

# Electrocatalytic oxidation of glyoxalate in alkaline medium on platinum adatom electrodes

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The influence of the foreign metal adatoms deposited at underpotentials on the oxidation of glyoxalate on platinum was studied in alkaline medium. Pronounced catalytic effects caused by underpotential submonolayers of Pb, Tl, Cd, Cu and Cr were observed. The enhancement of the oxidation processes by underpotential submonolayers has been interpreted according to the bifunctional theory of the electrocatalysis.

## 1. Introduction

Studies on electrode substrates covered by underpotential deposited (UPD) layers have great interest in electrosynthetic and fuel cell reactions. Small amounts of a foreign metal can give rise to substantial effects on the electrocatalytic behaviour of the electrode [1-3].

*In situ* application of reflectance spectroscopy [4, 5] revealed a large change of surface electronic properties of an electrode when foreign metal monolayers are deposited. The underpotential deposition of adatoms changes the double layer capacitance and the charge on the metal surface. Furthermore, the equilibrium of adatoms on the electrode surface may not be attained quickly enough and the competition with the anion adsorption from the bulk of the solution may occur. It has been well documented that submonolayer coverages of Sn, Pb, Cd and Tl on platinum electrodes increase considerably the overpotential for hydrogen evolution [6].

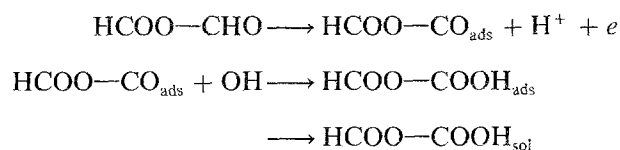
This enhancement can permit the electron-transfer processes to occur at much lower overpotentials and improve the selectivity of the electrocatalyst surface.

For the oxidation of simple organic compounds it was assumed that strongly chemisorbed particles play a predominant role. The large adatoms are believed to prevent the formation of strongly bound intermediates due to the suppression of the hydrogen adsorption on platinum [7], and strong adsorption of intermediates according to the third body mechanism [8]. According to a bifunctional mechanism the foreign metal adatoms catalyse the direct oxidation of the fuel and/or the adsorbate [9].

There are several papers devoted to the electrocatalytic action of UPD. Submonolayers are involved in the oxidation of simple organic substances such as carbon monoxide [10, 11], formic acid [12, 13], formaldehyde, methanol [14, 15], ethylene-glycol [16], 1,2-propanediol [17, 18], ascorbic acid [19] and hydrazine [20].

In previous work [21], the electrooxidation of glyoxylic acid was studied in 1 M HClO<sub>4</sub> on a platinized

platinum electrode. It was concluded that the reaction mechanism proceeds as follows:



Motoo *et al.* [24] showed that the glyoxylic acid oxidation in sulphuric acid is enhanced by oxygen-adsorbing adatoms through oxygen donation by them. The enhancement by As and Ru adatoms is far less than that expected from their oxygen adsorption potentials. A geometrical requirement for the transfer of oxygen atoms from the adatoms to the reaction intermediate is found to be another controlling factor for the enhancement by oxygen adsorbing adatoms.

The influence of the addition of adatoms on the cyclic voltammetry oxidation curves of glyoxylic acid on platinum in HClO<sub>4</sub> medium was studied by Pierre *et al.* [25]. In general an oxidation enhancement effect was observed.

The aim of the present work is an investigation of the electrocatalytic oxidation of glyoxalate on a platinum electrode in alkaline medium. The experiments were orientated towards obtaining facts that could improve our knowledge about the reaction mechanism. Furthermore the electro-oxidation on platinum-based electrodes modified by adatoms (Pb, Tl, Cd, Cu and Cr) was studied. Different UPD and redissolution potentials are characteristic of these adatoms. Likewise, the different number of platinum sites on which the adatoms were adsorbed is also a characteristic of the kind of adatom considered.

## 2. Experimental details

Linear and cyclic voltammetry were used throughout the work. The voltammograms were recorded using standard electronic equipment (a Bruker Mod. 310 potentiostat, a PAR Mod. 175 universal programmer and a Hewlett-Packard Mod 7047 A X-Y recorder).

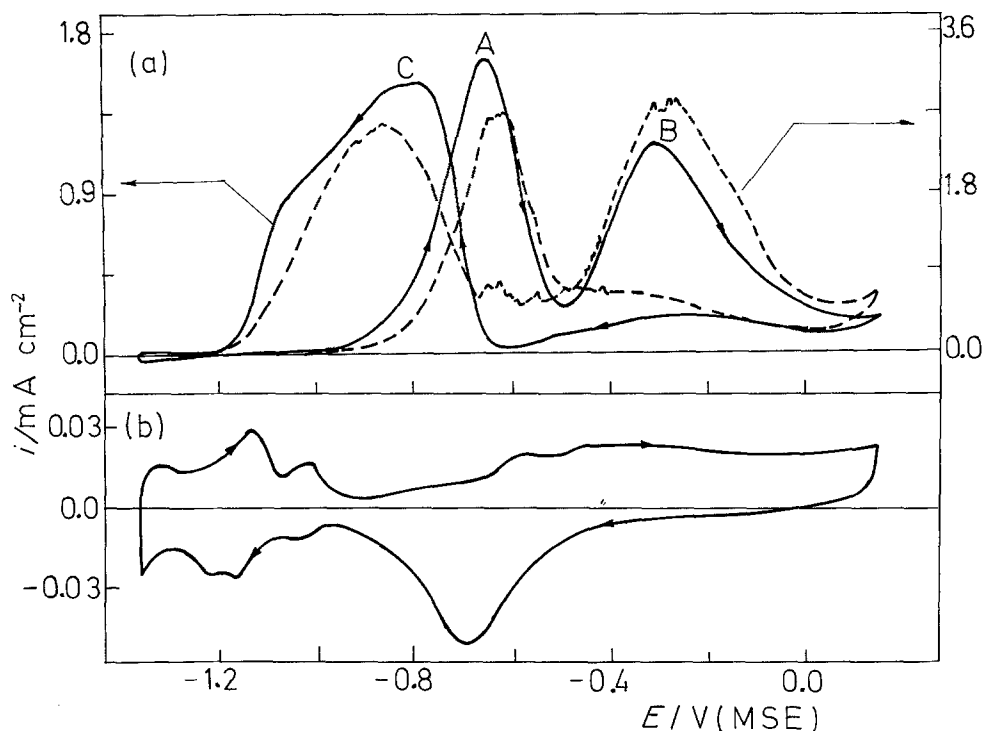


Fig. 1. Voltammograms of a platinum electrode in alkaline medium (0.1 M KOH, 25°C, 50 mV s<sup>-1</sup>). (a) With 0.1 M glyoxalate; (---) with stirring; (—) without stirring; (b) In the supporting electrolyte.

A three-electrode glass cell, with a platinum plate (99.998%) as working electrode (surface geometric 0.2 cm<sup>2</sup>), a platinum counter electrode and a mercurous sulphate electrode (MSE) as reference electrode were used. The electrochemical cell was held at a given temperature by circulation of thermostated water through the double wall of the cell. All measurements were carried out at 25 ± 0.2°C except in experiments in which temperature dependence was measured. Before the beginning of each experiment the solution was de-aerated with purified nitrogen.

Binary electrodes were prepared by UPD of the foreign metal adatoms on a small platinum plate from the electrolytic solution containing a soluble compound of the corresponding metal at a very low concentration (10<sup>-7</sup> to 10<sup>-4</sup> M).

Electrolytic solutions were prepared from doubly deionized redistilled water and Merck reagents ('p.a.' for potassium hydroxide, *zur synthese* for glyoxylic acid) were used. As the source of adatoms Pb(NO<sub>3</sub>)<sub>2</sub>, CdSO<sub>4</sub>, Tl<sub>2</sub>SO<sub>4</sub>, CuSO<sub>4</sub>, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, salts, containing ions of the metals investigated, were added to the solution.

The real surface of the working electrode was estimated by integration of the hydrogen region of a voltammogram recorded in a base electrolyte assuming 210 μC cm<sup>-2</sup> for an adsorbed hydrogen monolayer.

### 3. Results

#### 3.1. General aspects of the electrochemical behaviour of glyoxalate

Fig. 1 shows a typical voltammetric *i*-*E* curve obtained at a sweep rate of 50 mV s<sup>-1</sup> at 25°C in 0.1 M KOH.

It shows that the glyoxalate oxidation starts at -1.00 V/MSE and reaches a first peak at  $E_p^A = -0.65$  V versus MSE with  $i_p^A = 1.68$  mA cm<sup>-2</sup>. At more anodic potentials another peak appears at about -0.295 V versus MSE with  $i_p^B = 1.19$  mA cm<sup>-2</sup>. During the cathodic sweep no reduction peaks appear but an anodic current (peak C) is recorded in the potential range in which the surface oxides begin to be reduced. The *i*-*E* curve shows less marked current peaks in the potential region where the hydrogen adsorbs on platinum. When the solution is stirred the shape of the recorded voltammogram is similar to the above. Only an increase of the peak current densities  $i_A$ ,  $i_B$  and  $i_C$  is observed. During the repetitive potential cycling the peak heights A, B and C decrease, but the lowest values obtained are always higher than the peak heights registered on pure platinum. From the third cycle the general shape of the oxidation curves during both positive and negative sweeps does not change appreciably.

A change in the potential scan limits, gives rise to some changes in the recorded voltammograms as Fig. 2 shows. The decrease of the upper limit ( $E_a$ ), produces a diminution of the peak current on both anodic and cathodic sweeps. This fact may be due to the formation of strongly adsorbed intermediates produced by dissociative chemisorption of the organic substances which blocks the electrode surface and which would need more positive potentials to become oxidized. On the other hand, a shift of the cathodic limit to more anodic potentials does not lead to important changes. Only the peak currents in A and B increase quickly. It seems, therefore, that adsorbed hydrogen does not play a significant role in the poisoning process.

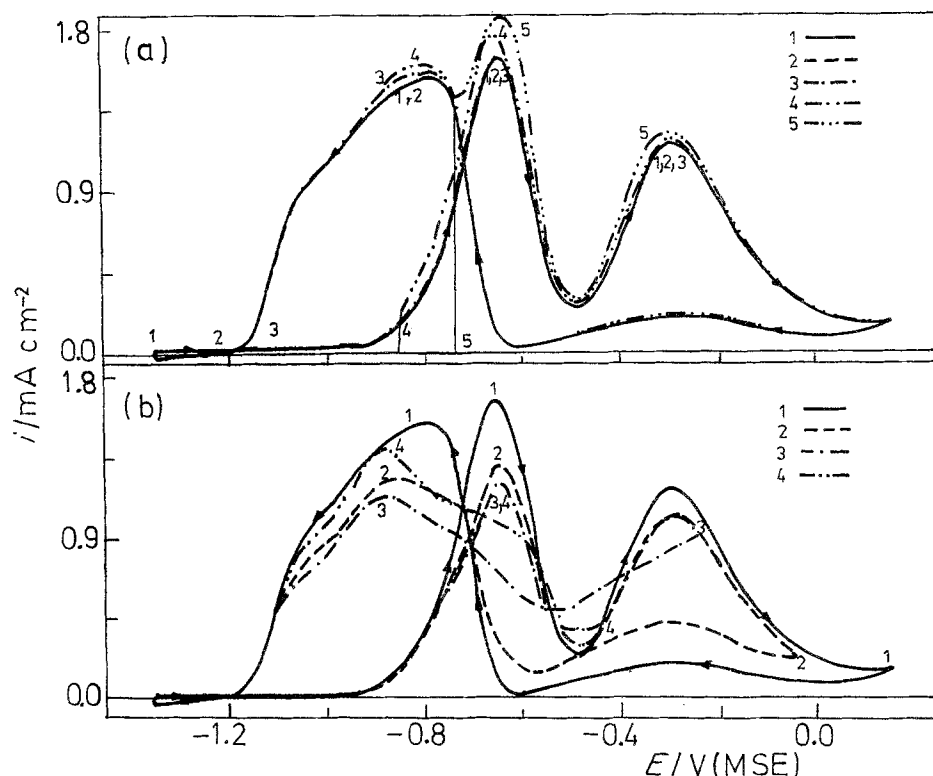


Fig. 2. Influence of the potential limits on the voltammograms of a platinum bead electrode in 0.1 M KOH +  $10^{-2}$  M glyoxalate ( $25^{\circ}\text{C}$ ,  $50\text{ mV s}^{-1}$ ): (a) negative limit  $E_c$  (b) positive potential limit  $E_a$ .

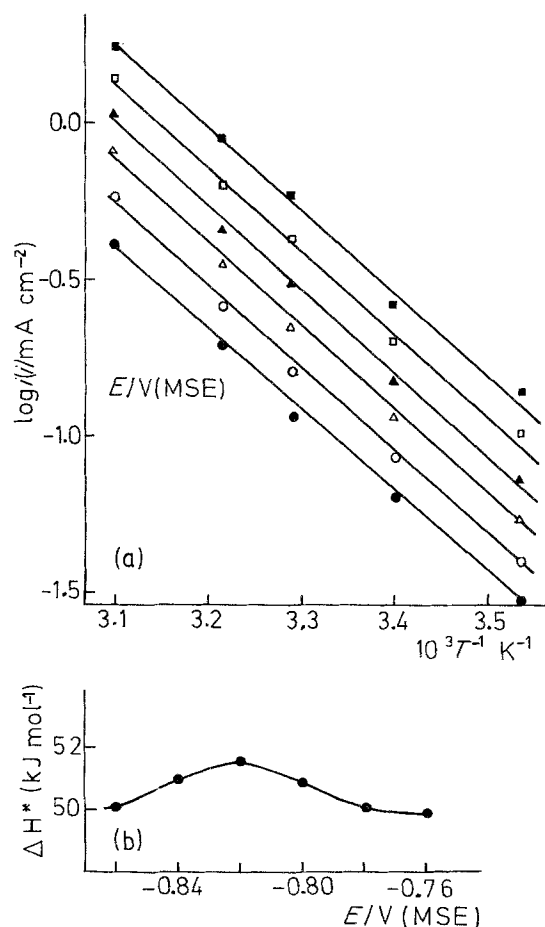


Fig. 3. (a) Dependence of  $\log i$  versus  $1/T$  plots for anodic oxidation of glyoxalate from  $10^{-2}$  M + 0.1 M KOH. (b) Dependence of  $\Delta H^*$  on electrode potentials for anodic oxidation of glyoxalate from  $10^{-2}$  M + 0.1 M KOH.  $E/V$  (MSE) (■)  $-0.76$ ; (□)  $-0.78$ ; (▲)  $-0.80$ ; (△)  $-0.82$ ; (○)  $-0.84$ ; (●)  $-0.86$ .

### 3.2. Influence of temperature on glyoxalate oxidation

The influence of temperature ( $10$  and  $50^{\circ}\text{C}$ ) on the oxidation rate of glyoxalate is illustrated in Fig. 3a, which shows a plot of the logarithm of the current densities ( $\log i$ ) against  $1/T$  (where  $T$  = absolute temperature). The current densities at a given electrode potential are increasing functions of temperature. The apparent activation energy for the process is approximately  $50\text{ kJ mol}^{-1}$  and not greatly dependent on the potential (Fig. 3b).

### 3.3. Effect of varying glyoxalate concentration

Fig. 4 gives the Tafel slopes obtained for glyoxalate oxidation at  $25^{\circ}\text{C}$  in 0.1 M KOH and different glyoxalate concentrations. The values of Tafel slope obtained are equal with the value of  $172 \pm 5\text{ mV}$  per decade. The concentrations of glyoxalate were varied from  $10^{-3}$  M to  $10^{-1}$  M. The resulting reaction order with respect to glyoxalate concentration is 0.6. This reaction order shows a slight variation with the potential in the range  $-0.95$  to  $-0.70\text{ V}$  versus MSE. The fact that the reaction order is never an integer confirms that the mechanism through which glyoxalate is transformed is of a complex nature. For glyoxalate concentrations equal to or higher than  $10^{-1}$  M an inhibition of the electrooxidation is observed.

### 3.4. Variation of the $\text{OH}^-$ concentration

The concentration of KOH was varied over the range  $0.03$  to  $1\text{ M}$ . The values of Tafel slopes obtained are

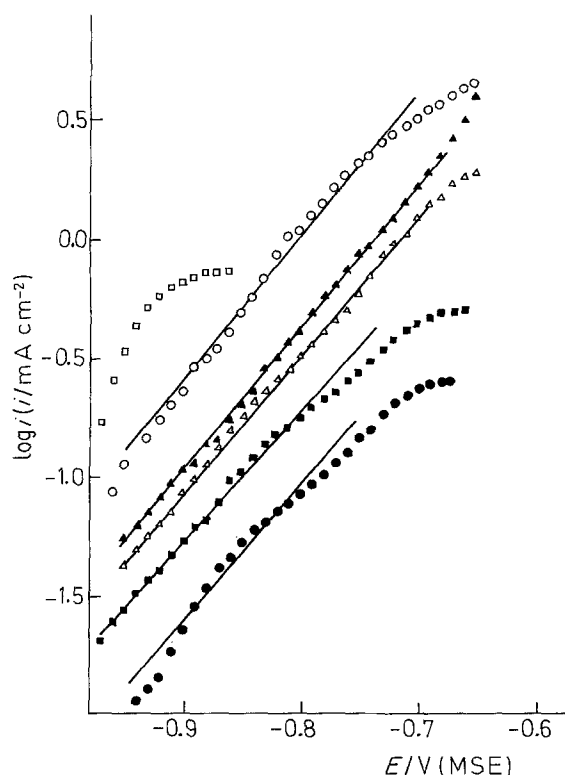


Fig. 4. Tafel slopes for different glyoxalate concentrations in 0.1 M KOH;  $v = 50 \text{ mV s}^{-1}$ . (●)  $2.5 \cdot 10^{-3} \text{ M}$ ; (■)  $5.0 \cdot 10^{-3} \text{ M}$ ; (△)  $1.0 \cdot 10^{-2} \text{ M}$ ; (▲)  $5.0 \cdot 10^{-2} \text{ M}$ ; (○)  $7.5 \cdot 10^{-2} \text{ M}$ ; (□)  $1.0 \cdot 10^{-1} \text{ M}$ .

equal with a value of  $172 \pm 5 \text{ mV}$  per decade (Fig. 5). A reaction order of around 0.3 (Fig. 6) with respect to the  $\text{OH}^-$  concentration is derived. This dependence could mean that the OH coverage or the  $\text{OH}^-$  ions present in solution are involved in the rate determining step. For  $\text{OH}^-$  concentrations lower than that of the glyoxalate an inhibition in the oxidation process is evident.

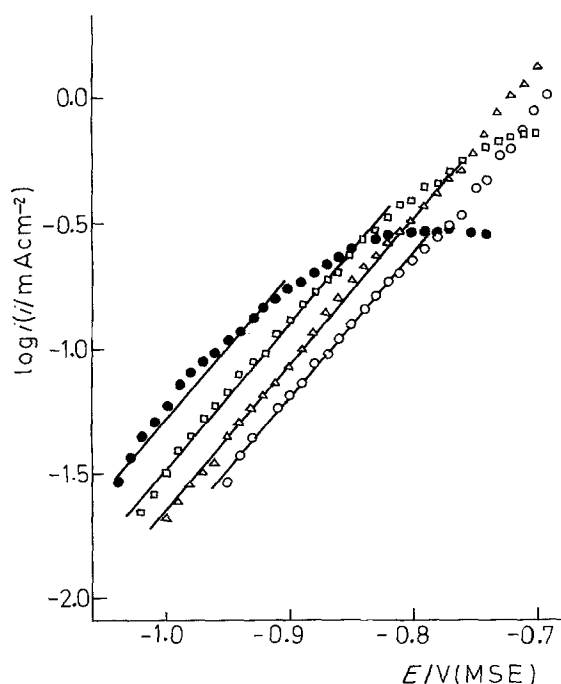


Fig. 5. Tafel slopes at different pH values  $C_{\text{glyoxalate}} = 10^{-2} \text{ M}$ . pH (●) 14.0; (□) 13.7; (△) 13.0; (○) 12.5.

Oxalate was obtained as final product after performing an electrolysis of the glyoxalate solutions for four days on a Pt electrode. The spectrophotometric method was used [24] for the identification of the final products.

### 3.5. Electro-oxidation of glyoxalate on platinum electrodes modified by foreign metal adatoms

Modification of the electrocatalytic activity of platinum electrodes for the electro-oxidation of glyoxalate was investigated using the following metal adatoms: Pb, Cd, Tl, Cu and Cr. The UPD range was between  $-0.330$  and  $-1.230 \text{ V}$  versus MSE, whereas the redissolution potential range is  $-0.880$  and  $0.100 \text{ V}$  versus MSE.

According to Furuya and Motoo [27] and Pletcher [14] the number of the platinum sites which are occupied by one metal adatom is: one (Cu), two (Cd, Pb) or three (Tl).

**3.5.1. Platinum-lead system.** Lead was deposited by UPD from a solution containing small amounts of  $\text{Pb}(\text{NO}_3)_2$  ( $10^{-7} \text{ M}$  to  $10^{-4} \text{ M}$ ). The lead adatoms inhibit the adsorption of the weakly and strongly bound hydrogen [16, 26]. The catalytic influence of the UPD of lead on the oxidation of glyoxalate in the absence and in the presence of lead is shown in Fig. 7. At pH 13 dissolved Pb(II) exists mainly as  $\text{HPbO}_2^-$ .

Lead adatoms cause a significant catalytic effect on glyoxalate oxidation (Fig. 7). This catalytic effect appears only as a modification in the voltammogram recorded during the anodic scan. The maximum catalytic activity occurs at  $5 \times 10^{-6} \text{ M}$  lead concentration (that is also the optimum concentration for 1,2-propanediol [17] and methanol [15] oxidation in 0.1 M KOH). For peak A the current density reaches a value of  $2.79 \text{ mA cm}^{-2}$  whereas the polarization curve is shifted to more negative potentials by about 150 mV. Peak B height diminishes with increasing lead concentrations. At higher concentrations (about  $10^{-4} \text{ M}$  in lead) the catalytic effect is diminished.

**3.5.2. Platinum-cadmium system.** Cadmium was deposited by UPD from a solution containing small amounts of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  ( $10^{-7} \text{ M}$  to  $5 \times 10^{-6} \text{ M}$ ). The hydrogen adsorption is not greatly modified by the presence of these foreign atoms on the platinum surface.

Fig. 8 shows how the presence of cadmium adatoms influences glyoxalate electro-oxidation. During the anodic sweep the current peak A becomes slightly increased, whereas peak B diminishes with increasing adatom concentration. The beginning of the glyoxalate oxidation is shifted by about 325 mV more cathodic when the cadmium concentration is  $10^{-6} \text{ M}$ . If the concentration of cadmium is increased up to  $5 \times 10^{-6} \text{ M}$  a significant inhibition in the electro-oxidation process is obtained, probably due to a blockage of the electrode sites by cadmium adatoms.

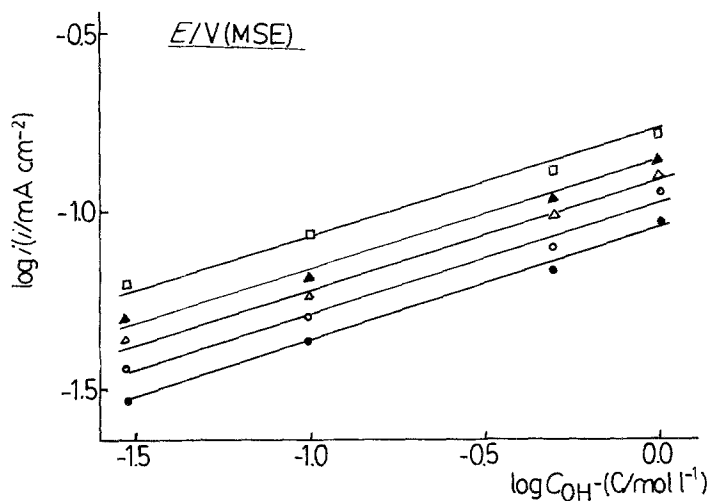


Fig. 6. Variation of  $\log i$  with  $\log C_{\text{OH}^-}$ .  $E/V$  (MSE) ( $\square$ )  $-0.900$ ; ( $\Delta$ )  $-0.920$ ; ( $\blacktriangle$ )  $-0.930$ ; ( $\bullet$ )  $0.940$ ; ( $\circ$ )  $0.950$ .

**3.5.3. Platinum–thallium system.** The UPD of thallium on a platinum electrode was obtained from a  $\text{Tl}_2\text{SO}_4$  solution at  $10^{-7}$  M to  $10^{-4}$  M concentrations. The hydrogen adsorption on platinum is greatly suppressed by thallium adatoms even for low concentrations of  $\text{Tl}_2\text{SO}_4$  [16].

In alkaline medium a considerable enhancement of the electrocatalytic activity is obtained even for small values of adatoms coverage. According to Fig. 9 the concentration which gives an optimum increase in the catalytic activity for the reaction studied would be  $5 \times 10^{-5}$  M in thallium. The current densities are increased up to  $2.20 \text{ mA cm}^{-2}$  for peak A, whereas peak B practically disappears. The shape of the polarization curve is also strongly modified. The oxidation starts at more cathodic potentials by about 200 mV and reaches its maximum at potentials about 400 mV

more cathodic. When the concentration of thallium is increased to  $10^{-4}$  M, bulk deposition takes place and the enhancement becomes slightly inhibited.

**3.5.4. Platinum–copper system.** Copper is dissolved in strong alkaline medium mainly as the soluble species  $\text{CuO}_2^{2-}$ . The UPD of copper adatoms was carried out from solutions containing small amounts of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  ( $10^{-7}$  to  $10^{-5}$  M). The adsorption of weakly bound hydrogen is greatly inhibited by copper adatoms. For concentrations higher than  $10^{-5}$  M bulk deposition occurs [16].

Fig. 10 shows that the presence of copper adatoms gives rise to an optimum catalytic effect for glyoxalate oxidation when copper adatoms are deposited onto platinum by UPD from  $10^{-5}$  M solution of  $\text{CuSO}_4$ . This UPD results in a cathodic shift for the start of the

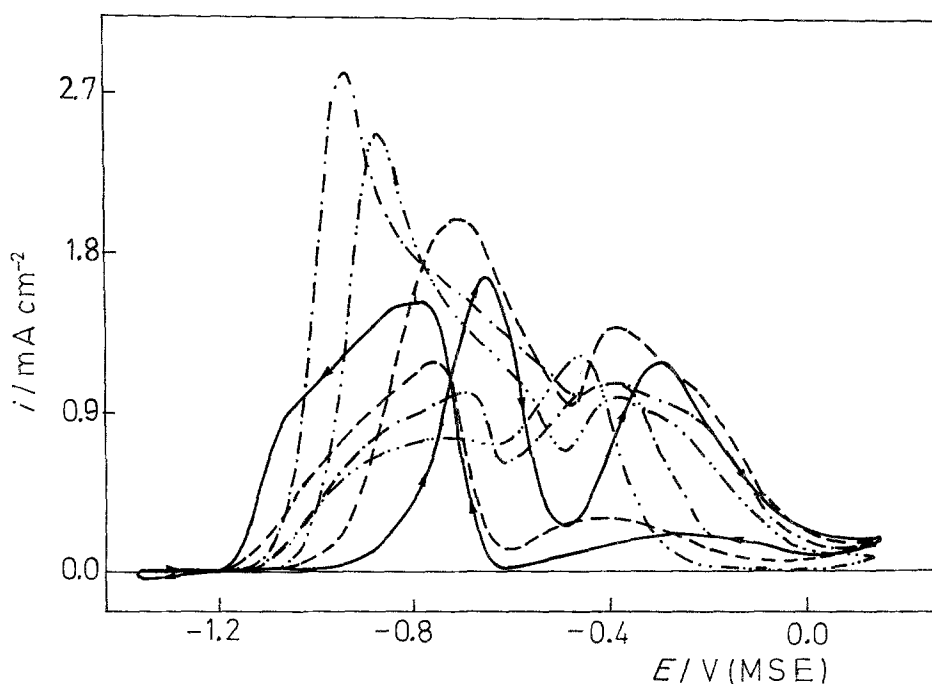


Fig. 7. Voltammograms of a platinum bead electrode modified by UPD of lead ( $0.1 \text{ M KOH}$ ,  $10^{-2} \text{ M glyoxalate}$ ,  $25^\circ \text{C}$ ,  $50 \text{ mV s}^{-1}$ ). Concentrations of lead as indicated. (—)  $0 \text{ M Pb}^{2+}$ ; (---)  $5.10^{-7} \text{ M Pb}^{2+}$ ; (-·-·-)  $5.10^{-6} \text{ M Pb}^{2+}$ ; (····)  $10^{-4} \text{ M Pb}^{2+}$ .

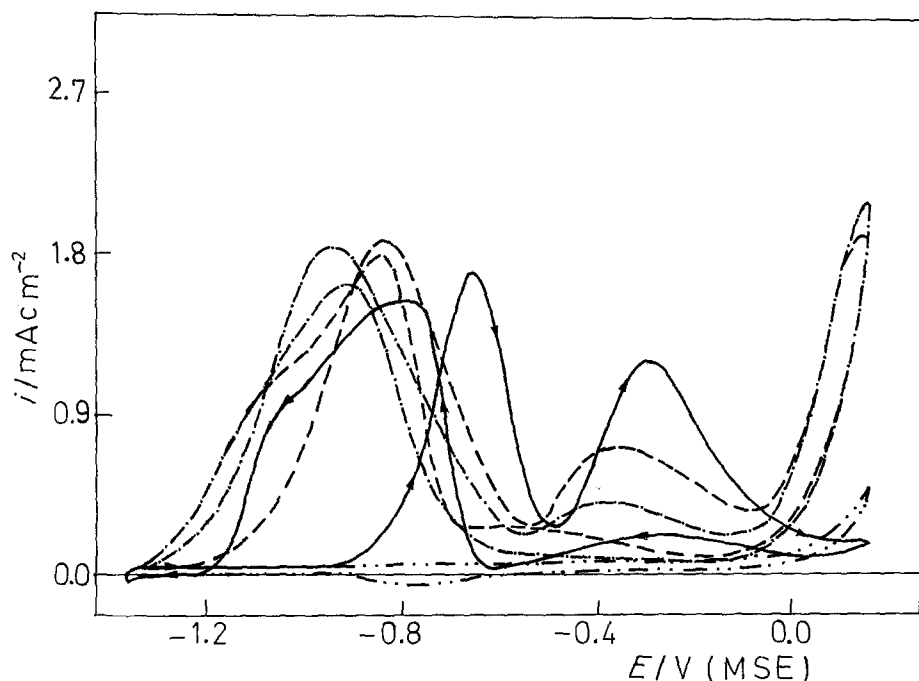


Fig. 8. Voltammograms of a platinum bead electrode modified by UPD of cadmium (0.1 M KOH,  $10^{-2}$  M glyoxalate,  $25^{\circ}\text{C}$ ,  $50\text{ mV s}^{-1}$ ). Concentrations of cadmium as indicated. (—) 0 M  $\text{Cd}^{2+}$ ; (---)  $5.10^{-7}$  M  $\text{Cd}^{2+}$ ; (-·-·-)  $10^{-6}$  M  $\text{Cd}^{2+}$ ; (····)  $5.10^{-5}$  M  $\text{Cd}^{2+}$ .

anodic curve. A strong decrease of the current densities obtained during the positive sweep for the peaks A and B is observed. Likewise, an increase in the adatoms coverage hardly modify the shape and current densities recorded during the cathodic sweep. However, for greater  $\text{Cu}^{2+}$  concentrations, current densities are considerably lowered due to a bulk deposition of copper in the form of multilayers.

3.5.5. *Platinum–chromium system.* The UPD of chro-

mium adatoms was performed from  $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  dissolved in the electrolyte solution (concentration was changed from  $10^{-7}$  to  $10^{-5}$  M). The hydrogen adsorption is not greatly disturbed by chromium adatoms. The presence of chromium adatoms on a platinum electrode hardly changes the shape of the polarization curves for glyoxalate electro-oxidation for all the chromium concentrations considered (Fig. 11). When an optimum concentration of  $10^{-6}$  M is used then  $i_p^A$  and  $i_p^B$  values increase around 30% and 49%

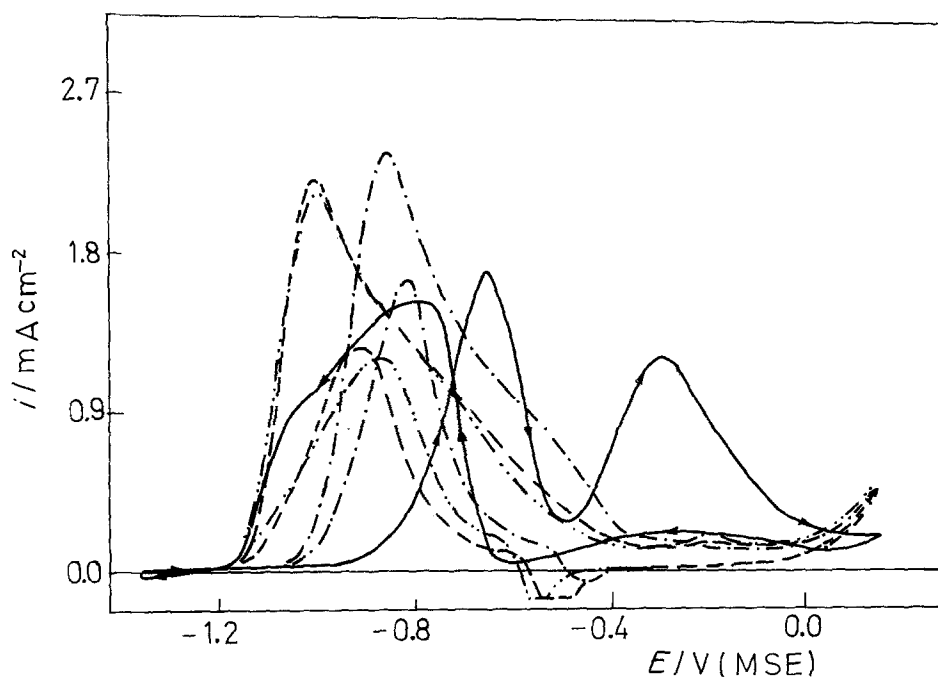


Fig. 9. Voltammograms of a platinum bead electrode modified by UPD of thallium (0.1 M KOH,  $10^{-2}$  M glyoxalate,  $25^{\circ}\text{C}$ ,  $50\text{ mV s}^{-1}$ ). (—) 0 M  $\text{Tl}^{+}$ ; (-·-·-)  $5.10^{-6}$  M  $\text{Tl}^{+}$ ; (---)  $5.10^{-5}$  M  $\text{Tl}^{+}$ ; (····)  $10^{-4}$  M  $\text{Tl}^{+}$ .

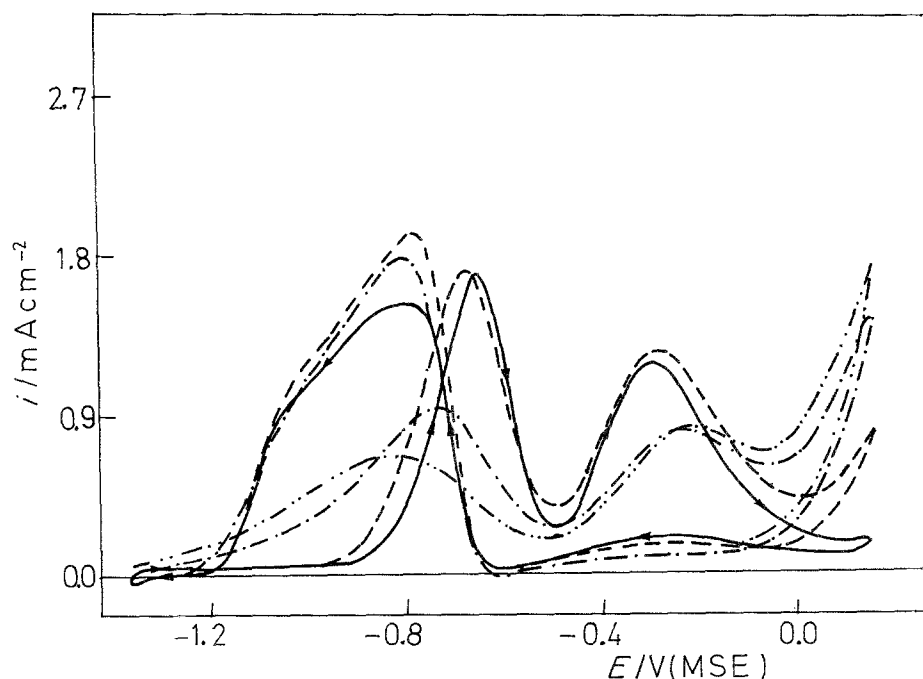


Fig. 10. Voltammograms of a platinum bead electrode modified by UPD of copper (0.1 M KOH,  $10^{-2}$  M glyoxalate,  $25^{\circ}\text{C}$ ,  $50\text{ mV s}^{-1}$ ). (—) 0 M  $\text{Cu}^{2+}$ ; (---)  $10^{-6}$  M  $\text{Cu}^{2+}$ ; (-·-·-·)  $5 \cdot 10^{-6}$  M  $\text{Cu}^{2+}$ ; (····)  $10^{-5}$  M  $\text{Cu}^{2+}$ .

respectively. For chromium concentration higher than  $5 \times 10^{-6}$  M the electrocatalytic activity is lower than that of pure platinum.

#### 4. Discussion

In order to compare the influence of the different adatoms investigated (Pb, Cd, Tl, Cu and Cr) on the electrocatalytic activity of a platinum electrode for glyoxalate oxidation, Fig. 12 shows all the polar-

ization curves obtained during the anodic sweep for the experimental optimum adatom coverages.

The addition of lead and thallium qualitatively exhibits the same effect. Quantitatively the effect is more pronounced for lead adatoms. The cadmium adatoms produce a strong shift of the polarization curves towards more cathodic potentials without increasing the current densities. Copper adatoms also shift cathodically the polarization curves, but current density decreases. As for chromium adatoms, their

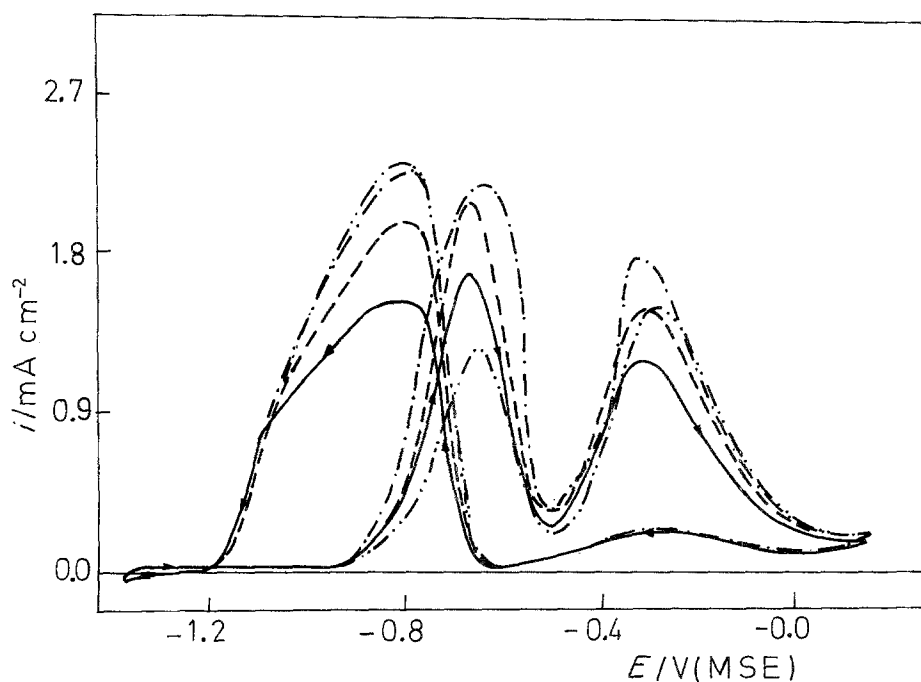


Fig. 11. Voltammograms of a platinum bead electrode modified by UPD of chromium (0.1 M KOH,  $10^{-2}$  M glyoxalate,  $25^{\circ}\text{C}$ ,  $50\text{ mV s}^{-1}$ ). (—) 0 M  $\text{Cr}^{3+}$ ; (---)  $10^{-7}$  M  $\text{Cr}^{3+}$ ; (-·-·-·)  $10^{-6}$  M  $\text{Cr}^{3+}$ ; (····)  $10^{-5}$  M  $\text{Cr}^{3+}$ .

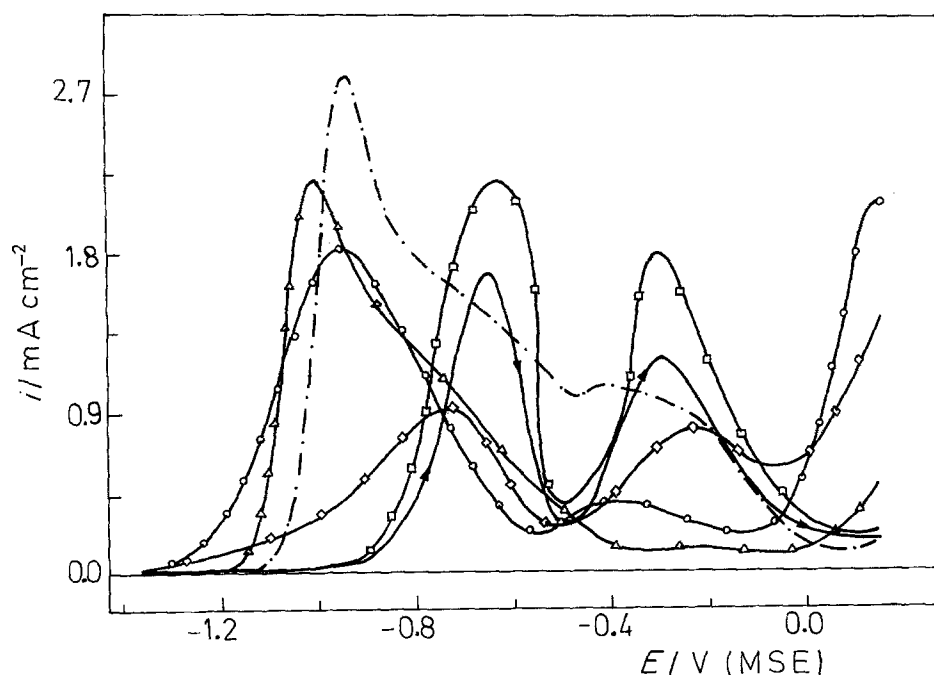


Fig. 12. Anodic polarization curves for the oxidation of  $0.1\text{ M KOH}$ ,  $10^{-2}\text{ M}$  glyoxalate on a pure platinum electrode (—) and on adatom modified platinum electrodes:  $5 \times 10^{-6}\text{ M Pb}^{2+}$  (---);  $10^{-6}\text{ M Cd}^{2+}$  (○);  $5 \times 10^{-5}\text{ M Tl}^{+}$  (Δ);  $5 \times 10^{-6}\text{ M Cu}^{2+}$  (◇);  $10^{-6}\text{ M Cr}^{3+}$  (□).

presence produces a slight increase in the current density. It is clear from the above results that the UPD of every metal ion studied catalyses the direct oxidation of glyoxalate for the optimum foreign metal concentration in solution.

The ratios  $i_{\text{Pt-X}}/i_{\text{Pt}}$  between the current densities for glyoxalate oxidation on the binary system Pt-X (where X = Pb, Cd, Tl, Cu, Cr) and the current densities on pure platinum at the same potential are plotted vs this potential in Fig. 13.

As for the platinum-lead electrode Fig. 13 shows that lead adatoms give a large enhancement in the catalytic activity. The  $i_{\text{Pt-Pb}}/i_{\text{Pt}}$  ratio at low overpotential for  $5 \times 10^{-6}\text{ M}$  lead is 250. This enhancement factor decreases for more anodic potentials. If the concentration of lead is larger than  $5 \times 10^{-6}\text{ M}$  the enhancement effect diminishes.

The platinum-cadmium system gives  $i_{\text{Pt-Cd}}/i_{\text{Pt}}$  ratios (Fig. 13b) greater than unity in the potential range up to  $-0.80\text{ V}$  versus MSE when the concentration of

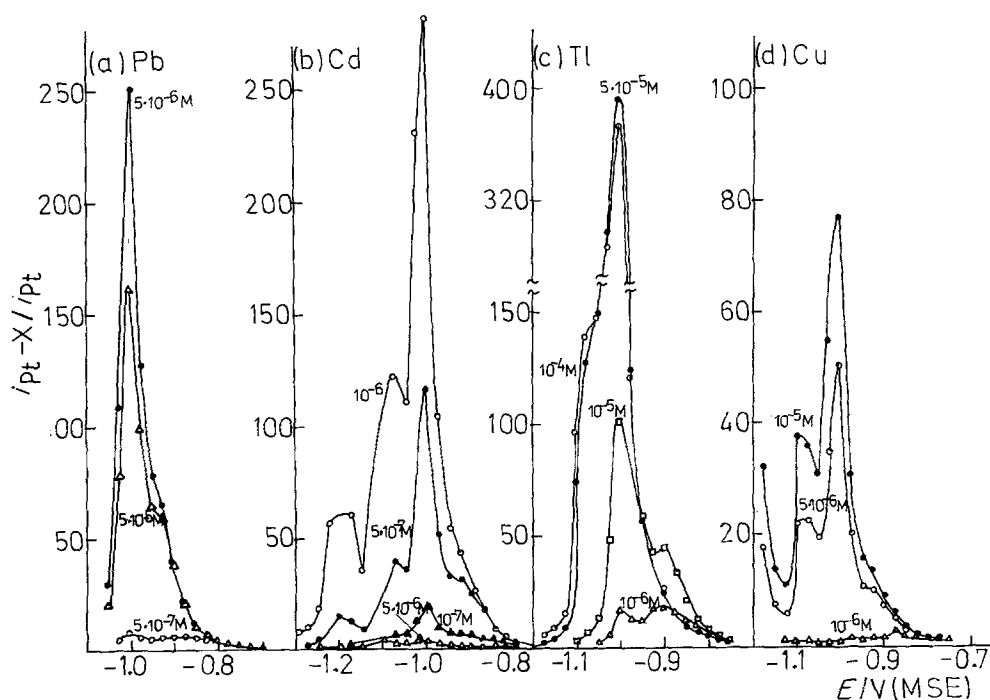


Fig. 13. Ratios between the current densities for  $10^{-2}\text{ M}$  glyoxalate oxidation on a binary electrode Pt-X at different concentrations of X in solution (concentrations are indicated). (a) With  $\text{Pb}^{2+}$ ; (b) With  $\text{Cd}^{2+}$ ; (c) With  $\text{Tl}^{+}$ ; (d) With  $\text{Cu}^{2+}$ .



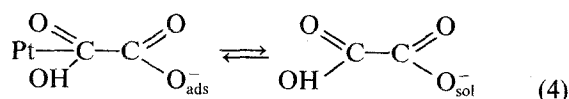
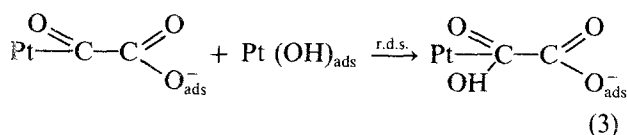
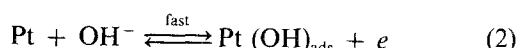
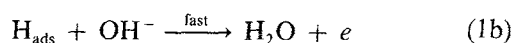
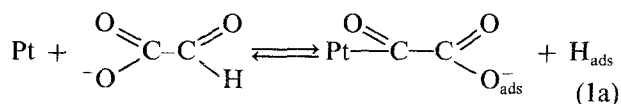
$\text{Cd}^{2+}$  is lower than  $10^{-6}$  M. For the optimum concentration an enhancement of about 280 is obtained at  $-1.00$  V versus MSE.

The platinum-copper electrode shows that copper gives rise to an enhancement in the catalytic activity since  $i_{\text{Pt-Cu}}/i_{\text{Pt}}$  are greater than unity for the potential range up  $-0.850$  V versus MSE and for concentrations larger than  $10^{-6}$  M. At more negative potentials the catalytic activity of the system becomes inhibited.

The platinum-thallium electrode gives  $i_{\text{Pt-Tl}}/i_{\text{Pt}}$  ratios greater than unity at low potentials and for  $5 \times 10^{-5}$  M in thallium the enhancement factor is about 390.

The enhancement of the activity for the platinum-chromium system is very low since the polarization curves are similar to those obtained on a pure Pt electrode.

In order to interpret these results qualitatively it is necessary to propose a possible mechanism for glyoxalate electro-oxidation in alkaline medium in the absence of the metal adatoms. It is known that many organic compounds oxidize on Pt electrodes after a first step of dissociative [27] adsorption. This mechanism could be:



Unlike the cases of the oxidation of alcohols [27] or 1,2-propanediol [17] in acid medium, in the mechanism proposed for glyoxalate oxidation in alkaline medium the first step (dissociative adsorption of glyoxalate) is supposed to be fast. In the proposed mechanism the rate-determining step (r.d.s.) is assumed to be the reaction between the OH coverage and the adsorbed intermediate resulting from the first step. That the r.d.s. should be step 3 is supported by the fractional values of the reaction orders with respect to OH and glyoxalate concentration as well as by the high value of the Tafel slope obtained.

In general it is admitted that the fractional reaction orders indicate complex mechanism in which adsorption steps play an important role [28]. Also, the fact that for pH values lower than 12.5 no electro-oxidation is detected seems to be in agreement with

the supposition of  $\Theta_{\text{OH}}$  playing an important role in the reaction mechanism, i.e. under a critical pH value  $\Theta_{\text{OH}}$  is lower than the required value for a more effective interaction with  $\Theta_{\text{glyoxalate}}$ . Furthermore, the high value measured for the apparent activation enthalpy ( $50 \text{ kJ mol}^{-1}$ ) could be the consequence of a r.d.s. in which both reactants are strongly adsorbed. Likewise,  $E_p$  for peak A shifts more anodic potential values when the glyoxalate concentration increases. An increasing glyoxalate concentration would displace the adsorption equilibrium, giving rise to higher  $\Theta_{\text{glyoxalate}}$  and therefore to a lower number of platinum sites free to become covered with OH radicals. If step 3 is supposed to be the r.d.s. the decrease in  $\Theta_{\text{OH}}$  would demand the application of a higher anodic overpotential in order to carry out the electro-oxidation. Finally, peak A appears at potential values at which a partial coverage of the platinum surface with OH occurs.

The absence of any poisoning species formed by interaction between any glyoxalate adsorption residue and adsorbed hydrogen is shown in Fig. 2a. It can be seen that the variation of the cathodic scan limit scarcely influences the peak currents. The oxidation mechanism must lead from the glyoxalate to the oxalate anion since this is the final product detected. Our experiments show that oxalate is not very oxidizable on a platinum electrode in alkaline medium in the potential range studied. The likelihood of a posterior oxidation of the oxalate formed to  $\text{CO}_2$  or  $\text{CO}_3^{2-}$  is very small.

#### 4.1. Effect of the different metal adatoms on the proposed mechanism

It is now possible to give a qualitative explanation of the effect of the different metal adatoms studied here.

According to the experimental results all the foreign metals studied lead to an enhancement of the electrocatalytic activity of the platinum electrode as shown in the anodic sweeps all together (see Fig. 12). The reason why the foreign metal adatoms enhance the electrocatalytic activity of metal substrates could be the following:

(i) A prevention of the formation of strongly bound intermediates due to the suppression of H adsorption on platinum.

(ii) Formation of a bifunctional catalyst providing different active sites for the adsorption of molecules or radicals participating in the electrode reaction.

(iii) Prevention of electrode surface poisoning by strongly adsorbed intermediates according to the so called third body mechanism.

In alkaline solution, there is no proof of a poisoning effect. Adsorption of the glyoxalate intermediate and of hydroxyls is very important for the oxidation mechanism. When the OH species are coadsorbed on the platinum the organic intermediate is oxidized at more positive potentials.

In the presence of a metal adatom, M, the r.d.s. (3) may be replaced by the following:

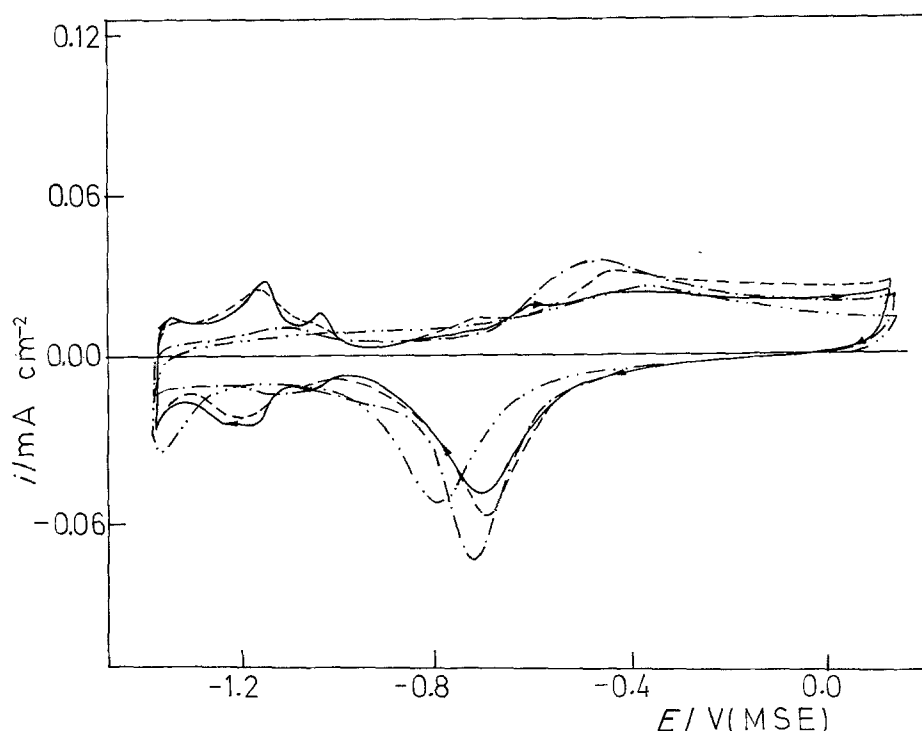
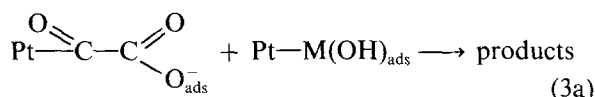
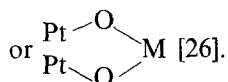


Fig. 14. Voltammograms of a platinum bead electrode modified by UPD of cadmium in 0.1 M KOH, 25°C, 50 mV s<sup>-1</sup>. (—) 0 M Cd<sup>2+</sup>; (---) 10<sup>-7</sup> M Cd<sup>2+</sup>; (-·-·-·) 10<sup>-6</sup> M Cd<sup>2+</sup>; (·····) 5.10<sup>-6</sup> M Cd<sup>2+</sup>.



It is possible that the metal adatom could adsorb on platinum during the anodic sweep giving rise to a coverage in the form of species such as Pt-O-MOH



According to the bifunctional theory of the electrocatalysis developed by Watanabe and Motoo [31], the maximum rate is obtained when  $\Theta_{\text{org}} = \Theta_{\text{OH}} = 0.5$ .

The first group of the foreign metals (lead, thallium) studied gives rise to a great enhancement of the catalytic activity. The redissolution of the bulk foreign metal takes place at about -0.880 V versus MSE before the oxidation of glyoxalate leaves free platinum sites which are able to adsorb glyoxalate molecules. According to the reaction scheme proposed, in step 3 the oxygen containing species OH, would react with

neighbouring glyoxalate adsorbate  $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \end{array}-\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O}^-_{\text{ads}} \end{array}$

groups in a surface reaction leading to the oxidation of glyoxalate to oxalic acid. On a platinum electrode this OH or O is donated by platinum at more anodic potentials than -0.800 V versus MSE.

There is no evidence that Pb(0) and Tl(0) adatoms cause OH radicals to be adsorbed at more negative potentials than on a bare platinum surface but in the range 0.730, -0.430 V versus MSE, the hydroxyl radicals are able to adsorb on the few metal adatoms remaining at a platinum surface, and the reaction 3a is favoured.

The second anodic peak B which inhibits in the Pt-O region in the absence of UPD layers could be assigned to strong interactions between cations and Pt-O [30].

In the second group of the metal adatoms cadmium favours the formation of (OH)<sub>ads</sub> at lower potentials than that on pure platinum because they display some ionic character [31]. Fig. 14 shows the enhancement of the Pt-OH coverage formation brought about by the presence of cadmium adatoms on the platinum surface which are more easily oxidizable than platinum. A shift of the polarization curve towards more cathodic potentials is recorded although the magnitude of the current is very slightly modified in this case.

For copper adatoms redissolution occurs in the potential range of glyoxalate oxidation (for Cu(II) concentrations lower than 10<sup>-6</sup> M). The coverage with organic substance seems not to change appreciably with the adatom surface concentration for concentrations in solution lower than 10<sup>-6</sup> M. For concentrations greater than 10<sup>-6</sup> M a negative shift of the beginning of the anodic curve is obtained. This behaviour is similar to that observed with cadmium adatoms although the current density is not so high in this case.

Chromium adatoms do not greatly change the polarization curve. Adatom redissolution occurs in the potential range (-0.800 to -0.700 V versus MSE) in which glyoxalate oxidation starts and for this reason the organic substance coverage,  $\Theta_{\text{org}}$ , is not modified.

In conclusion, all metal adatoms studied in the present work increase the electrocatalytic activity of a platinum electrode in alkaline medium for glyoxalate oxidation. The greatest electroactivity is obtained at very small concentrations of the precursor salts. When

the coverage is increased the UPD layer may form a superlattice structure with properties close to the bulk metal. This enhancement may be explained through the bifunctional theory of electrocatalysis.

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