{ cm}^{-1}$  can be tentatively assigned to the presence of bicarbonate anion formed from  $\text{CO}_2$  at high potentials in this medium.

#### 4. Conclusions

Irreversibly adsorbed species on Pt(100), Pt(111) and Pt(110) electrodes coming from dissociative adsorption of ethanol have been studied by cyclic voltammetry in alkaline media ( $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  solutions). Adsorbed CO appears as the main adsorbed species. From the results of in situ FT-IR spectroscopy it can be concluded that the adsorption of ethanol gives linearly adsorbed CO on Pt(110) and multi-bonded CO on Pt(100) in these media.

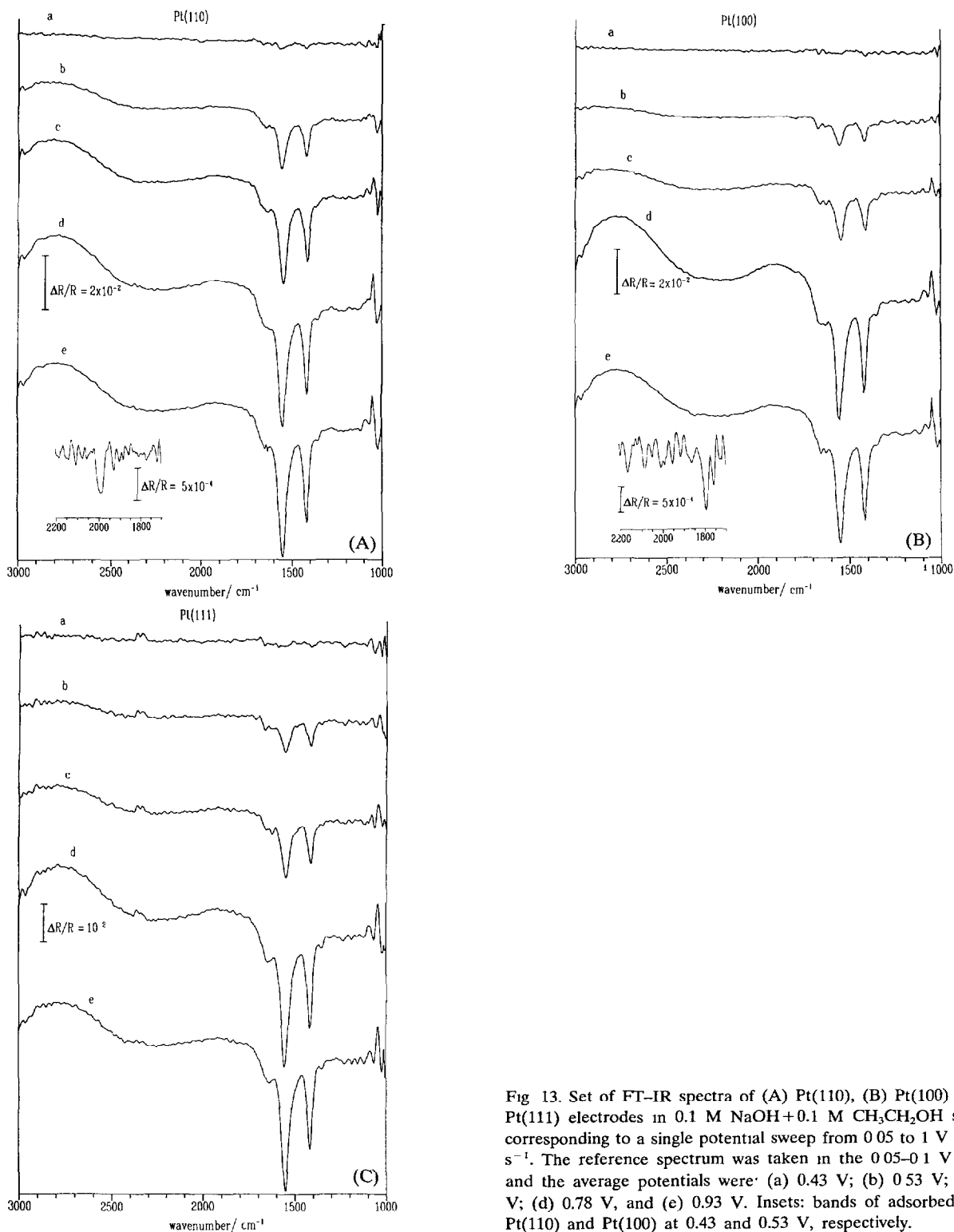


Fig 13. Set of FT-IR spectra of (A) Pt(110), (B) Pt(100) and (C) Pt(111) electrodes in 0.1 M NaOH + 0.1 M  $\text{CH}_3\text{CH}_2\text{OH}$  solution, corresponding to a single potential sweep from 0.05 to 1 V at  $1 \text{ mV s}^{-1}$ . The reference spectrum was taken in the 0.05–0.1 V interval and the average potentials were: (a) 0.43 V; (b) 0.53 V; (c) 0.63 V; (d) 0.78 V, and (e) 0.93 V. Insets: bands of adsorbed CO on Pt(110) and Pt(100) at 0.43 and 0.53 V, respectively.

From the results obtained in the bulk ethanol oxidation, Pt(100) and Pt(110) are deactivated due mainly to structural surface modification. This surface modification is only clearly observed for the Pt(110) electrode. The Pt(111) electrode shows the best behaviour for ethanol oxidation. In NaOH solution the Pt(111)

electrode is continuously deactivated by poisoning of the surface when the potential limit is 1 V. This deactivation does not appear if the potential limit is 1.2 V (Table 2). From the FT-IR study acetate is the main product in the oxidation of ethanol in these media.



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