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Oxidation of formic acid at a high surface area supported platinum modified by foreign metal adatoms

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The anodic oxidation of formic acid was studied on platinum distributed in the form of small particles in a porous substrate modified by metal adatoms deposited at underpotentials. The rate of the reaction was greatly enhanced on the commercial catalyst Powercat 3000 (PC 3000). The hydrogen adsorption and the underpotential deposition of several metals at PC 3000 were shown to be dissimilar to that at smooth polycrystalline Pt. Steady-state and long-term experiments were performed to determine the stability of this electrode.

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1. Introduction

High surface area electrodes are necessary for efficient operation of fuel cells. A number of porous structures have been used to meet this requirement. These porous structures are usually composed of a porous carbon substrate and a catalyst layer which consists of carbon supported platinum catalyst and polytetrafluorethylene (PTFE), which gives hydrophobicity to the catalyst layer. Carbons used in fuel cell electrodes are subjected to pretreatment to increase the surface area, improve the performance and extend the life time. Heat treatments of high surface area carbons produce significant changes in both the surface area and the surface oxide content in the temperature range between 400 and 1000° C (673 and 1273 K). A removal of oxide opens up the micropores to give this surface enhancement. It also improves the interparticle contact and makes the carbon powder more conductive [1]. More recently, other forms of carbon have been used as a support [2]. One such commercial electrode, the Stonehart and Assoc. "Powercat 3000" (Stonehart and Assoc. Inc., Madison Connecticut, USA) has been used in this work.

The oxidation of formic acid has been the subject of longstanding interest [3–6]. A general problem in the electro-oxidation of HCOOH and other small organic molecules is a progressive decrease of the rate (current density) of reaction at a given potential and temperature [7]. The decrease in oxidation rate of HCOOH is due to a surface-poisoning of the electrode by strongly bound intermediates, which are difficult to oxidize [4, 5].

Foreign metal adatoms cause considerable catalytic effects in the oxidation of formic acid on platinum. The presence of adatoms has a direct effect on the rate of HCOOH oxidation by preventing the formation and adsorption of poisoning species during oxidation [8, 9]. The purpose of this work was to study the effects of foreign adatoms on the oxidation of HCOOH on high surface area catalysts. The results on flat surfaces [8] suggest that, if similar effects were obtained with high surface area electrodes, then electrodes of practical interest could be realized. The investigation was focused on the effects of Pb, Bi and Sn adatoms.

2. Experimental details

The electrolytic cell was of standard design. The working electrode was a small piece of PC 3000, geometric area of 0.4 cm^2. This commercial catalyst contained 0.5 mg Pt cm^{-2} of electrode, with a specific Pt surface area of 130 $m^2 g^{-1}$. The counter electrode was platinum while the saturated mercury-mercuric sulphate electrode was used as a reference. All potentials given here refer to the standard hydrogen electrode.

The electrolyte used was 1 M perchloric acid prepared from triply distilled water and Merck $HClO_4$. Formic acid was added to the electrolyte, to form concentrations of 1 M. Purified nitrogen was bubbled through the electrolyte before measurements and, during the experiments, a nitrogen blanket was maintained over the solution.

Potential sweep, steady-state polarization and long-term polarization experiments were made first in the absence and then in the presence of known amounts of a cation in solution, whose catalytic effect was to be tested. The cation concentration was varied in the range 0.01 to 1 mM.

All the cations used were in the solution during the experiment, except for the experiments with Sn. This cation was adsorbed on the electrode for 15 min at a potential of 0.5 V from 0.5 mM solution following the procedure of Janssen and Moolhyssen [10]. The working electrode was then transferred to the cell containing the solution under study and the measurements were run.

3. Results and discussion

3.1. *Underpotential deposition (u.p.d.) of Pb and Bi on PC 3000*

The base cyclic voltammogram of PC 3000 in perchloric acid differs considerably from that for smooth

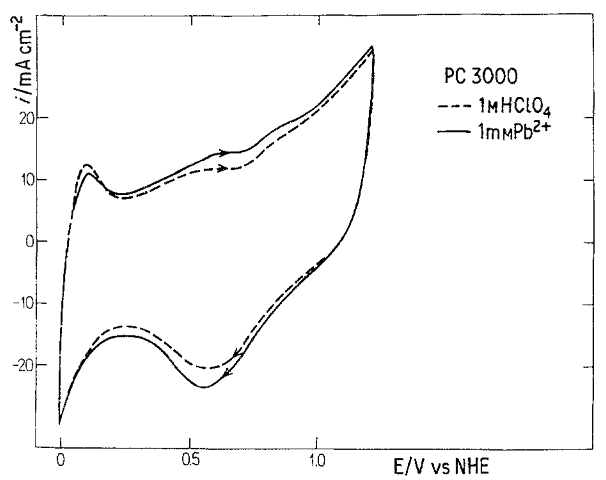

Fig. 1. Cyclic voltammogram of underpotential deposition of lead on PC 3000 electrode in 1 M $HClO_4$, containing none (dashed line) and 1 mM Pb^{2+} (full line). Sweep rate 20 mV sec^{-1}.

polycrystalline platinum. The method of preparation of the high surface area electrocatalyst, PC 3000, the crystallite size and specific electrocatalyst-support interactions give Pt surface sites with specific activity. So, the significant difference between the base curve for Pt dispersed on porous carbon substrate and smooth polycrystalline Pt is not surprising. Most recently Arvia *et al.* [11] have also reported a sizeable difference in hydrogen adsorption on high-surface area and smooth platinum electrodes.

Figs 1 and 2 show the cyclic voltammograms of PC 3000 in the absence (dashed line) and in the presence (full line) of Pb and Bi cations in solution. In each case the reduction of platinum oxide is followed by the u.p.d. of cations. To date no comments have been made about the difference of u.p.d. at supported high surface area Pt and smooth polycrystalline Pt. The u.p.d. of Pb and Bi on PC 3000 is much smaller than on the smooth Pt electrode. A small suppression of hydrogen adsorption by a submonolayer of Pb adatoms is also observed (Fig. 1). Lower currents are obtained in the presence of Bi than Pb (Fig. 2), in the region of hydrogen adsorption. The u.p.d. of Bi is clearly seen in the region of its dissolution.

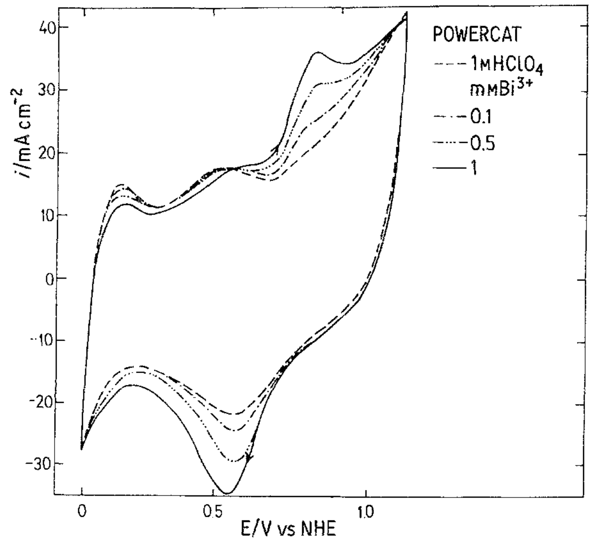

Fig. 2. Cyclic voltammogram of underpotential deposition of bismuth on PC 3000 electrode in 1 M $HClO_4$, containing none (dashed line) and 0.1 mM Bi^{3+} (full line). Sweep rate 20 mV sec^{-1}.

In order to determine the real surface area of a platinum electrode it is customary to determine the coverage of adsorbed hydrogen and then, by taking 210 μC cm^{-2} as a monolayer coverage, calculate the roughness factor, i.e. the real surface area. This method would certainly give unrealistic results for the roughness factor for PC 3000, as well as for the measurements of the coverage of Pb or Bi adatoms. Figs 1 and 2 show that the best defined process for PC 3000 is the oxide reduction. Hence, the peak for the Pt-oxide reduction has been determined, and by taking two electrons per site, i.e. 420 μC cm^{-2} for a monolayer of Pt-oxide, the roughness factor of roughly 400 has been calculated.

The Bi coverage could be estimated from the peak at 0.9 V. Its dissolution on smooth Pt commences at more negative potentials [9]. That peak is not, however, well defined in Fig. 2. The peak at 0.9 V gives, for three different Bi concentrations of 0.1, 0.5 and 1 mM, coverages of 36, 108 and 180 mC cm^{-2} respectively. If divided by a roughness factor of 400 these values give approximate coverages of 0.09, 0.27 and 0.45 respectively.

3.2. *Oxidation of formic acid on PC 3000*

The effect of Pb on the oxidation of formic acid on the electrode PC 3000 is shown in Fig. 3 where the potential sweep curves are given for 1 M HCOOH in the absence (dashed line) and in the presence (full line) of lead cations in the electrolyte. The catalytic effect of Pb is high. However, the ratio of current peaks is not as high as for smooth Pt. Nevertheless, the currents of several hundreds of mA cm^{-2} for the oxidation of the organic molecule are very high, even for a high surface area electrode. The peak potentials for the anodic and cathodic scans are almost the same. No *IR* compensation or correction was made with the curves in

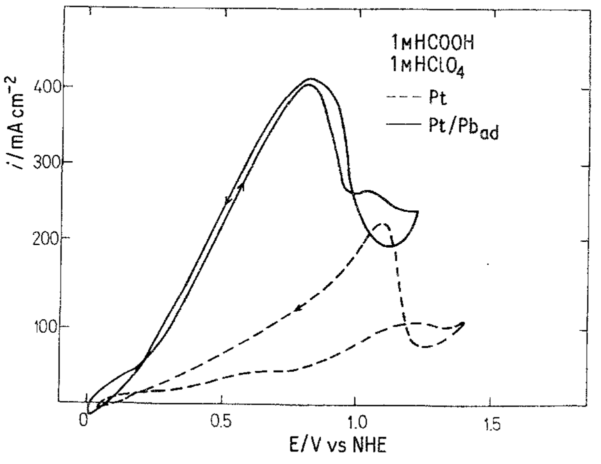

Fig. 3. Catalytic effect of lead on formic acid oxidation at PC 3000 in 1 M $HClO_4$. Cyclic voltammogram in the absence (dashed line) and in the presence (full line) of 0.5 mM Pb^{2+}. Sweep rate 50 mV sec^{-1}.

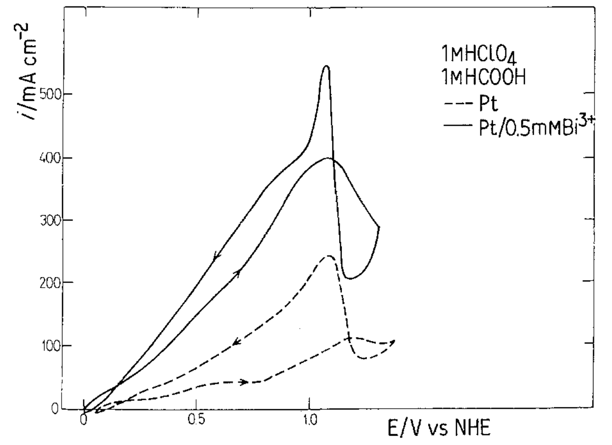

Fig. 4. Catalytic effect of bismuth on formic acid oxidation at PC 3000 in 1 M $HClO_4$. Cyclic voltammogram in the absence (dashed line) and in the presence (full line) of 0.5 mM Bi^{3+}. Sweep rate 50 mV sec^{-1}.

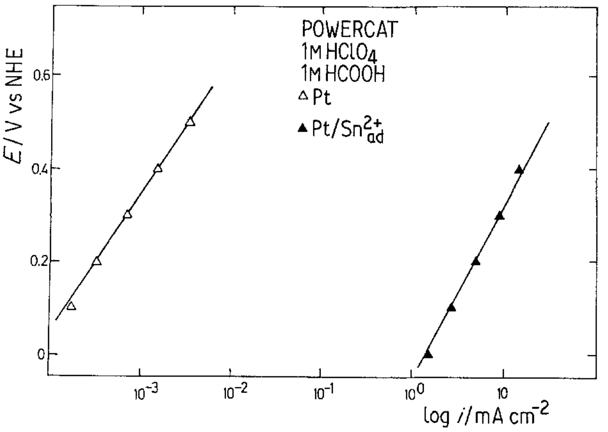

Fig. 6. Tafel plots for oxidation of 1 M HCOOH in 1 M $HClO_4$ at PC 3000 in the absence (△) and in the presence of Sn adatoms (▲) previously adsorbed for 15 min at 0.5 V from solution containing 0.5 mM Sn^{2+}.

Fig. 3. So the curve in the presence of PGb adatoms, at those high current densities, is probably shifted to more positive potentials. Therefore, the actual catalytic effect is higher than that seen in Fig. 3.

Fig. 4 shows the effect of Bi on formic acid oxidation on the PC 3000 electrode. The first anodic peak is shifted to more positive potentials and a sharp cathodic peak with a shoulder is observed. In the case of Bi also currents of several hundreds of mA cm^{-2} are obtained, and the same explanation, as above for Pb, can be applied.

3.3. *Steady-state polarization measurements*

Investigation of HCOOH oxidation on PC 3000 was also carried out by recording the steady-state curves for the oxidation of formic acid in the absence and in the presence of lead and tin adatoms. The Tafel relationships obtained for different concentrations of Pb^{2+} ions present in solution and Sn^{2+} ions previously adsorbed on the electrode surface are shown in Figs 5 and 6. The measurements were carried out after reaching the quasi-equlibrium by waiting 90 s at each potential. In both cases high Tafel slopes were obtained. The slope for PC 3000 is ~400 mV dec^{-1}. In the presence of lead adatoms it is 425 mV dec^{-1}. The catalytic effect of lead under these conditions shifts the Tafel line by about one order of magnitude on the current scale. Similar results have been obtained for 0.5 and 1 mM solutions.

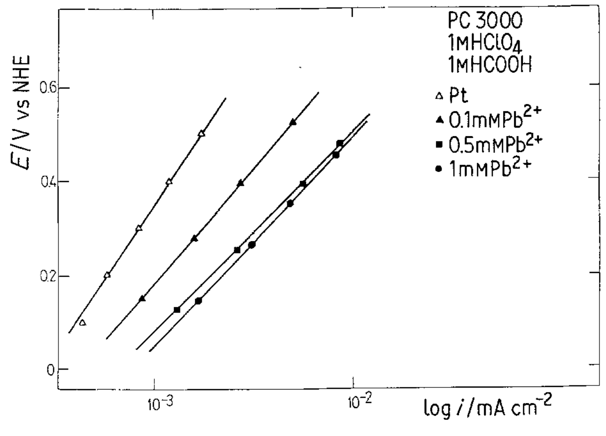

Fig. 5. Tafel plots for oxidation of 1 M HCOOH in 1 M $HClO_4$ at PC 3000 in the absence (△) and in the presence of (▲) 0.1; (■) 0.5 and (●) 1 mM Pb^{2+}.

The high Tafel slopes, higher than 120 mV dec^{-1}, may have several origins, including the uncompensated *IR* drop, a change in the potential distribution in the double layer and increased concentration of the reaction products in the pre-electrode layer. A large *IR* drop would cause curved *E*-log *i* plots, so its contribution is probably small. The other two sources probably contribute more to the increase in the Tafel slope.

Following the work with Pt-Sn alloys by Cathro [12] several experiments have been carried out with Sn adatoms. The catalytic effects observed differ considerably, ranging from a factor of 10 [13] to 50–100 [10] and even larger [14]. This cannot be explained only by a different method of preparation of Sn adatoms, although the 'immersion' technique of Janssen and Moolhysen [10] gave consistently larger effects in this laboratory than the u.p.d. of Sn adatoms in the presence of Sn ions in the electrolyte. Motoo and Watanabe [14] have reported catalytic effects on the oxidation of HCOOH, caused by alloying Pt with Sn adatoms. The alloy is not stable and 'cycling' the potential into a region of oxide formation on Pt causes a complete dissolution of Sn [14]. The mechanism of the catalytic effect of tin has been explained by reversible adsorption of oxygen by the tin adatom, which participates in the oxidation of the chemisorbed organic species [13]. A considerable enhancement of four orders of magnitude is obtained in the presence of tin adatoms in the work under the conditions given in Fig. 6. This striking effect also has been obtained if the potential is scanned at a small rate of 0.1 mV sec^{-1} with slopes of 340 mV dec^{-1}.

The longstanding interest of electrochemists in the mechanism of the oxidation of HCOOH stems from its role as a possible fuel and a model molecule since it appears as an intemediate in the oxidation of larger organics. There was no consensus on the mechanism of this reaction which has been aggravated most recently by different reports on the nature of the

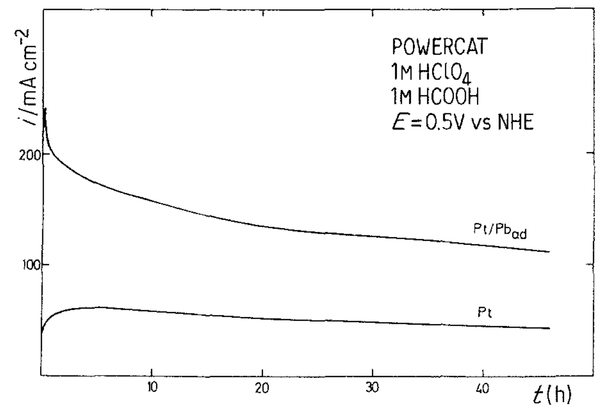

Fig. 7. Long-term experiments during oxidation of 1 M HCOOH in 1 M $HClO_4$ at PC 3000. Electrode potential 0.5 V; 0.5 mM Pb^{2+} in solution.

strongly bound intermediate. The data obtained by Bewick *et al.* [15] by EMIRS (electrode modulated infrared spectroscopy) indicate CO, while Heitbaum *et al.* [16] by DEMS (differential electrochemical mass spectroscopy) show evidence of COH as the strongly bound intermediate.

For this discussion it suffices to recall that the first step in the oxidation of HCOOH on Pt is

$$HCOOH \longrightarrow -COOH + H^+ + e \qquad (1)$$

It is accepted that the reaction goes further in two pathways.

$$-COOH \begin{cases} \nearrow \text{strongly bound species} \\ \searrow CO_2 + H^+ + e \end{cases} \qquad (2)$$

The intermediate COH can be formed [5, 17] in reaction

$$-COOH + 2H_{ad} \longrightarrow \equiv COH + H_2O \qquad (3)$$

The explanation of the catalytic effects of foreign metal adatoms is based on the elimination of reaction 3 by suppression of hydrogen adsorption, and by decrease of adsorption of the strongly bound intermediates outside the H-adsorption region. For Sn adatoms, a coadsorbed O or OH has been assumed to take part in the oxidation of the poisoning species [8, 14]. One can write for CO and COH,

$$SnOH + COH \longrightarrow Sn + CO_2 + 2H^+ + 2e \qquad (4)$$

$$SnOH + CO \longrightarrow Sn + CO_2 + H^+ + e \qquad (5)$$

Sn adatoms probably act through reactions 4 and 5 and suppress reaction 3, which explains its higher effect in comparison with the effect of Pb adatoms. A determination of the stability of the catalytic activity of surfaces modified by Pb, Bi and Sn is necessary for assessing their potential for application.

3.4. *Long-term stability of modified PC 3000 and reactivation*

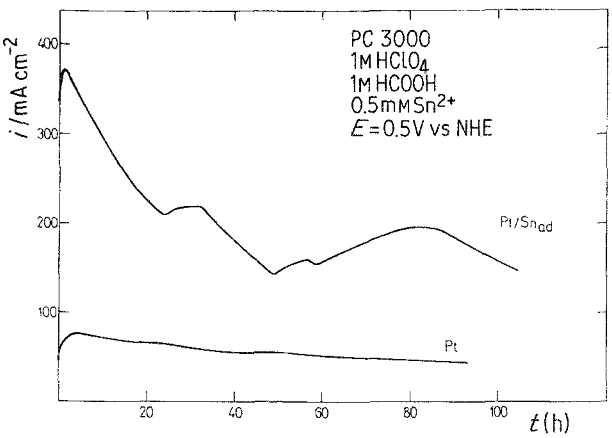

Fig. 8. Long-term experiments during oxidation of 1 M HCOOH in 1 M $HClO_4$ at PC 3000. Electrode potential 0.5 V; Sn adatoms previously adsorbed for 15 min at 0.5 V from solution containing 0.5 mM Sn^{2+}.

The catalytic activity of PC 3000 was measured in the absence and in the presence of Pb and Sn adatoms. Lead was in equilibrium with 0.5 mM Pb^{2+}. The resulting current versus time responses on a potential step to 0.5 V were recorded. This potential has been selected as the peak potential, although one can expect a longer stability of catalytic effects at less positive values. The Sn adatoms were preadsorbed, as explained above, and the measurements were done without cations in solution. The curves are shown in Figs 7 and 8 respectively. In general, initial currents were of the order of 0.3–0.4 A cm^{-2} and decreased gradually in the case of Pb within 44 h of experiment. An initial increase of the current is probably due to a wetting of a highly hydrophobic surface which increases the contact area of reactant and catalyst. After 20 h both curves assume a very slow rate of change indicating that such differences in the activity of PC 3000/Pb and PC 3000 could last longer than 45 h.

The case of PC 3000/Sn is somewhat different. The variation of the current with time is not gradual but rather irregular. It is surprising that the shape of the curve up to 40 h has been reproduced. A sizeable activity of electrode is seen even above 100 h. There are probably three causes of a gradual decrease in activity. The main one, certainly is the poisoning of catalyst particles by strongly bound intermediates. Secondly, Sn and Pb species can be either blocked or desorbed from such a surface, and finally the exhausting of HCOOH in electrolyte also contributes to the decrease in activity.

Reactivation of a PC 3000 electrode was attempted by cycling it up to 1.2 V in order to oxidize strongly bound intermediates. The addition of fuel and cations to form adatoms were tried too. Each time an increase in current density was observed, but a relatively rapid drop to the previously obtained currents was found. Some disintegration of PC 3000 was noticed after 120 h of continuous operation. The above reactivation procedure is not adequate for the Sn-activated catalysts since it irreversibly oxidizes Sn adatoms, while the Sn cations in solution give smaller enhancement than activation by immersion. Further work is needed to devise a more efficient method of activation.

3.5. *The XPS measurements*

An effort was made to determine the state of Pt crystallites on PC 3000 by the XPS technique in a Riber 600 XPS-AES-LEED system. Preliminary results show that only C could be seen on such a surface; Pt could not be identified.

4. Conclusions

The activation of the high-area Pt catalyst, such as PC 3000, by foreign metal adatoms formed by underpotential deposition seems promising for practical application. A sizable activation by Pb and Sn adatoms could be considerably enhanced by optimizing the size of the catalyst particles, hydrophobicity of the electrode surface and the method of preparation and maintaining of foreign metal adatoms.

Acknowledgements

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