

de Investigação Científica no âmbito do Centro de Processos Químicos da Universidade Técnica de Lisboa. Graças à colaboração do Doutor Luis J. Alcácer foi possível utilizar o equipamento de voltametria cíclica existente nas instalações do Laboratório Nacional de Engenharia e Tecnologia Industriais em Sacavém. Os autores desejam exprimir os seu reconhecimento por estes apoios.

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THE EFFECT OF SOLUTION COMPOSITION ON THE CATALYTIC ACTIVITY OF
Pt/Pb ADATOM ELECTRODES FOR FORMIC ACID OXIDATION

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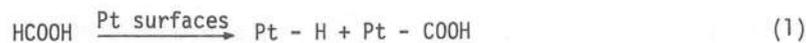
The oxidation of formic acid at Pt electrodes partially covered by Pb adatoms has been studied in perchlorate media of pH 0-2. It is shown that although the rate of oxidation of formic acid can be fast (i.e. effectively diffusion controlled) in all these solutions, there is a definite medium effect on the predissociation step $\text{HCOOH} \rightarrow \text{H}_{\text{ADS}} + \text{COOH}_{\text{ADS}}$.

It is also shown that low concentration of chloride ion (10^{-5}M) have a very adverse effect on the catalytic activity of the Pt/Pb surfaces.

INTRODUCTION

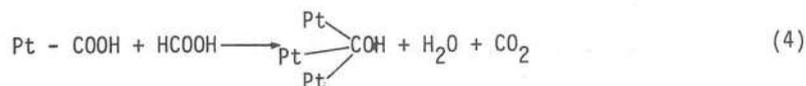
An earlier paper¹ has reported a study using potential sweep and, particularly, potential step methods, of the oxidation of formic acid at a Pt electrode partially covered by Pb adatoms. It was concluded that

(a) the oxidation of formic acid occurs by the mechanism first proposed by Capon and Parsons² i.e.



where the predissociation reaction (1), which leads to rapidly oxidised adsorbed intermediates, and diffusion of formic acid to the electrode surface have similar rates.

b) the role of the Pb adatoms is to prevent the formation of surface poisons by reaction such as



which otherwise rapidly reduce the rate of oxidation of formic acid. Whatever, the exact structure of the poison, it was suggested that its formation requires 3 or more adjacent Pt sites on the surface and that the Pb adatoms arrange themselves on the surface to allow a large number of sites where there are two adjacent Pt atoms (for reaction (1) to occur) but few sites with three adjacent Pt atoms where poison can form^{1,3}.

This paper examines the effect of electrolyte composition and pH on the rate of oxidation of formic acid at Pt/Pb adatom surfaces.

Certainly, in reactions where the properties of the surface are crucial, the adsorption of anions and organic species must be expected to have a large effect on reactions involving adsorbed intermediates⁴⁻⁶. In this

paper chloride ion was selected as an anion known to adsorb at Pt.

EXPERIMENTAL

The experimental results are very adversely affected by impurities in solution and also depend on the history of the Pt surface. Hence all solutions and glassware were carefully prepared by procedure described in detail in a previous paper¹.

The electrochemical measurements were carried out with a Hi-Tek potentiostat type DT 2101 and function generator, type PPR1. I-t transients were recorded using a Gould type OS 4100 Digital Storage Oscilloscope, I-E curves using a Hewlett Packard XY recorder and charges using a Hi-Tek gated integrator. The electrochemical cells (two were used in parallel, one filled with the solution under study and the other filled with 1M HClO₄) had two compartments. The working electrode was a Pt wire of geometric area 0.29 cm² and it was transferred between cells as necessary to maintain a check on its real surface area and state of cleanliness. The reference electrode was a laboratory constructed H₂ electrode separated from the working electrode by a Luggin Capillary. The counter electrode was a Pt gauze in the form of a cylinder around the working electrode.

Before each set of experiments the Pt working electrode was cleaned chemically with H₂SO₄ / HNO₃ and then washed thoroughly with triply distilled water. The electrode was then cleaned periodically by potential cycling at 10Vs⁻¹ between +20 and +1600mV in the base electrolyte. Experiments were only continued if the cyclic voltammogram had the classical shape for a clean system, see figure 1.

The real surface area was obtained by dividing the charge under the hydrogen desorption peaks by that for the formation of a monolayer of adsorbed hydrogen, i.e. 210 μC cm⁻². The roughness factor was always close to 2.

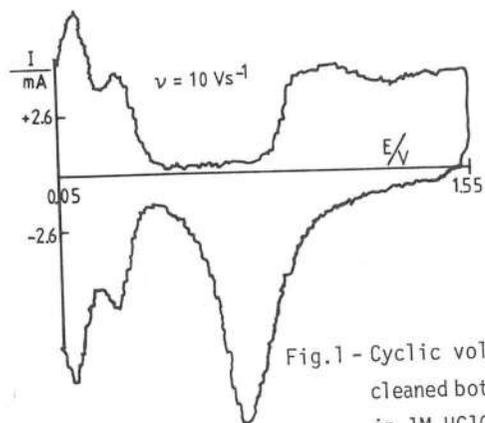


Fig.1 - Cyclic voltammogram for a Pt wire electrode, cleaned both chemically and electrochemically, in 1M HClO₄. Potential scan rate 10 Vs⁻¹.

RESULTS AND DISCUSSION

Figure 2 shows a cyclic voltammogram for the solution 1M HClO₄ + 10⁻³M Pb(NO₃)₂ run at 0.2 Vs⁻¹.

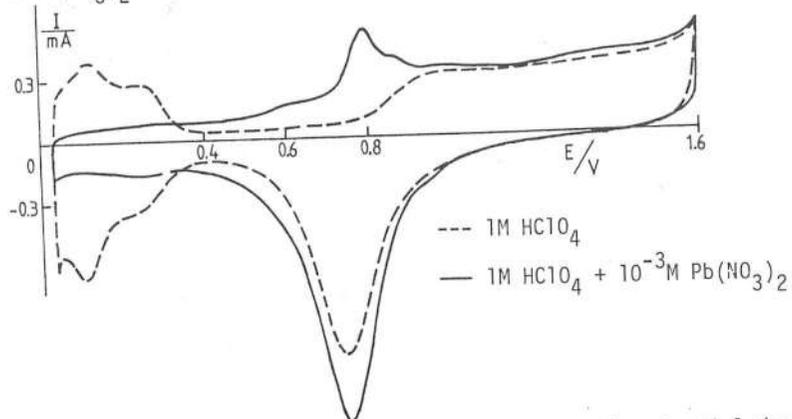


Fig. 2 - Cyclic voltammograms to show the underpotential deposition of Pb on Pt. Potential scan rate 0.2 Vs⁻¹.

The charge for the formation of an underpotential lead monolayer is observed between +0.8 and +0.4V, but the peaks for the removal of this monolayer are more clearly seen on the sweep towards positive potentials. The complete monolayer of Pb can also be seen to almost entirely prevent the formation of adsorbed hydrogen (see the potential region +0.3 to 0V) and this shows that

with lead the monolayer has a closely packed structure. The voltammogram is closely similar to those reported by earlier workers^{1,7}. Similar cyclic voltammograms were also obtained for solutions 0.1M HClO₄ + 0.9 NaClO₄ and 0.01M HClO₄ + 0.99M NaClO₄. In each case, the coverage of the Pt surface by Pb adatoms were determined by a potential step procedure¹ and $\theta_{Pb} = 0.5$ was found to occur close to +0.6V for all three solutions. Figure 3 shows cyclic voltammograms for the solutions 1M HClO₄ + 0.1M HCOOH, 1M HClO₄ + 10⁻³M Pb(NO₃)₂ + 0.1M HCOOH and 0.01M HClO₄ + 0.99M NaClO₄ + 10⁻³M Pb(NO₃)₂ + 0.1M HCOOH.

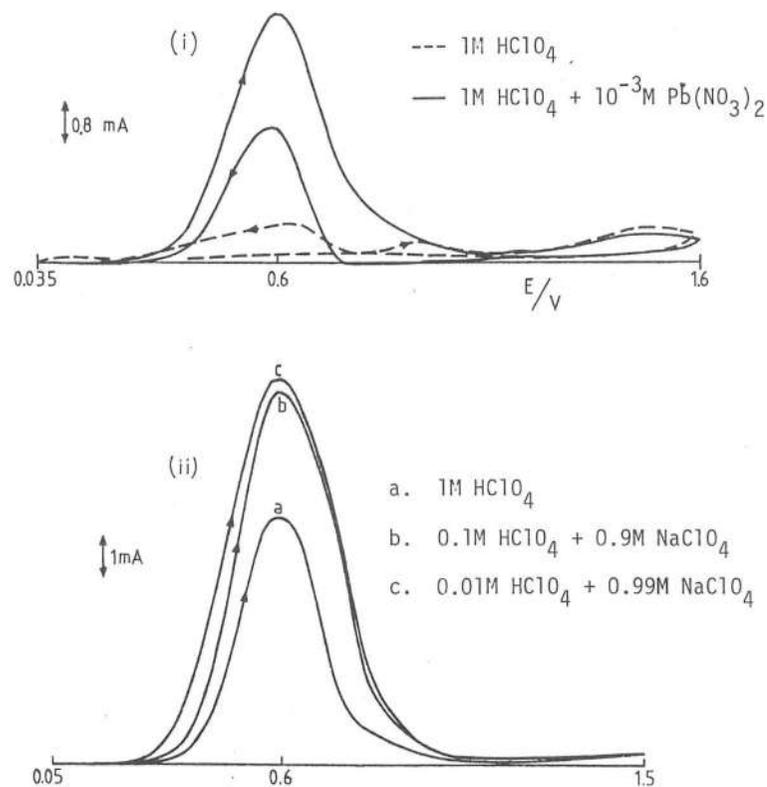


Fig. 3 -(i) Cyclic voltammograms showing the influence of Pb adatoms on the oxidation of formic acid (0.1M). Pt electrode. 0.1Vs⁻¹.

(ii) Linear potential sweeps to show the influence of pH. Solutions contain 0.1M HCOOH and 10⁻³M Pb(NO₃)₂. Pt electrode. 0.1Vs⁻¹.

The catalytic effect of the presence of the lead ion in solution is immediately obvious and has been noted before^{1,3,7}. The peak in the voltammograms reflect changes in θ_{Pb} , the fraction of surface covered by Pb adatoms and for both solutions the maximum occurs at the potential where $\theta_{Pb} = 0.5$. When $\theta_{Pb} > 0.5$, some of the surface contains no Pt atoms on which oxidation of formic acid can occur, while for $\theta_{Pb} < 0.5$ enough Pt atoms are exposed for poison to begin to form. This figure shows for the first time, however, that pH also influences the I-E responses and the solution of pH 2 leads to a large peak.

The effect of solution composition was then continued using potential step techniques. The I-t transients in response to potential steps from +0.2V to +0.6V were recorded for perchlorate solutions of pH 0, 1 and 2 but of constant ionic strength (1M) and each containing $10^{-3}M Pb(NO_3)_2$ and 0.1M HCOOH. The transient for pH 0 is shown in figure 4.

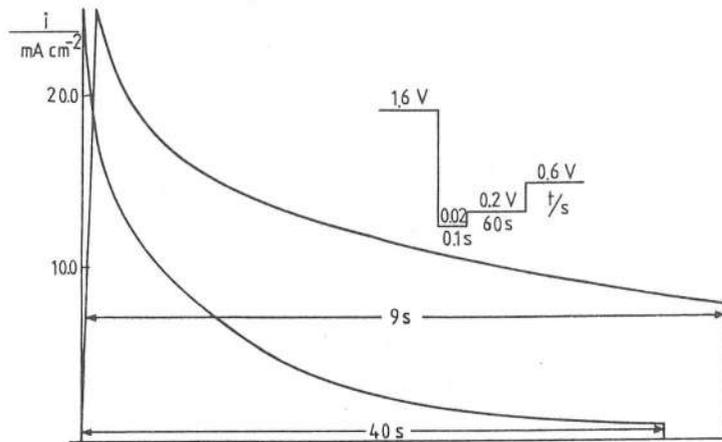


Fig. 4 - I-t transients in response to the potential step 0.2V \rightarrow 0.6V. Pt electrode in solution 1M HClO₄ + $10^{-3}M Pb(NO_3)_2$ + 0.1M HCOOH.

The major feature of this curve is the very high current density compared to experiments in the absence of Pb²⁺. Moreover the catalytic activity is maintained for extended periods of time. Indeed, analysis of the transients, figure 5, shows that after a few seconds, the current becomes and remains

controlled by the rate of diffusion in solution of formic acid.

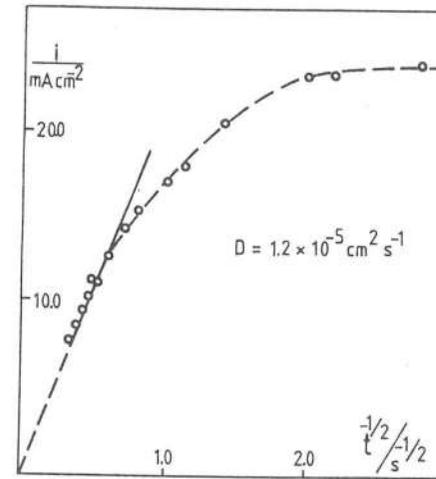


Fig. 5 - Data of figure 4 replotted as i vs $t^{-1/2}$.

The deviation from diffusion control at short times has been attributed to kinetic control by the rate of predissociation of the C-H bond in formic acid, reaction(1) and the procedure of Delahay and Oka⁸ and the equation of Pletcher and Solis¹ may be used to obtain the value of the rate constant for reaction (1). Such analysis were carried out for each of the perchlorate solutions and the results were reported in table I.

T A B L E I

Solution*	$10^5 D_{HCOOH} / cm^2 s^{-1}$	$10^2 k^+ / cm s^{-1}$
1M HClO ₄	1.2	1.6
0.1M HClO ₄ + 0.9M NaClO ₄	1.0	3.2
0.01M HClO ₄ + 0.99M NaClO ₄	1.0	>5.0
1M HClO ₄ + $10^{-5}M Cl^-$	1.4	0.7

* All solutions also contain $10^{-3}M Pb(NO_3)_2$ + 0.1M HCOOH.

+ Calculations of K assume $\theta_{Pb} = 0.5$ at the potential of I_{max} .

It can be seen that the rate constant for the predissociation reaction (1), K , increases with pH and, indeed, at pH 2, the value is too high to be determined by the technique employed, i.e., the $I-t$ transients appear to be mass transfer controlled over the whole time regime employed. The value for the diffusion coefficient for formic acid does not vary within experimental error.

The catalytic activity of the Pt/Pb atom electrodes were investigated as a function of potential by carrying out a series of potential step experiments and determining the charge passed during the first 1s of oxidation. The results are presented in figure 6.

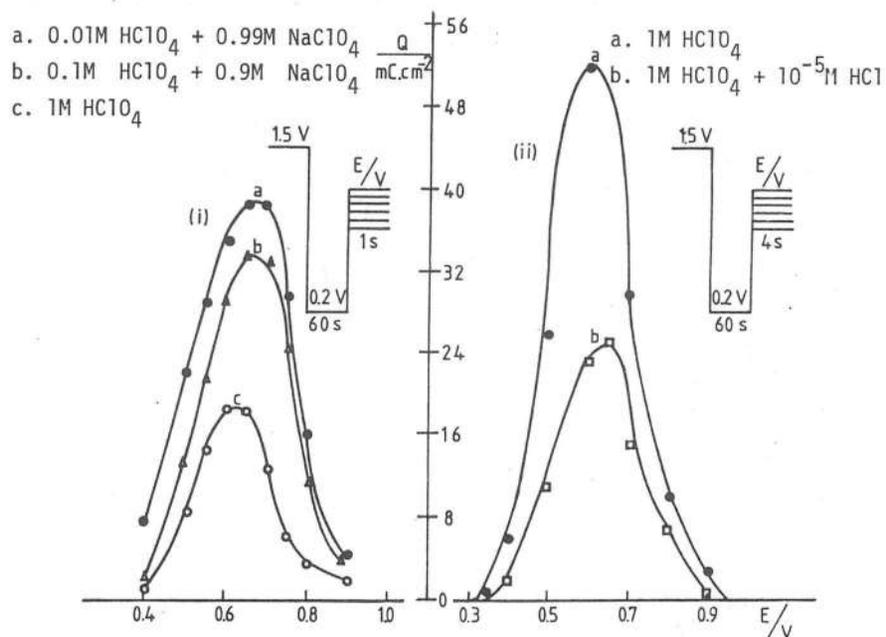


Fig. 6 - (i) Effect of pH on the Q vs E plots for a series of potential steps. The first 1s of the transients was integrated. Pt electrode. All solutions contain 0.1M HCOOH and 10^{-3} M $\text{Pb}(\text{NO}_3)_2$.

(ii) Effect of Cl^- on the Q vs E plots. The first 4s of the transients were integrated. Pt electrodes. Solutions contain 0.1M HCOOH and 10^{-3} M $\text{Pb}(\text{NO}_3)_2$.

It should be noted, however, that this data totally emphasizes the differences in the kinetics of reaction (1) and in almost all the pulse experiments carried out, the current would take up the same values, the diffusion limited current, after a period of 1-50 s (depending on the solution). It can be seen from the figure that the activity increases with pH as expected from the data in table I. It is also instructive to estimate the charge for this experiment if the current is always diffusion controlled. This charge is obtained by integrating the well known equation for the current i.e.

$$Q = \int_0^t \frac{AnFD^{1/2}c}{\pi^{1/2}} t^{-1/2} dt = \frac{A 2nFD^{1/2}c}{\pi^{1/2}} t^{1/2}$$

and the charge obtained by substituting $n = 2$, $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and making allowance for the fact that figure 6 is plotted in terms of real surface area (the diffusion current depends only on geometric area), is 40 mC cm^{-2} . This is very close to the value obtained for the peak charge at pH 2. At this pH and potential, the current is mass transfer controlled at almost all times. In contrast, the value of K at pH 0 is low enough that there is a kinetic limitation of the current for a large part of the 1s experiment. The dependence of the charge on the potential, of course, again arises because of the variation of the lead coverage with potential.

The effect of chloride ion was also studied and some results for 10^{-5} M Cl^- are reported in table I and figure 6. It can be seen that chloride strongly depresses the catalytic activity of the surface and higher concentrations are totally catastrophic.

CONCLUSIONS

The rate constant for the dissociation of the C-H bond of formic acid at Pt increases with pH in the range 0-2. This leads the current and hence the oxidation charge for formic acid at short times to vary with pH. However, because of the values of K , the current becomes diffusion controlled

after a period in all solutions investigated; hence the transients beyond a certain time are the same for all solutions. In perchloric acid solutions, Pb atoms are clearly an effective catalyst for formic acid oxidation but Cl^- ion has a deleterious effect on the activity of the system.

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FOTOFEITOS EM FILMES ANÓDICOS DE COBRE

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INTRODUÇÃO

A corrosão e passivação de metais depende da termodinâmica dos sistemas e, variando o pH e o potencial, pode passar-se duma situação corrosiva a passiva.

O estudo dos filmes anódicos tem sido feito utilizando diferentes métodos - in-situ e ex-situ - e sabe-se que muitos dos filmes passivantes apresentam propriedades semicondutoras. O uso da espectroscopia de fotocorrente, como método in-situ, tem revelado que os conceitos da electroquímica de semicondutores podem ser estendidos a estes sistemas.

Devido, provavelmente, às conhecidas propriedades semicondutoras tipo-p do Cu_2O , a passivação electroquímica do cobre tem, recentemente, suscitado grande interesse [1-3], em particular o comportamento electroquímico do cobre em soluções alcalinas [4,5]. Conhecem-se, pois, as variações electroquímicas e dispõe-se de informação sobre os passos da oxidação do eléctrodo de cobre [6-8]. No entanto, não foi ainda estabelecida uma plena sequência para o ciclo completo.

Neste trabalho, utilizaram-se medidas de fotocorrente que, além duma informação quantitativa, permitem propôr uma tal sequência.

† O estudo do sistema concernente a esta comunicação mereceu, dos autores indicados, posterior desenvolvimento. O trabalho será publicado em revista da especialidade.