

ANODIC OXIDATION OF CARBON MONOXIDE AND FORMIC ACID  
ON PLATINUM COVERED WITH SULFUR

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### 1. Introduction

In recent years it was demonstrated by investigations of several authors (1)-(5) that CO is oxidized on platinum electrodes in an acid electrolyte at temperatures below 100°C. However, the current density achieved was only of the order of some ma/cm<sup>2</sup>. In order to increase the current densities temperatures of up to 150°C were applied using phosphoric acid as electrolyte (6). In this way the current density was raised to about 50 ma/cm<sup>2</sup>. We reported about the results obtained with our type of Raney-platinum electrodes (7) which allowed current densities of about 200 ma/cm<sup>2</sup> to be drawn using carbon monoxide as fuel in 3N H<sub>2</sub>SO<sub>4</sub> at temperatures below 100°C (8,9).

However, polarization was large compared with that encountered in the oxidation of hydrogen; attempts at the simultaneous oxidation of hydrogen and carbon monoxide resulted in an enrichment of carbon monoxide in the effluent gas mixture.

The strong polarization encountered in the anodic oxidation of CO is due to an adsorption product which is slowly adsorbed on the electrode, thus blocking it. We found, however, that the blocking effect is not encountered on a platinum electrode onto which sulfur has been pre-adsorbed (10).

This paper describes the results of adsorption measurements and of the electrochemical oxidation of carbon monoxide and formic acid. The influence of sulfur on the adsorption is discussed and a modification of the oxidation mechanism is proposed\*).

### 2. Experimental Conditions

The electrochemical measurements were performed by means of a half-cell arrangement. The reference voltages indicated in this paper relate to a hydrogen electrode in the same solution as the test electrode. The disk-shaped electrodes were prepared by compacting a mixture of 50 volume per cent gold powder or platinum powder as skeleton material and 50 volume per cent of a powdered platinum-aluminum alloy having a platinum content of 15 atomic per cent. The aluminum was leached out with potassium hydroxide solution. The skeleton material - platinum and gold - appeared to have no effect on the results of our measurements. The Raney platinum had a specific surface area of about 30 m<sup>2</sup>/g. For measurements with formic acid, immersed electrodes were used, while bubbling electrodes were used in the case of carbon monoxide. The electrolyte was boiled thoroughly and protected from atmospheric oxygen by feeding nitrogen into the closed vessel above the electrolyte. The electrodes used for the determination of periodic current-voltage curves had a platinum content of about 50 mg/cm<sup>2</sup>. Electrodes with

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\*) For papers concerning oxidation of formic acid and carbon monoxide cf. references (12) to (33)

a platinum content of 180 mg/cm<sup>2</sup> were used only in measurements of stationary current-voltage curves with carbon monoxide and for determining the quantity of the carbon monoxide chemisorbate. The potentiodynamic current-voltage curves were plotted by means of a mechanically operated xy-recorder.

### 3. The Sulfur Chemisorbate

If a platinum electrode is exposed to an atmosphere of hydrogen sulfide, it is covered with a sulfur chemisorbate. A characteristic feature pointing to the presence of this adsorbate is the observation made in measurements of periodic potentiodynamic current-voltage curves that the peaks corresponding to the oxidation of H<sub>ad</sub> atoms (34) become smaller or vanish completely (Fig. 1). Complete disappearance of the maxima is consistent with complete sulfur coverage of the electrochemically active platinum surface. The degree of coverage can thus be derived from the periodic current-voltage curve by determining the ratio between the atoms of the platinum surface available for hydrogen adsorption before and after coverage of the platinum with sulfur\*).

Above a specific reference voltage, which ranges between 600 and 800 mv depending on the degree of coverage, the sulfur chemisorbate is oxidized anodically. Complete oxidation occurs at 1450 mv, so that the normal current-voltage curve of platinum is obtained after reversal of the voltage. The charge required for the oxidation of sulfur can be determined from the difference of those areas in the voltage range between 600 and 1450 mv which are enclosed by the curves (Fig. 1, area hatched horizontally). It was found that the required charge is about four times as large as the charge necessary for oxidation of the corresponding number of H<sub>ad</sub> atoms. From this finding and from the observation that gas is evolved at the electrode during oxidation, we infer that for each platinum atom one sulfur atom is adsorbed which is oxidized to give sulfur dioxide.

In contrast to the oxygen adsorbate, the sulfur adsorbate is stable even at a voltage of -100 mv, although the thermodynamic limits for the stability of elemental sulfur are 150 and 450 mv. Methods for covering the platinum with sulfur, other than the exposure of the electrode to an atmosphere of hydrogen sulfide, include its exposure to sulfur vapor or sulfur solution (in CS<sub>2</sub>) and the cathodic reduction of sulfuric acid or sulfurous acid at high current densities.

### 4. Influence of the Sulfur Chemisorbate on the Anodic Performance

#### 4.1 Carbon Monoxide

On a platinum surface covered with a sulfur chemisorbate, the rate of the anodic oxidation of carbon monoxide is much higher than on an uncovered surface. At a temperature of 90°C even small quantities of sulfur increase the current density considerably (Fig. 2), but as in the case of 30°C the maximum current density is achieved only at nearly complete monatomic coverage of the catalyst.

This increase in current density with increasing sulfur coverage of the platinum is observed between 30 and 90°C in the whole voltage range up to at least 500 mv (Fig. 3). As soon as monatomic

\* ) This is based on the assumption that one hydrogen atom is chemisorbed per platinum atom.

coverage is exceeded, the current density again decreases.

At an uncovered electrode the current density is much more dependent on the temperature than at an electrode covered with sulfur. From the different slopes of the straight lines in an Arrhenius diagram a decrease in the activation energy of about 7 kcal/mole is calculated. By calculating just the difference of the activation energy, the contribution of the overvoltage to the activation energy is approximately eliminated.

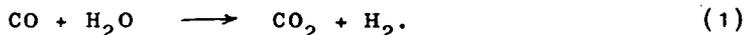
#### 4.2 Formic Acid

In the anodic oxidation of formic acid, the influence of the sulfur adsorbate on the reaction rate is even more pronounced than in the oxidation of carbon monoxide (Fig. 4). If the electrode is covered with sulfur, the current density depends more strongly on the concentration of formic acid than in the absence of sulfur (Fig. 5), i.e. the rate constant of the oxidation reaction is raised. From the ratio of the rate constants the decrease in the activation energy can be estimated to be 8.4 kcal/mole. In contrast to CO oxidation, the maximum influence is reached throughout the temperature range investigated at a coverage of only 40 per cent and not at nearly complete coverage (Fig. 6).

From the varying dependence of the current density on the temperature the decrease in activation energy for the oxidation of formic acid on a platinum electrode with a 45 per cent sulfur coverage is calculated to be about 8 kcal/mole. This value is in fair agreement with that calculated for the oxidation of carbon monoxide.

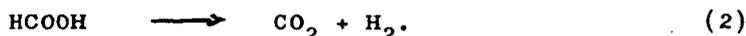
#### 5. Reaction under Open Circuit Conditions

Under open circuit conditions the following shift reaction takes place at a Raney platinum electrode:



On pure platinum this reaction is very slow. In the presence of a sulfur adsorbate, however, its rate is substantially increased. This reaction takes place even if the carbon monoxide is mixed with hydrogen or carbon dioxide. The reaction rate can be measured at temperatures as low as 30°C.

Formic acid decomposes on a platinum electrode under open circuit conditions according to the following reaction:



The rate of this reaction again is increased by the sulfur chemisorbate. In 3N H<sub>2</sub>SO<sub>4</sub> + 2M HCOOH at 90°C the reaction rates differ by a factor of about 25. The composition of the effluent gases at a temperature of 70°C was determined to be 40.4 volume per cent H<sub>2</sub>, 41.6 volume per cent CO<sub>2</sub>, and 18 volume per cent O<sub>2</sub>/N<sub>2</sub>. No CO (<0.2 per cent) was formed during the decomposition of formic acid, because the shift reaction takes place at a platinum electrode partly covered with sulfur.

#### 6. Adsorption Measurements

The potentiostatic current density-time curves (Fig. 7a) reveal that the inhibition of the anodic oxidation of formic acid at a platinum electrode is due to a comparatively slow blocking of the electrode [see e.g. (13)]. For plotting these curves, the electrode was held at one of the voltages indicated in Fig. 7 by means

of a potentiostat. Oxidizable contaminations had been previously removed by anodic stripping (up to 1,600 mv). Inhibition occurs also under open circuit conditions: if the circuit is closed one hour after addition of formic acid, the small stationary current density is observed immediately, e.g. at a voltage of 300 mv. Our porous electrodes required about two hours to be completely covered with the formic acid chemisorbate. Thereafter,  $H_{ad}$  atoms are no longer detectable at the platinum surface.

This inhibition effect is not observed at potentials above, say, 600 mv.

No inhibition is observed either if the electrode is partly covered with pre-adsorbed sulfur (Fig. 7b): the comparatively high current densities are reached immediately and decrease only insignificantly.

Similar inhibition effects which can be avoided by pre-adsorption of sulfur, are observed during the anodic oxidation of carbon monoxide.

For measuring the quantity of adsorbate, potentiodynamic curves have been plotted at low voltage speed after thorough rinsing of the electrode with pure sulfuric acid. These curves clearly show the influence of the hydrogen and oxygen adsorbate on the oxidation and permit the double layer capacity to be readily determined. Furthermore, these curves provide information about the position of the oxidation maximum and the electrochemical stability of the organic adsorbate.

The charge necessary for the oxidation of adsorbed hydrogen is derived from the potentiodynamic curve obtained for the clean platinum electrode by subtraction of the charge of the double layer from the total charge. The double layer capacity results from the current flowing between 400 and 700 mv. Prior to adsorption measurement the electrode is placed in dilute sulfuric acid. In order to remove all adsorption layers, it is exposed first to a voltage of 1,400 mv, then to 200 mv, and finally to 500 mv. Then, formic acid is added under open circuit.

Between 0.1 and 2M, the quantity of chemisorbed formic acid is independent of the concentration of formic acid in the electrolyte. However, it is necessary for this result that the adsorption equilibrium has been reached. At 30°C the oxidation of the adsorption product (Fig. 8) starts at about 400 mv, and at 70°C it starts at about 300 mv. Thus, the chemisorbate is stable up to this potential. The maximum oxidation currents are observed at 660 mv and 530 mv for 30 and 70°C, respectively.

The quantity of adsorbate was derived from the measured charge, taking into account the integral capacity of the double layer of the uncovered platinum surface. The potential of zero charge for platinum has been assumed to be 400 mv [see also (31)]. In accordance with Brummer (15), the specific charge required for oxidation of the adsorbate totals 1.5 e/Pt atom. The amount of HCOOH chemisorbed on a platinum electrode partly covered with sulfur is smaller than that on the uncovered electrode (Fig. 9a) and decreases with increasing degree of coverage. For a coverage of 70 per cent, this effect is easily recognized by the smaller oxidation peak. If the quantity of chemisorbed HCOOH is related to the platinum surface

not covered with sulfur, the charge required for oxidation corresponds to a transfer of 2.1 e/Pt atom. At a sulfur coverage of only 40 per cent, 1.7 e/Pt atom are required for the oxidation of the HCOOH chemisorbate.

$H_{ad}$  atoms are never detectable on the platinum surface once the equilibrium of formic acid adsorption has been reached. Thus, the surface is always covered with a chemisorbate (in the voltage range between 0 and about 400 mv), either with a pure HCOOH adsorbate or with a mixed HCOOH and S adsorbate. In steady state, oxidation of formic acid occurs on the platinum surface covered with a mixed chemisorbate at a higher rate than on platinum covered with the pure HCOOH chemisorbate. In the case of the periodic curve (Fig. 9b) the current necessary for the oxidation of the chemisorbate is superposed on the steady state current-voltage curve.

For the adsorption of carbon monoxide on the electrode, the gas was pressed through the porous electrode at a very low flow rate under open circuit conditions. The amount of adsorbate was determined at the completely immersed electrode which had been rinsed thoroughly with boiled sulfuric acid prior to the measurement.

At 70°C the oxidation maximum is observed at a voltage of 530 mv. At 30°C the peak is shifted to 650 mv (Fig. 10). Thus, the maxima are reached almost exactly at the same voltage as in the case of oxidation of the HCOOH chemisorbate.

The quantity of CO chemisorbate again decreases with increasing coverage of the platinum with sulfur (Fig. 11). At a coverage of about 100 per cent the adsorbed amount is insignificant.

In the case of uncovered platinum, 1.5 e/Pt atom are required for the oxidation of the CO chemisorbate. At a sulfur coverage of 60 per cent the charge corresponds to a transfer of 1.9 e/Pt atom.

#### 7. Oxidation Mechanism and Influence of the Sulfur Adsorbate

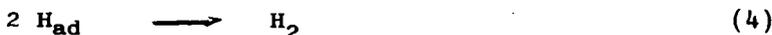
The most important question in the discussion of the mechanism underlying the anodic oxidation of formic acid and carbon monoxide on platinum is the influence of the adsorbate or intermediate blocking the electrode.

It is important to note that the chemisorbate is oxidized in both cases only at a voltage above 300 mv, being stable at lower voltages, and that in both cases only one oxidation peak occurs at the same potential. Another significant finding is that no  $H_{ad}$  atoms are found on the surface of the electrode after the adsorption equilibrium has been reached.

As an explanation of the fact that for each platinum site less than 2 e are required for the oxidation of the inhibitory chemisorbate, several authors - e.g. (15) - state that the platinum surface is covered only partially with chemisorbate. This is contradictory to our finding that no  $H_{ad}$  atoms can be detected after the equilibrium has been reached, not even at a voltage as small as 100 mv. The reactions assumed by many authors for the adsorption of formic acid

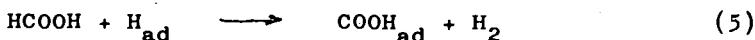


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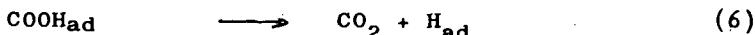


are certainly initiated on a completely free platinum surface.

The hydrogen thus formed is physically dissolved in the electrolyte or escapes as a gas: this is the process of dedhydration. In the hydrogen-covered regions of the electrode, however, the following reaction will take place:

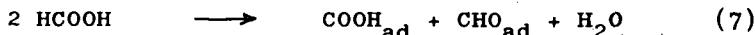


On the free platinum surface the decomposition of the carboxyl radical proceeds in accordance with the reaction



With increasing inhibition of the electrode by the chemisorbate, the formic acid will be dehydrated according to the electrochemical mechanism postulated by Gottlieb (23) and finally, though at a very low rate, it will be dehydrated even on the platinum surface covered with chemisorbate.

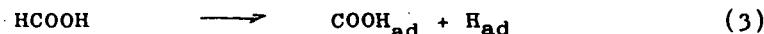
However, the poisoning of the platinum by reaction (3) does not provide an explanation for all the findings. Since the average charge of the adsorbate per platinum site is larger than 1 but smaller than 2, it has to be assumed that a further reaction takes place; the most plausible appears to be dismutative adsorption:



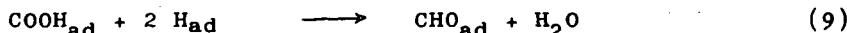
Each species has one platinum bond;  $\text{COOH}_{\text{ad}}$  has one oxidation equivalent per C atom,  $\text{CHO}_{\text{ad}}$  has three. This means that, on the average, two equivalents are available for each C atom, which would also be the case in the adsorption of  $\text{HCOOH}_{\text{ad}}$ . It is unlikely that even glyoxylic acid (15) with a C-C bond is formed, because it has no free electron for the bond with platinum [see also (17)]. If  $\text{H}_{\text{ad}}$  atoms are to be found on the surface, the formic acid may also be hydrated to give the radical of formaldehyde in the reaction assumed by Podlowchenka et al. (17):



The combination of reactions (3) and (8) would result in (7):



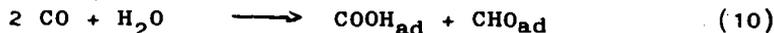
This would, however, involve an additional platinum site for  $\text{H}_{\text{ad}}$  in contrast to the direct process of (7). Besides, the following reaction may occur:



The platinum atoms set free during this reaction would then be again available for reaction (3).

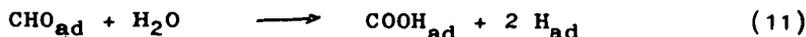
The chemisorbate obtained after the adsorption of CO is identical with the HCOOH adsorbate. This is due to the fact that the oxidation peak is reached in both cases at 530 mv and that the same charge is required for the oxidation. Besides, the required charge depends to the same extent on the sulfur coverage.

Dismutative adsorption also appears most plausible for the adsorption of CO:



because it furnishes the same mixture of species as the adsorption of formic acid. In addition, there is always a sufficient amount of adsorbed water on the electrode immersed in the electrolyte.

Reaction (10) may be followed by the shift reaction observed on platinum, for example, in accordance with the following equation:



followed by



and



These reactions should occur as long as there are free platinum sites to take up the  $\text{H}_{\text{ad}}$  atoms. When all the platinum atoms are covered with the mixture of  $\text{CHO}_{\text{ad}}$  and  $\text{COOH}_{\text{ad}}$ , the rate of the shift reaction becomes insignificant.

However, this hypothesis postulating a chemical mechanism for the shift reaction and formic acid decomposition is rather improbable if we consider our finding that a sulfur adsorbate strongly increases the rate of these reactions. This is true despite the fact that - as in the case of carbon monoxide - the sulfur adsorbate occupies practically all the platinum sites when maximum rates are reached.

Our experiments rather suggest that the electrochemical oxidation of formic acid and carbon monoxide at potentials below 300 mv and the decomposition of formic acid or the shift reaction observed in steady state do not take place on the free platinum surface, but on a chemisorbate covering the platinum surface. We postulate that

- reactions on sulfur-free platinum always take place on the complete "monomolecular" chemisorbate of formic acid or carbon monoxide (at an extremely low reaction rate);
- reactions on platinum covered with sulfur take place on the mixed chemisorbate of sulfur and formic acid, or of sulfur and carbon monoxide;
- reactions involving oxidation of carbon monoxide take place even on a surface completely covered with sulfur chemisorbate.

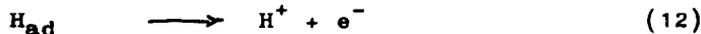
This concept contradicts the dehydrogenation mechanism of the oxidation, which would have to involve the following reactions



and

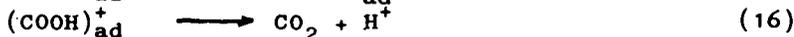
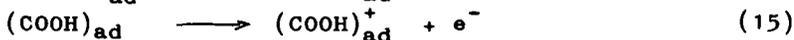
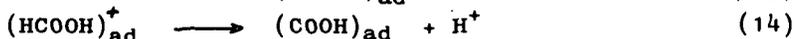


with



as the potential-determining step. A prerequisite for this mechanism would be dissociative adsorption, which is assumed to be possible only on the free platinum surface.

Anodic oxidation of formic acid may rather be expected to take place on the chemisorbate or chemisorbate mixture in accordance with a modified electron-radical mechanism (20,26,27):



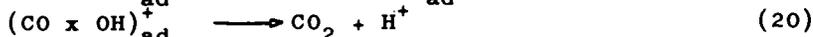
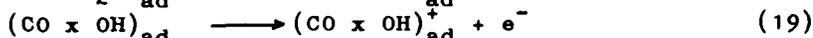
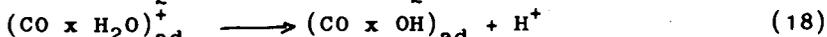
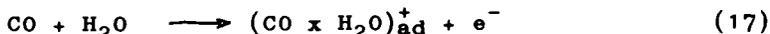
where either equation (13) or equation (15) determines the potential. In no instance will  $(\text{COOH})_{\text{ad}}$  be identical with  $\text{COOH}_{\text{ad}}$ , since the chemisorbate covering the electrode permits physisorption rather than chemisorption.

Dehydrogenation of formic acid in the steady state of the electrode involves reactions (13) to (16) as the anodic step of the total electrochemical reaction, with



as the cathodic partial step [see (23)]. The charge transfer reaction occurs more readily at the sulfur sites than at the formic acid chemisorbate, so that dehydrogenation is measurable even at room temperature.

The electron-radical mechanism for the anodic oxidation of carbon monoxide may be described as follows:



The intermediates are reaction complexes which are probably not identical with the corresponding complexes involved in the oxidation of formic acid, since the relationship between the course of the reaction and the sulfur coverage of the electrode is different in each individual case.

Carbon monoxide appears to be physisorbed on the sulfur sorbate, so that the charge transfer reaction can take place. The sulfur adsorbate appears to be unsuitable for the physisorption of formic acid; it is rather to be assumed that a carbonyl group is necessary to which the formic acid molecule is attached by hydrogen bonding, thus coming into the neighborhood of the chemisorbed sulfur by which the electron transfer is effected.

This model requires further substantiation by experiment. For a closer characterization of the chemisorbate it is in particular necessary to know the number of charges required for the formation of one molecule of carbon dioxide.

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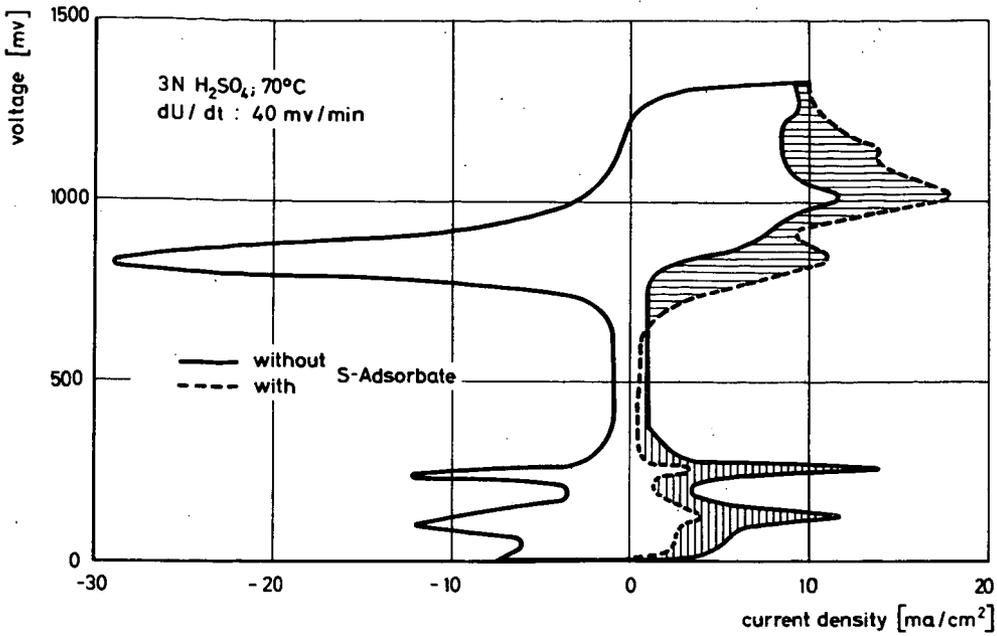


Fig. 1 Oxidation of a sulfur chemisorbate on Raney-Pt in  $3N H_2SO_4$  at  $70^\circ C$ ; voltage speed:  $dU/dt = 40 \text{ mV/min}$

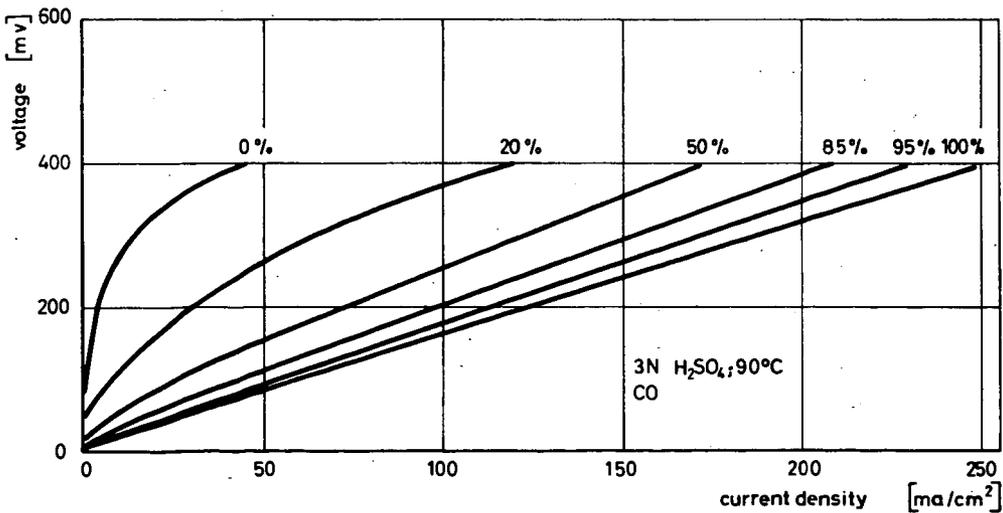


Fig. 2 Shift of current density-voltage plots of a Raney-Pt electrode in the case of CO-Oxidation caused by chemisorbed sulfur

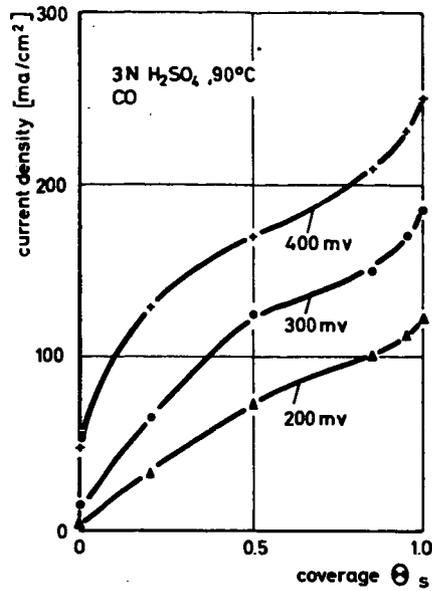


Fig. 3 Effect of chemisorbed sulfur on the performance of CO at a Raney-Pt electrode

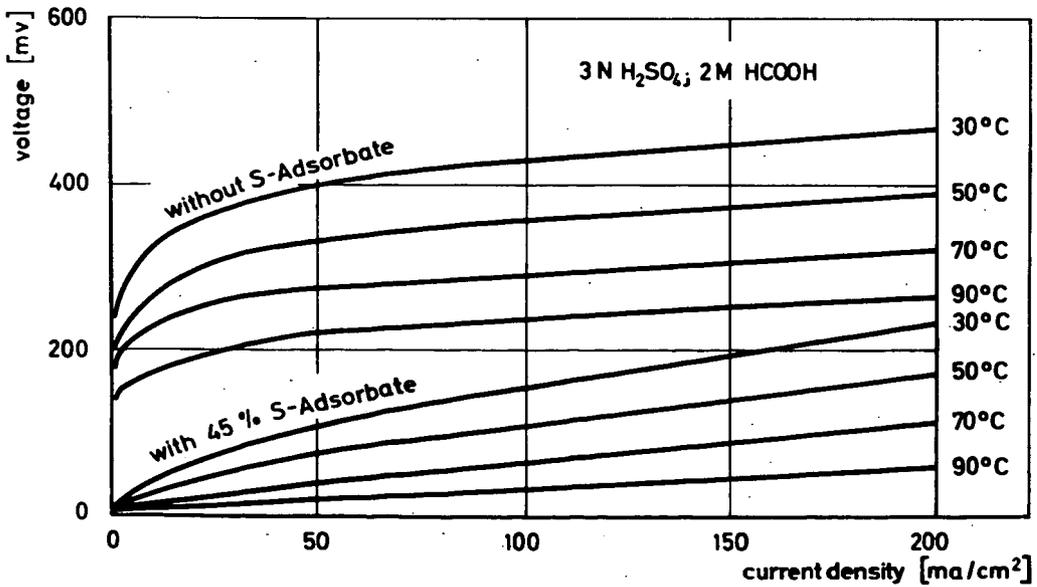


Fig. 4 Shift of current density-voltage plots at a Raney-Pt electrode in the case of HCOOH-Oxidation caused by chemisorbed sulfur

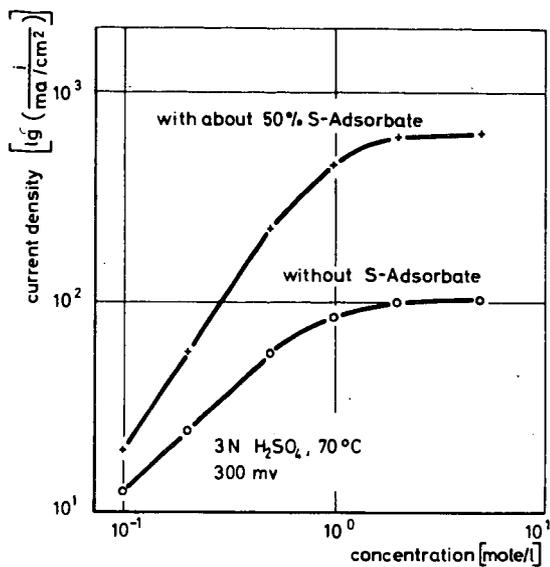


Fig. 5 Current density at a Raney-Pt electrode as a function of HCOOH concentration

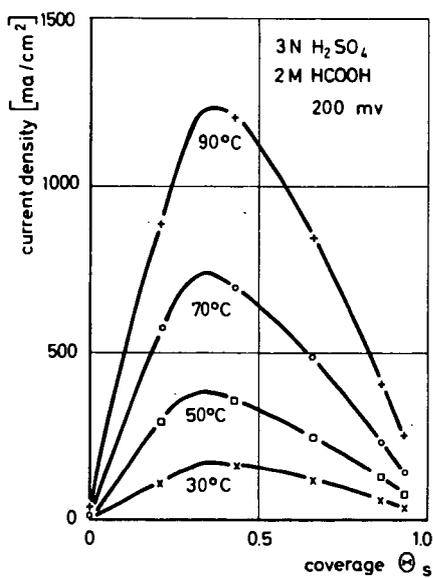


Fig. 6 Effect of chemisorbed sulfur on the performance of HCOOH at a Raney-Pt electrode

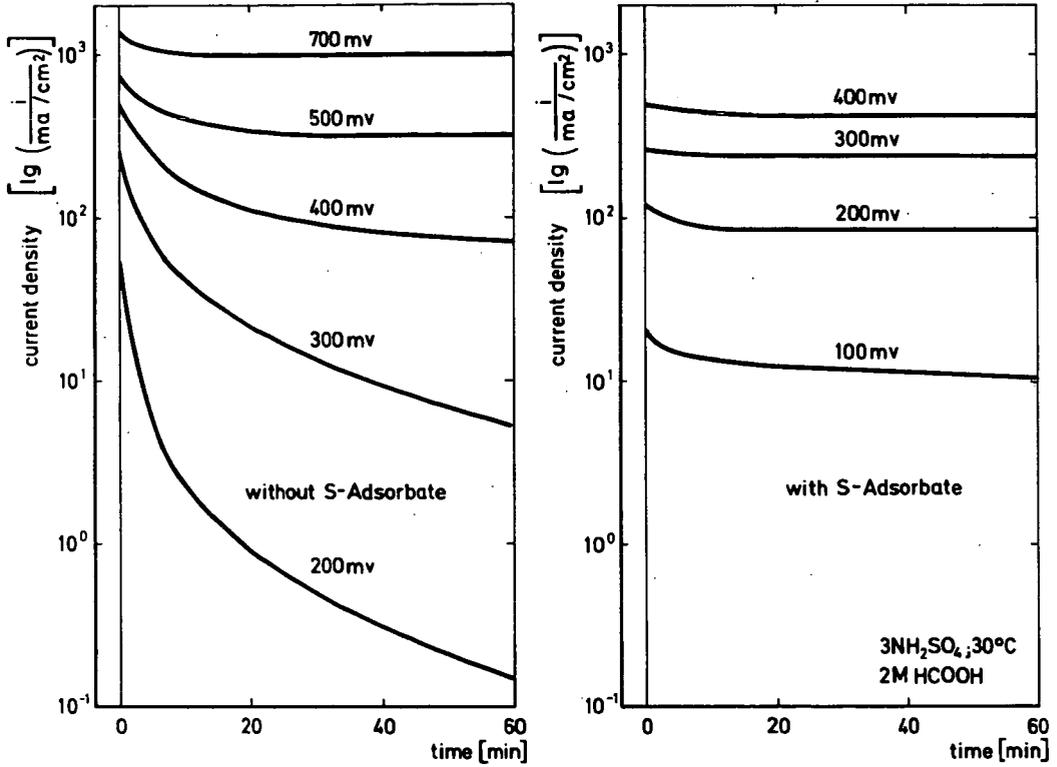


Fig. 7 Decay of current density at a Raney-Pt electrode during oxidation of HCOOH

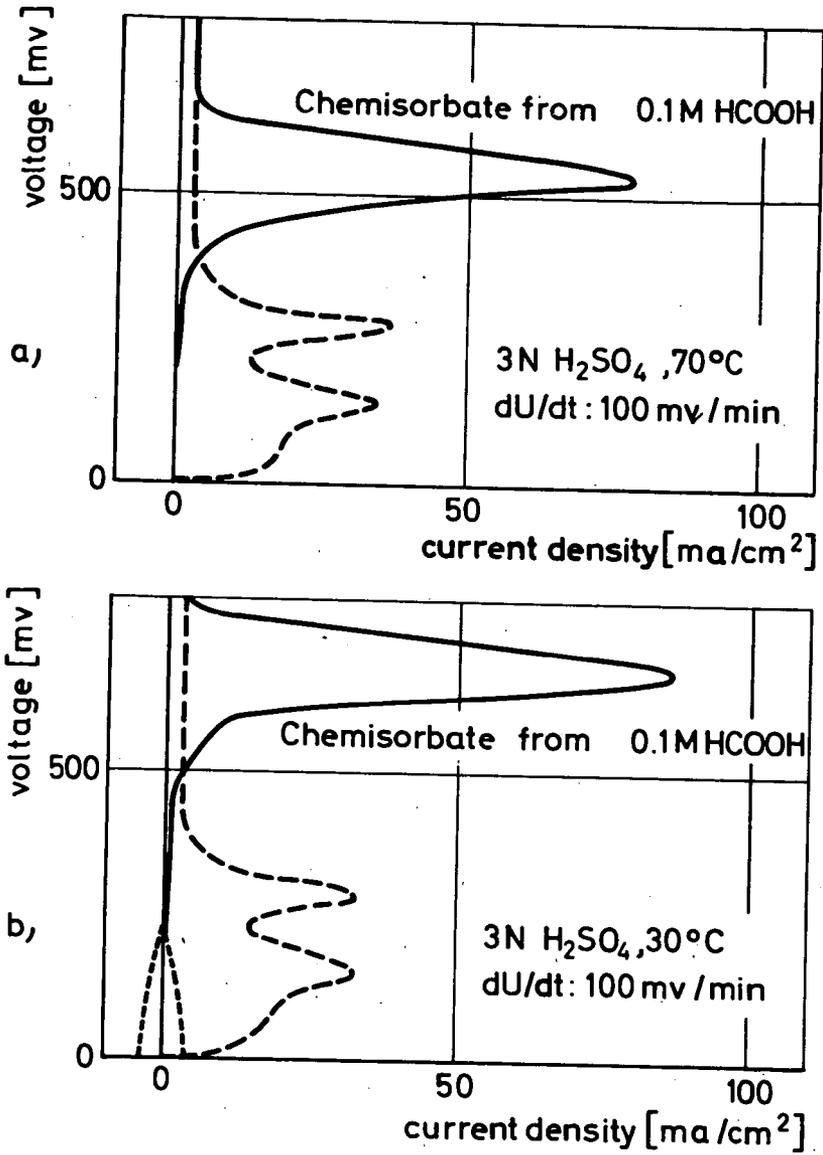


Fig. 8 Oxidation of the HCOOH chemisorbate on Raney-Pt  
 a) at 70°C (single sweep); b) at 30°C (single sweep)

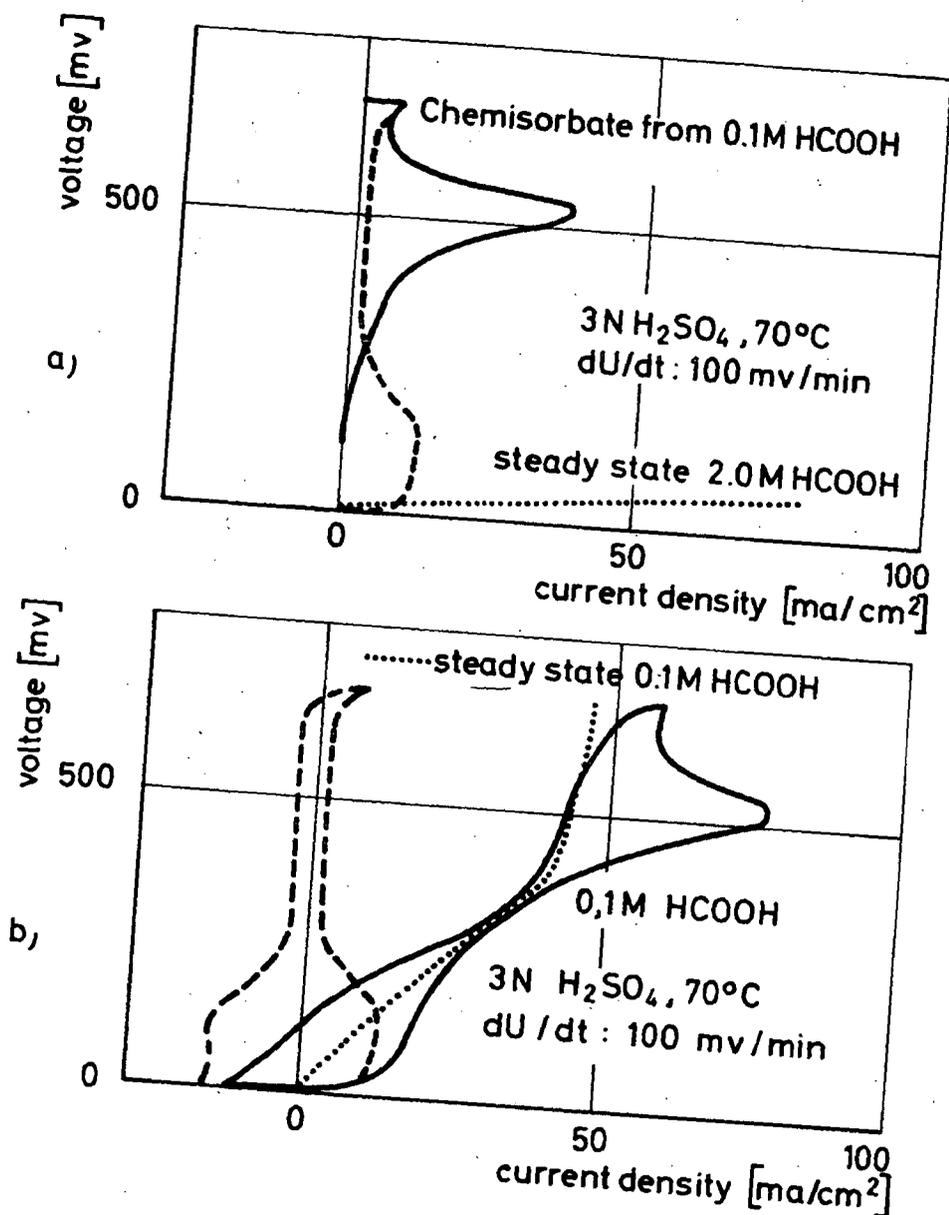


Fig. 9 Oxidation of HCOOH at a Raney-Pt electrode covered with a sulfur chemisorbate ( $\theta_S = 70$  per cent)  
 a) oxidation of the HCOOH chemisorbate (single sweep);  
 b) oxidation in the presence of 0,1 M HCOOH (periodic curve)

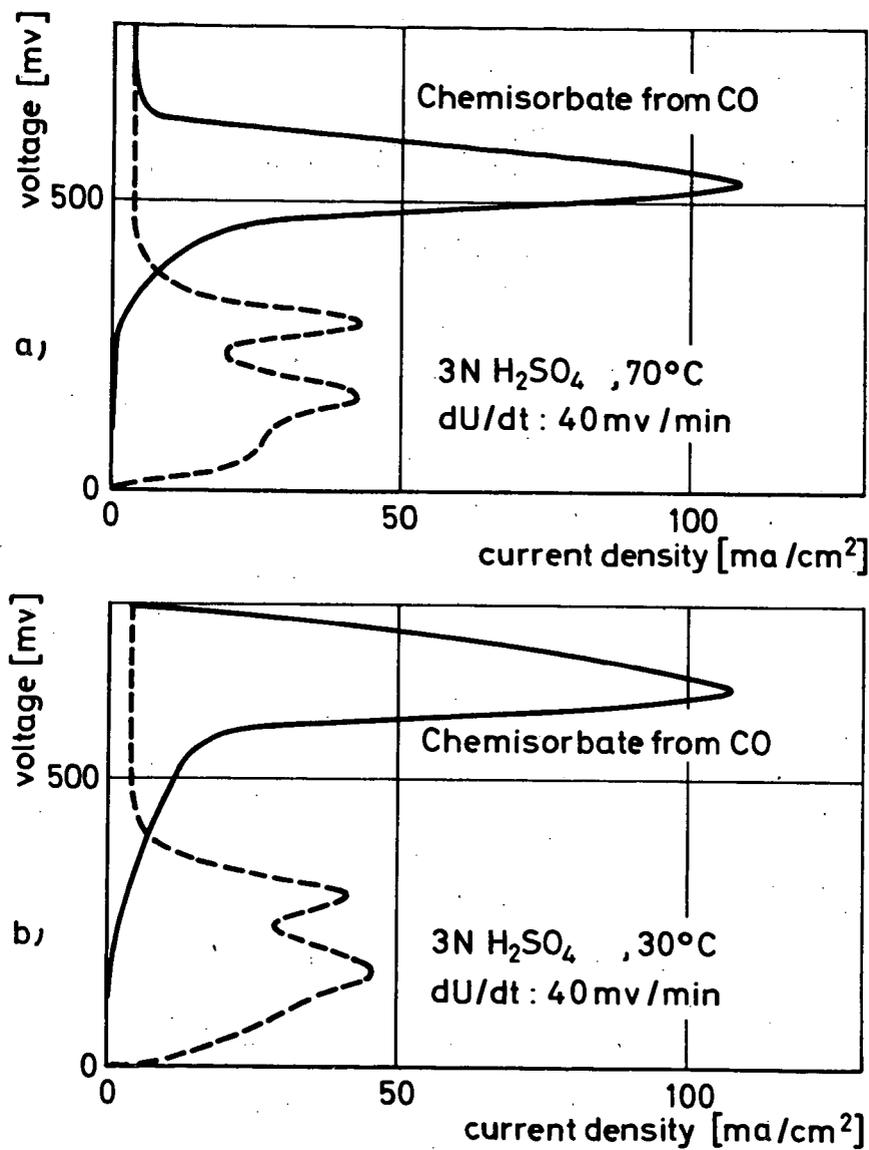


Fig. 10 Oxidation of CO chemisorbate on a Raney-Pt electrode  
a) at 70°C (single sweep); b) at 30°C (single sweep)

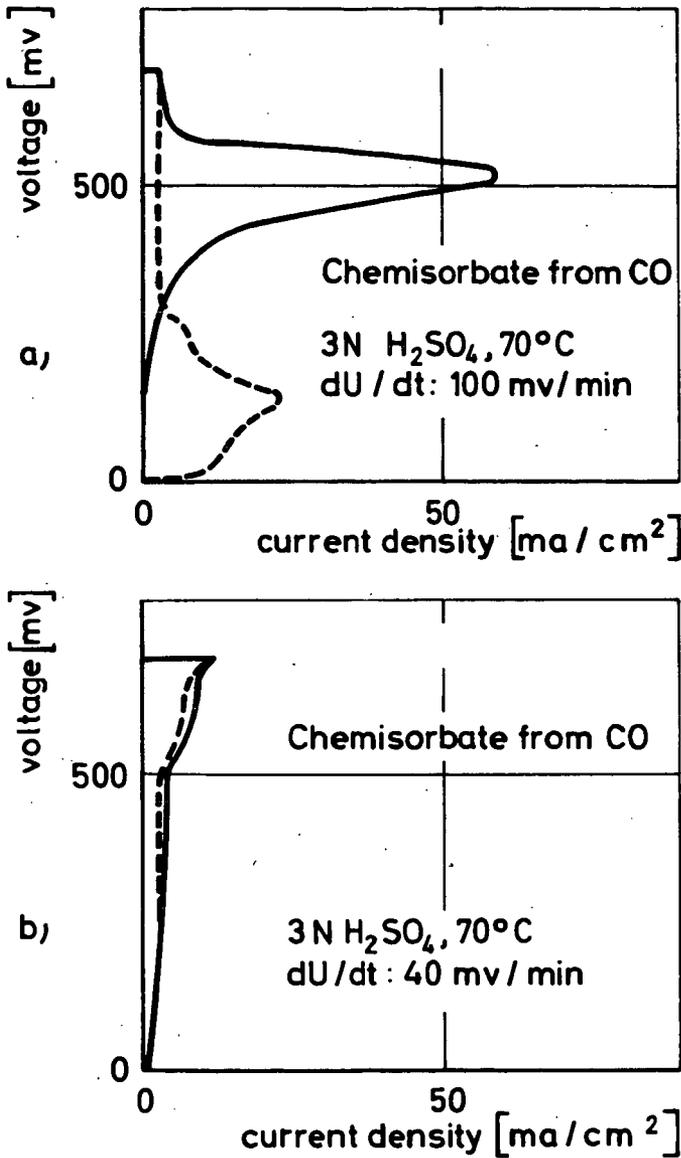


Fig. 11 Oxidation of the CO chemisorbate on a Raney-Pt electrode covered with an additional sulfur chemisorbate a)  $\theta_S = 60$  per cent (single sweep); b)  $\theta_S \approx 100$  per cent (single sweep)