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POTENTIAL OSCILLATIONS BY THE ANODIC METHANOL OXIDATION

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ABSTRACT - In the anodic methanol oxidation in aqueous sulphuric acid on smooth Pt-electrodes using the chronopotentiometric method, oscillations of potential in the $V=V(t)$-curves have been observed. The evolution of such potential oscillations with the value of the current impulse imposed on the electrodes has been discussed and a reaction mechanism of the methanol oxidation has been proposed in accordance with the experimental results.

KEYWORDS - Methanol oxidation, potential oscillations, chronopotentiometry

INTRODUCTION

The energy problem either taken alone or considered together with the protection of the environment has attracted the attention of many people all over the world. The aim has been to find alternative non-pollutant sources of energy. Among non-pollutant alternative sources of energy are the fuel cells. Given the possibility to the consumption in fuell cells of small organic molecules such as methanol, formic acid and formaldehyde (CH_3OH, HCOOH, H_2CO) to get clean electric energy, a lot of papers on their anodic oxidation have been published. Most of the publications in the last ten years have been concerned with the identification of the intermediate species and/or "poisons", with the aim of proposing an acceptable reaction mechanism. Great value has been assigned to the "in situ" spectrometric results, especially those obtained by EMIRS, Electrochemically Modulated IR Spectroscopy, IRRAS, Infra Red Reflection-Absorption Spectroscopy, DEMS, Differential Electrochemical Mass Spectroscopy and ECTDMS, Electrochemical Thermal Desorption Mass Spectrometry. There seems to be no doubt about the participation of the carbon monoxide CO, as intermediate species (or "poison"), adsorbed on the electrode linearly (CO-Pt) or in bridge $CO(Pt)_2$, in the electrochemical oxidation of the three above mentioned molecules. As regards the methanol oxidation, it seems that the aldehyde carbonyl group CHO (or COH) is an intermediate species too ("poison" or not) [1,2,3,4,5, 6, 7]. The instability of the electrode process, appearing as current or potential oscillations, is an experimentally observed fact which has attracted the atention of several investigators [8-13, 17-30]. Such instability concerning the anodic methanol oxidation, by chronopotentiometry, at platinum-electrodes in sulphuric acid solution, appearing as potential oscillations in the V=V(t)-curves, will be discussed here. When a potentiostatic or potentiodynamic method such as the potential sweep voltammetry is being used, the same instability appears naturally as current oscillations, if the required conditions are met. The above mentioned instability has already been reported concerning the anodic oxidation of formaldehyde and formic acid [3, 12-16], but until now no report of it has been made as far as we know, concerning the anodic oxidation of methanol. The required conditions for the appearance of those oscillations in the anodic methanol oxidation by chronopotentiometry on Pt-electrodes in sulphuric acid solutions are not those reported to the formiate oxidation [1].

EXPERIMENTAL

The instruments used in the measurements described here were: (a) a potentiostat **Wenking**, (b) an oscillograph **Tetronix** type 533A, or a XY-register **Hewlet & Packard** type 7033B, (c) a function generator **Exact Electronics** type 250, (d) an electric voltage source **Rohde & Schwarze** type NGU BN95140 and (e) a glass cell as shown in fig.1 .

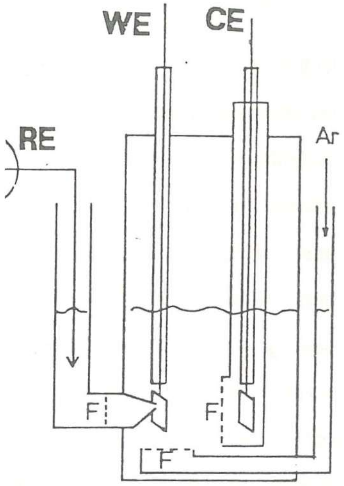

Fig.1- Glass cell. CE, counter electrode; WE, working electrode; RE, reference electrode; F, glass filter.

The potentiostat was used mainly to keep the working electrode at a fixed potential for a short period before imposing the current impulse [35]. The value of the current impulse, which was a function of the externally selected values of potential and resistance, was precisely measured.The cell resistance was negligible compared with that of the whole circuit. In order to take a V=V(t)-curve,the current source and the oscilloscope were connected and the potentiostat disconnected simultaneously, using a mercury key.

The sulphuric acid solutions were prepared with a. g. reagent (Riedel de Häen) and de-ionized distilled water. The methanol (dried) was supplied by Merck.

Before every set of galvanostatic measurements, a potential sweep voltammetry diagram was registered in order to calculate the roughness factor, after having activated the working electrode properly by varying the potential between the values of H_2 and O_2 evolution. The potential was measured against the calomel electrode. The geometric area of the working electrode was 2.2 cm^2. Thereafter methanol was added to the central body of the cell in fig.1. The solution was deaerated by argon or another suitable inert gas, in order to withdraw the oxygen from it before adding methanol to the cell and thereafter with the view to accelerating its diffusion. The current pulse was stopped immediatly after the transition time had been reached, in order to avoid reaching the potential of the oxygen evolution value [32, 33, 34].

RESULTS AND DISCUSSION

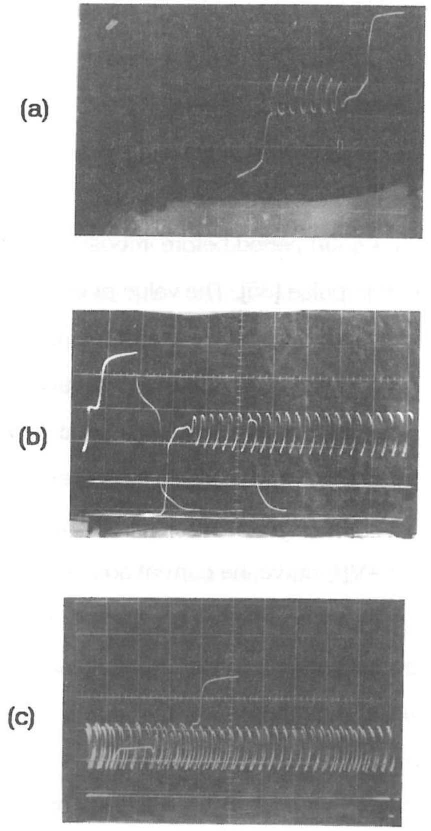

Fig.2 - Chronopotentiograms on Pt at 25º C; vert. axis:200 mV/cm; hor. axis: 5 s/cm; j = 10.05 mA.

In this paper we report the potential oscillations observed in the chronopotentiometric V=V(t)-curves by the anodic methanol oxidation in sulphuric acid solutions on platinum electrodes and show their importance by proposing a reaction mechanism. Such oscillations have well defined properties, shape, frequency and amplitude, whose evolution as a function of time and current impulse value is easy to follow. Sets of chronopotentiometric measurements were made at different temperatures and sulphuric acid concentrations. Some V=V(t)-curves were selected for discussion. In fig.2 a, b, c, there are three V=V(t)-curves, where the above mentioned oscillations can be seen. All the curves were recorded using the same galvanostatic pulse value, j = 10.05 mA, but changing the methanol concentration: fig.2a, c_1 = 0.25 M, fig.2b, c_2 = 0.50 M, fig.2c, c_3 = 0.75 M (the measurement was continued at c_4=1.00 M, the transition time was then measured also by a chronometer). A saturated calomel electrode was used as reference electrode. In all these diagrams the vertical and the horizontal axis are 200 mV/cm and 5 s/cm worth, respectively. The working temperature was 25º C.

Taking eq.(1)

V=V(t)-curves is an increasing function of the methanol concentration,fig.4. The experimental points fit a first degree polynomial quite well. Fig.5 shows the evolution of the number of periods of the oscillatory part of the V=V(t)-curve with increasing methanol concentration.The experimental points fit quite well to a third degree polynomial. Now let us discuss the V=V(t)-curves obtained at 30º C, in methanol $2.5 \cdot 10^{-2}$ M in 0.5 M H_2SO_4, on Pt-electrodes.

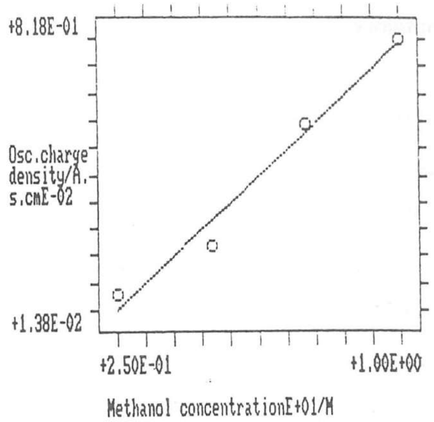

Fig.4 - Oscillating charge density against methanol concentration.

The activation condition of the working electrode is shown in fig.6. A charging curve in 0.5 M H_2SO_4 without methanol, can be seen in fig.7 (curve 1). In the same figure (curve 2) a chronopotentiogram obtained after adding methanol until $2.5 \cdot 10^{-2}$M can be seen. Comparing the chronopotentiogram (curve 2, fig.7) with the charging curve (curve 1, fig.7), it becomes clear that the methanol oxidation occurs between about 360 mV and 425 mV, against a saturated calomel electrode These potentials belong to the double layer charging potential interval, as can be seen in fig. 6. and fig. 7 (curve 1). At 410 mV (s.c.e.) the electrode starts oscillating. As has been pointed out earlier, the chronopotentiogram has two distinct parts: pre-oscillating and oscillating. In the oscillation part of the curve most points of the oscillation peaks go more or less symmetrically and attain potentials from 500 mV to 550 mV

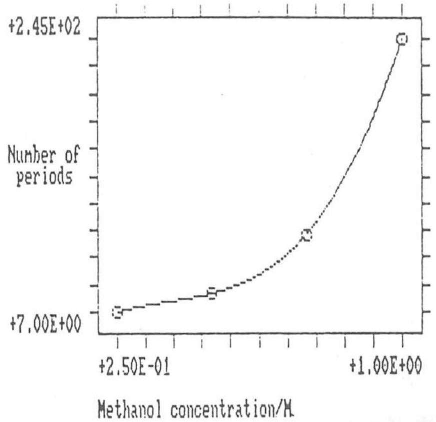

Fig. 5 - Number of periods/methanol concentration.

$$j \cdot t_t^{1/2} = (1/2)\cdot(n\, F\, \pi^{1/2}\, D_{red}^{1/2}\, C_{red}^{o}), \qquad (1)$$

obtained for a redox reaction like

$$S_{red} \;=\; S_{ox} + n\, e^-, \qquad (1a)$$

whose rate depends only on the diffusion of the species (S_{red}) to the electrode, and introducing in it the experimental values of current density j, transition time t_t, and methanol concentration in the bulk solution C^o, concerning the V=V(t)-curves in fig.2 on the whole, the curves in fig.3 were obtained. In fig.3, the product $j \cdot t_t^{1/2}$ appears as an increasing function of the methanol concentration and of the square root of the transition time, curve 1 and 2, respectively, fitting well to first degree polynomials: $y_i = a_i + b_i x$. Both can be taken as calibration curves for determining the methanol concentration in identical working conditions (electrode surface, pH and temperature). We intend to show the instability of the above mentioned anodic process, expressed by the oscillations in the V=V(t)–curves in fig.2. They cannot be forgotten by proposing a reaction mechanism and a valid mechanism cannot contradict them.

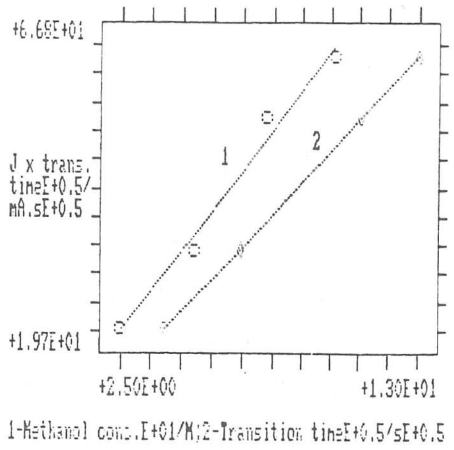

Fig.3 - Curve 1: $j \cdot t_t^{1/2}$/meth. conc.; curve 2: $j \cdot t_t^{1/2} / t_t^{1/2}$.

It can now be observed that these curves (fig.2) are made up of two different parts: non-oscillating and oscillating. Both parts are an increasing function of the methanol concentration, but in the present experimental conditions the increase of the oscillatory part of the V=V(t)–curves is clearer than the increase of the other part, as can be seen, by comparing diagrams a, b and c, in fig.2 . The oscillatory charge corresponding to the oscillatory part of the

(s.c.e.). These potentials values are closer to those where the electrode starts oxidizing, and definitely under the forward metanol oxidation peak.

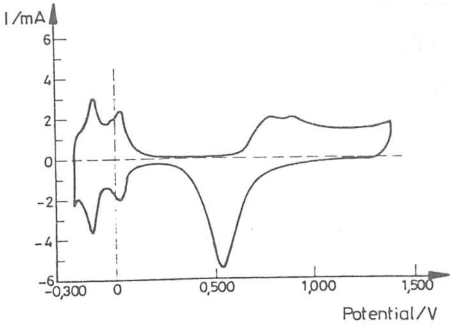

Fig.6-Cyclic voltam. in 0.5 M H_2SO_4, on Pt,at 30º C. Vel.:128 mV/s. Vert. axis:1 mA/cm.Hor. axis:100 mV/cm. R= 4 Ohm

In fig. 8 another V=V(t)-curve is shown. This curve was obtained at a higher current value and recorded at a small velocity (8.25 s/cm against 30.0 s/cm). In this way, the oscillating part of the chronopotentiogram can be seen more clearly, and the exact form of the single oscillations emerges. As can be seen, they are not quite symmetrical in themselves but are composed of a rising part of two different slopes, the peak becoming less and less sharp, and a suddenly descending forward edge. The oscillation amplitude increases gradually with time, which should have an indirect influence upon the period and frequency. Fig.9a, b, shows the evolution of the V=V(t)-curves with increasing applied current: the shape of the oscillations emerge clearly as described earlier, but it can be seen that the oscillation number decreases gradually with increasing applied current value. For an exact value of applied current (exact value of electrode roughness, temperature,

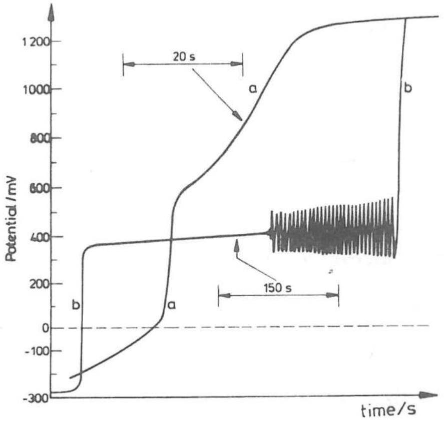

Fig.7- a) Charging curve in .5 M sulph. acid,on Pt,at 30º C.Vert.axis: 100 mV/cm.Hor. ax.:4 s/cm.b) V=V(t)-curve, in $2.5 \cdot 10^{-2}$ M CH_3OH, in 0.5 M H_2SO_4, on Pt, at 30º C. Ap. current: j=2.75 mA. Vert. ax.: 100 mV/cm. Hor.ax.:30 s/cm.

pH and methanol concentation) the oscillating part of the V=V(t)-curve disappears, as can be seen in fig.10 a, b, c. In the first chronopotentiogram of this figure (a), a last oscillation can be seen. The following chronopotentiograms (b) and (c) do not show any complete oscillation,but two potential steps, the last of them in the potential range between about 480 mV and 560 mV (s.c.e.), immediatly under the second forward methanol oxidation peak. The first potential step, the longest one, in the potential range between 368 mV and 430 mV (s.c.e.) lies under the potential range of the first methanol oxidation peak (in some circumstances appearing as a swelling in the forward potential sweep and more clearly in the reverse one, after the electrode has become free from the oxide). It is futher interesting to consider the V=V(t)-curves in figs.11 and 12 obtained on Pt-electrodes, at 30^{o}C, in $2.5 \cdot 10^{-2}$ M methanol in 0.25 M sulphuric acid. In fig.11 we can observe the oscillation shape and how it disapears. In fig.12 the two potential steps remaining after the disappearance of the oscillating part of the chronopotentiogram can be seen most clearly. Now it is

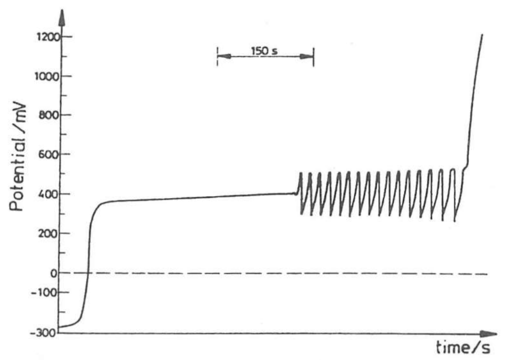

Fig.8 - Chronopotentiograms. Vert. axis: 100 mV/cm; hor. axis: 30 s/cm; j=3.5 mA.

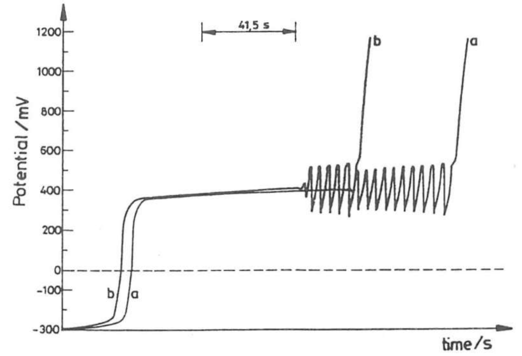

Fig.9 -V=V(t)-curves; a) j = 3.60 mA; b) j = 3.70 mA; vert.axis: 100 mA/cm; hor.axis: 8.3 s/cm.

interesting to discuss some quantities connected to the above described chronopotentiograms so that some conclusions may be drawn:

1. Current intensity multiplied by the square root of the transition time, as a function of the current intensity, $j \cdot t_t^{1/2}/ j$ (eq.1).

Fig.13 shows the value of the applied current impulse multiplied by the square root of the transition time as a function of the value of the current impulse. Two lines having different negative slopes can be distinguished, revealing a situation deviating from the simplest case described by eq.1 [35,36]. We must, however, expect such as the situation in which the step determining the speed of the process, preceding the electronic transference, is made up of a chemical reaction of the first order occurring in the solution. The two straight lines with different slopes in fig.13,are an indication of the possible existence of two chemical reactions in the solution, each in turn becoming the rate determining step, depending on the value of the current pulse imposed on the cell [38]. In this case, eq.(2) can be used:

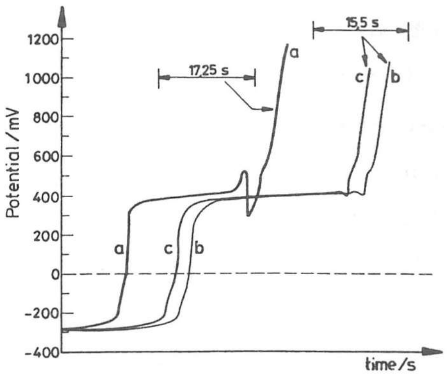

Fig 10 - Chronopotentiograms. a) j=4.80 mA;b) j=5.00 mA;c) j=5.50 mA; vert. ax.: 100 mV/cm; hor.ax.: a) 3.45 s/cm; b) and c) 3.1 s/cm.

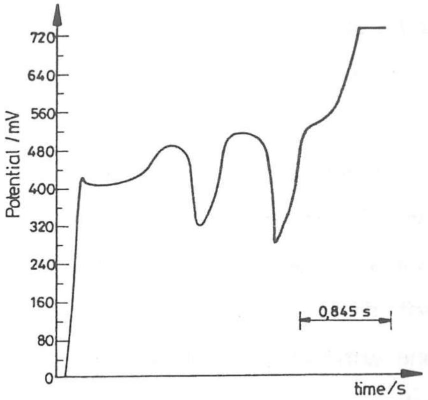

Fig.11- Chronopotentiogram on Pt, at 30^o C; j=5.75 mA;vert. ax.:40 mV/cm; hor. ax.: 0.169 s/cm.

$$j \cdot t_t^{1/2} = n F C^0 (\pi D/4)^{1/2} - (j/2) \pi^{1/2} [K a_{H^+}(k_f a_{H^+} + k_b)]^{-1/2}, \tag{2}$$

with C^0 the methanol concentration in the solution, D the diffusion coefficient, n the number of charges transferred in the corresponding step, F the Faraday constant, j the current density, a_{H^+} the proton activity, K the equilibrium constant, k_f and k_b the forward and backward rate constants for the chemical reaction in the solution, t_t the transition time [37, 38].

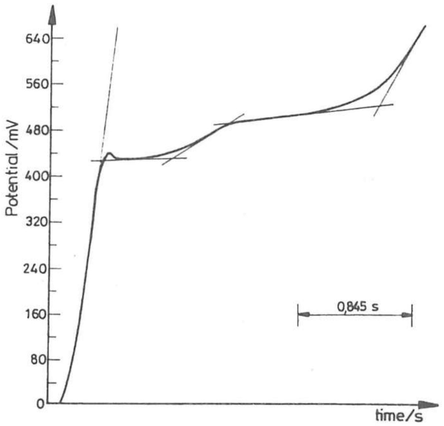

Fig.12-Chronopotentiogram on Pt,at 30° C; j=7.0 mA; vert.ax.: 40 mV/cm; hor. ax.: 0.169 s/cm.

2. Evolution of the pre-oscillatory and oscillatory parts of the V=V(t)-curves,as a function of the applied current intensity.The charge transferred to the electrode during the pre-oscillatory (Q_1) and oscillatory (Q_2) part of the V=V(t)-curves, as a function of the applied current intensity, is represented in fig. 14. The experimental points fit quite well to straight lines with different negative slopes, the one with higher experimental charge values and a higher slope belonging to the pre-oscillatory part of the V=V(t)-curves. A comparison of the two shows that in this experiment the duration of the pre-oscillatory part diminishes more quickly as the current is increased than does the duration of the oscillatory part.

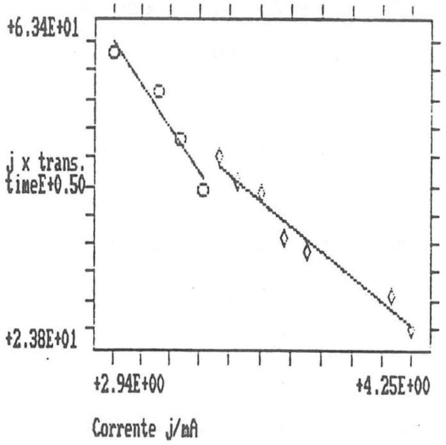

Fig13-$j.t_t^{1/2}/j$ [$mA.s^{1/2}/mA$]. Values from the set of meas. figs. 7-10.

3. Number of periods. The number of oscillations decreasing with increasing current intensity can be seen from the chronopotentiograms.Fig.15 shows the number of periods in those V=V(t)-curves as a function of the current impulse value. The experimental points fit to a third degree polynomial quite well.

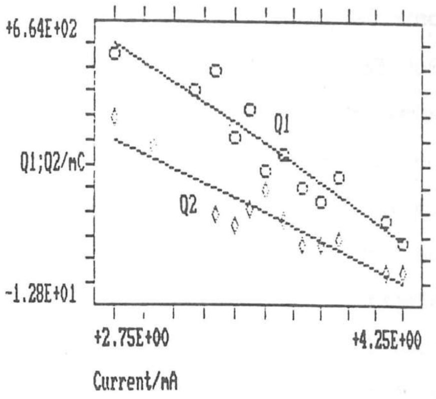

Fig.14 - Charges Q_1, Q_2 [mC] of the pre-osc. and osc. p. of the V=V(t)-curves versus applied currrent j [mA], for the same set of measurements.

4. Frequency. The oscillation amplitude increases, in the oscillatory part of the chronopotentiograms as time passes. If the potential change making the oscillations does not accelerate, the period increases and the frequency decreases. It was found that the mean value of the frequency does not change significantly from one chronopotentiogram to another, in a set obtained in the same circumstances of electrode roughness, temperature, methanol and sulphuric acid (pH) concentration.

REACTION MECHANISM

Many researchers have dealt with the methanol oxidation on platinum electrodes in sulphuric acid solutions.There is a consensus in accepting a first dissociative step eq.(3), where the molecule splitting four (or three) hydrogen atoms becomes an intermediate product strongly adsorbed on the electrode, be-

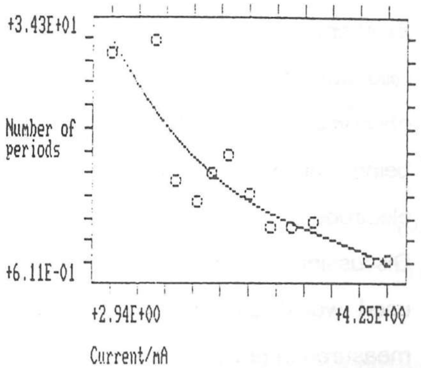

Fig.15 - Number of periods versus applied current [mA].

fore giving the final product (CO_2). Some authors like Biegler and Koch [38], Beden et al. [2,15], Leiva and Giordano [40],J.O´M.Bockris et al.[6], believe that the intermediate species adsorbed on the electrode is carbon monoxide (CO), bound to the electrode linearly or in bridge. Other people like Bogotzky et al.[41], Breiter [42], W. Vielstich et al. [7], J.Heitbaum et al. [3] say the intermediate species is CHO. J. Heitbaum, W. Vielstich, v.g., using differential electrochemical mass spectroscopy (DEMS) and electrochemical thermal desorption mass spectrometry (ECTDMS) in potentiodynamic conditions (a) detected experimentally hydrogen in the intermediate adsorbed species on the electrode and identified it as CHO; b) supported by results obtained experimenting with D_2O, CD_3OH and CH_3OD, expressly stated that the hydrogen atom is connected to the carbon, but not to the oxygen atom. (c) and calculated three electrons per site as necesary to oxidate to carbon dioxide the adsorbed intermediate species.

On the other hand J.O´M. Bockris using Fourier transform infrared spectroscopy (FTIR), in stationary conditions found that (i) C-H vibrations could not be detected for the adsorbed species on platinum in contact with methanol containing solutions, (ii) the aldehyde carbonyl groups adsorb around 1700 cm^{-1}, whereas the absorbance maxima observed by him are 2150 cm^{-1} and 1790 cm^{-1} and (iii) 3 (three) electrons per site are required for oxidation of this species (CHO) to carbon dioxide, whereas the experimentally observed value is 1.2 - 1.5, in agreement with the thesis of carbon monoxide being the intermediate adsorbed species, linearly or bridge-bonded to the electrode [6].

Discussing his results Bockris says [6] : " The steady-state measurements used would be expected to give different results from those which are measured in potential sweep measurements on Kunimatsu et al. [44, 45]. The potentiodynamic sweep technique used by others results in measurement and consequently the collection of data before the steady-state situation has been achieved. It is very likely that a proposed mechanism for a reaction based on

data taken before the stady-state condition is achieved will be substantially different, even contraditory, to a mechanism which might be proposed for the same reaction based on data that are collected after the steady state is reached." (End of citation)

Our data have been obtained by chronopotentiometry, a technique permitting the system to adjust itself to well defined quasi-steady-state conditions. We could not identify the species adsorbed on the electrode as those using any spectroscopic method did. But different from the spectroscopic steady-state measurements, our experimental results contain indirect information about electrochemical active non-adsorbed species in quasi-steady-state conditions. In accordance with this information the adsorption never comes out itself as a determining step of the rate of the process. So the reaction mechanism that we propose does not need to be completely in accordance with that based on spectroscopic steady-state measurements, because our working conditions were similar but not identical, and it will be different from that based on data obtained before a steady-state situation has been achieved as they were obtained by the potential sweep method used by Kunimatsu et al., or by the potentiodynamic sweep technique used by others [3, 7].

Before applying a galvanostatic impulse the electrode was held for about five minutes at - 300 mV (s.c.e). We believe that in this time some carbon monoxide was produced and adsorbed, obstructing partially the electrode, according to

$$CH_3OH \xrightarrow{k_1} CO_{ad} + 4\,H^+ + 4\,e^- \qquad (3)$$

$$CO_{ad} = CO_{sol} \qquad (4)$$

The carbon monoxide dissolves partially and remains in equilibrium according to eq.(4). By applying the current impulse, the potential of the electrode rises till a potential value of about + 300 mV (s.c.e.), depending on the current intensity. At this potential, the electrode being partially blocked by the species CO_{ad}, the following reaction will continue:

$$CH_3OH \xrightarrow{k_2} (COH)_{ad} + 3\,H^+ + 3\,e^- \qquad (5)$$

$$(COH)_{ad} = (COH)_{sol} \qquad (6)$$

$$(COH)_{sol} + H_2O = H_2OCOH = HCOOH^- + H^+ \qquad (7)$$

$$HCOOH^- \longrightarrow HOCOH + e^- \qquad (8)$$

$$HCOOH \underset{k_f}{\overset{k_b}{\rightleftharpoons}} COOH^- + H^+ \qquad (9)$$

$$COOH^- \longrightarrow COOH + e^- \qquad (10)$$

$$COOH \underset{k'_f}{\overset{k'_b}{\rightleftharpoons}} COO^- + H^+ \qquad (11)$$

$$COO^- \longrightarrow CO_2 + e^- \qquad (12)$$

During the galvanostatic experiment the potential rises as far as about +410 mV (s.c.e.), the radicals OH_{ad} begin to be produced on the electrode [43] and react there with the species CO_{ad} and COH_{ad} according to

$$H_2O \longrightarrow OH_{ad} + H^+ + e^- \qquad (13)$$

$$CO_{ad} + OH_{ad} \longrightarrow COOH \qquad (14)$$

$$COH_{ad} + OH_{ad} \longrightarrow HCOOH \qquad (15)$$

As has been pointed out earlier, our experimental results as, e.g., the evolution of the curves $j{\cdot}t_t^{1/2}/j$ in fig.13, do not denote the existence of slow adsorption reactions, which are sometimes the determinant step of the rate of the process [35]. Therefore the adsoption and desorption of the species CO, COH, and OH must be rapid (eqs.4, 6, 14, 15). That the CHO is the intermediate or poisoning

poisoning species has not been definitely confirmed. The species COH has also been suggested as such by many authors [1]. If the potential gets a suitable value for the reactions (13), (14) e (15), they occur very fast. The electrode suddenly becomes clean and has a sudden increase in its effective area. Consequently a decrease in the current density causes a sudden potential decrease in the V=V(t)-curves. After that, the equilibria (4) and (6) move rapidly to put the system back in the previous situation. The reaction (5) does not stop until the transition time has been completed, but the methanol concentration near the electrode surface is by this time very small compared with the methanol concentration in the solution. The potential therefore increases again until the value where the species CO_{ad} and COH_{ad} react rapidly with OH_{ad} on the electrode surface, which becomes cleaned suddenly. The increase in its effective area causes a decrease in the current density and a decrease in the potential of the V=V(t)-curves, etc., etc, causing the oscillations observed.

The rise in the oscillation amplitude can be explained by the fact that the increasing diffusion overpotential is at the top of the oscillations in the potential range of the forward methanol oxidation peak, where reactions (13), (14), (15) occur. There may also be a slight occurence of,

$$CO_{ad} + O_{ad} + 2\,e^- \longrightarrow CO_2\,. \qquad (16)$$

The oscillation amplitude "increases" downwards due to an increasing cleanness of the electrode from one oscillation to another, producing an increasingly large effective area which has the direct effect of decreasing the current density and consequently the potential of the V=V(t)-curves.

The shape of the oscillation is due to the fact that it was formed by an ascending charging curve followed by a sudden potential drop caused by a sudden increase in the effective electrode area, as already explained.

CONCLUSION

The potential oscillations in the chronopotentiometric V=V(t)curves discussed here are an experimentally established fact which must be taken into consideration when proposing a reaction mechanism for the anodic methanol oxidation in sulphuric acid solutions on platinum electrodes. The experimental conditions under which we worked were not exactly the same as those of many researchers dealing with this matter, nor is the experimental information about the system and its evolution that we obtained the same as that acquired by the potential sweep or cyclic voltammetry. The spectroscopic information about intermediate species adsorbed on the electrode is very important, but not sufficient for us to be able to say the last word about a reaction mechanism. The reaction mechanism we propose cannot be exactly the same as those previously proposed.

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