

## LIMITING OXYGEN COVERAGE ON SMOOTH PLATINUM ANODES IN ACID SOLUTION

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Despite numerous studies on the properties of the oxygen-containing film formed on anodic platinum surfaces (see GILMAN<sup>1</sup> and HOARE<sup>2</sup> for recent reviews) there is still no measure of agreement on the nature and extent of the adsorbed layer. It is generally accepted that in acid solution oxygen adsorption commences about 0.8 V with respect to a reversible hydrogen electrode (RHE), and that the amount of oxygen which can be detected by cathodic stripping increases with potential to quantities in excess of one oxygen atom/platinum atom. The coverage-potential relationship has been given as approximately linear, with no apparent limiting coverage, by a number of authors<sup>3-9</sup>. On the other hand MAYELL AND LANGER<sup>10</sup> and FLEISCHMANN *et al.*<sup>11</sup> have reported a maximum followed by a plateau at high potentials.

The various postulates concerning the nature of the adsorbed layer can be conveniently classified into four groups.

(1) Oxygen-containing species are chemisorbed and the surface can accommodate more than one oxygen atom/surface platinum atom.

(2) Oxygen atoms are chemisorbed on the surface but those in excess of one/surface platinum atom are absorbed into the underlying metal lattice ("dermasorbed").

(3) Chemisorption occurs at potentials below about 1.4 V but when the O/Pt ratio exceeds unity, the adlayer is considered to be a phase oxide.

(4) Distinct PtO (or PtOH) phases of various stoichiometries are proposed for all potentials.

GILMAN<sup>1</sup> has pointed out the difficulty in defining properties that provide a precise basis for distinguishing between chemisorbed oxygen and phase oxide. However, the commonly accepted criteria<sup>1</sup> are that chemisorption is essentially due to bonding between oxygen and the surface without disruption of the metal lattice, while a phase oxide has the lattice structure and thermodynamic properties of the bulk oxide. Consequently, a limiting coverage is required for chemisorption whereas no such restriction is necessary in the case of phase oxide.

The results obtained at high potentials seem critical in distinguishing between the above categories. The finding by FLEISCHMANN *et al.*<sup>11</sup> of a maximum coverage of about 25 mC cm<sup>-2</sup> appears to support the phase oxide concept, but in view of the very large quantitative discrepancies between these results and the work of MAYELL AND LANGER<sup>10</sup> we considered it important to re-examine the high potential region. In both the above works the precautions taken to eliminate possible contributions from reduction of molecular oxygen seem to be inadequate. GILMAN<sup>7</sup> has already

shown that, owing to the well known irreversibility of "oxide" reduction, the potential can be held for some time at 1.5 V without loss of "oxide" formed at higher potentials where oxygen is evolved. This allows purging of the solution and eliminates the problem of dissolved oxygen. Galvanostatic or voltammetric stripping can then be used to determine the cathodic charge passed in reducing the "oxide" layer ( $Q_{ox}$ ) and at the same time to measure the true electrode area from the hydrogen region of these curves. Monitoring of electrode area is important wherever programs involving anodic-cathodic treatments are used<sup>12,13</sup>.

Experiments were carried out at 25° in 1 M H<sub>2</sub>SO<sub>4</sub> prepared from doubly distilled water and B.D.H. AristaR reagent. Solutions were degassed with purified nitrogen. A three-compartment glass cell of conventional design was used. The reference electrode, mercury/mercurous sulphate in 1 M H<sub>2</sub>SO<sub>4</sub>, had a potential of 0.68 V vs. RHE in 1 M H<sub>2</sub>SO<sub>4</sub>, to which all potentials are referred. The potential was controlled by a Wenking fast rise potentiostat and programmed with a Tacussel GSTP2 function generator together with a bias unit of potential dividers and switches to provide potential steps. Current-voltage curves were recorded on a Moseley 7035A X-Y recorder.

The electrode was a length of 38-gauge platinum wire (geometric area 0.0182 cm<sup>2</sup>) sealed into soft glass tubing. After heating to yellow heat in a coal gas/air flame the electrode was activated by triangular potential cycling between 0.05 and 1.54 V for a total of 350 cycles. The surface at this stage is at a constant and reproducible activity<sup>13</sup>. After this pre-treatment the saturation hydrogen coverage,  $Q_H^s$ , was 4.6  $\mu$ C (253  $\mu$ C/geometric cm<sup>2</sup>), giving a roughness factor of 1.2.

The programs used to generate and determine the adsorbed oxygen are shown in Fig. 1. Program B was used for  $\phi_{ox} \geq 1.68$  V. Vigorous deoxygenation was carried out during the period,  $t_d$ , which was 30 sec except at the highest potential

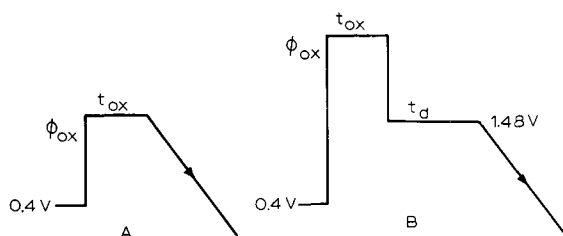


Fig. 1. Potential programs used to generate and determine the adsorbed oxygen layer.

studied (3.0 V) where so much oxygen was evolved that the purging time had to be increased to 300 sec. The nitrogen bubbling was stopped and the solution allowed to become quiescent before the linear potential sweep was applied. Shorter values of  $t_d$  caused difficulty in selection of a base-line for integration of the "oxide" reduction peak because of the presence of a cathodic wave for residual dissolved oxygen. However, no decrease in  $Q_{ox}$  with increasing  $t_d$  could be detected and, correspondingly, the current during this period was below the detection limit of the apparatus ( $5 \cdot 10^{-9}$  A). This confirms that program B is appropriate for precise determination of  $Q_{ox}$  at high potentials.

Figure 2 shows cathodic sweeps for two values of  $\phi_{ox}$  and constant  $t_{ox}$  (10 sec).

Base-lines for integration of  $Q_{\text{ox}}$  and  $Q_{\text{H}^{\text{s}}}$  are shown on the curves. The potential-dependence of  $Q_{\text{ox}}$  for  $t_{\text{ox}} = 10$  sec is plotted in Fig. 3 as a ratio of  $2 Q_{\text{H}^{\text{s}}}$ ; a value of unity then corresponds theoretically to a coverage of one oxygen atom to each surface platinum atom. It can be seen that at potentials above 2.2 V, the oxygen coverage reaches a limiting value of  $Q_{\text{ox}}/2 Q_{\text{H}^{\text{s}}} = 2.47 \pm 0.05$ . However, even at the highest potential examined (2.98 V),  $Q_{\text{ox}}$  for  $t_{\text{ox}}$  of 10 sec is not quite the steady value. Figure 4

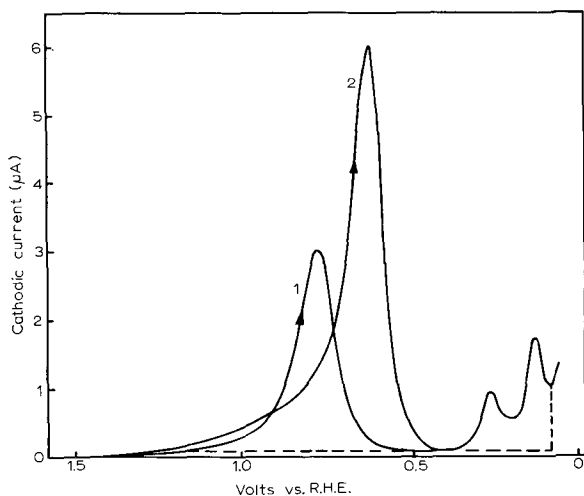


Fig. 2. Cathodic current-potential curves showing oxygen reduction (potential  $> 0.4$  V) and hydrogen adsorption (0–0.4 V) peaks for  $t_{\text{ox}}$  of 10 sec and  $\phi_{\text{ox}}$  of (1), 1.48; (2), 2.46 V. Linear potential sweep, 41.3 mV/sec. Dotted lines are base-lines used for integration of the curves.

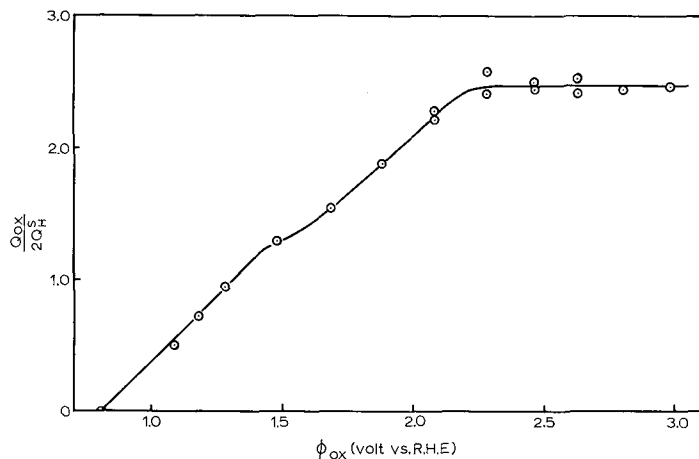


Fig. 3. Dependence of oxygen coverage on potential of "oxide" formation,  $\phi_{\text{ox}}$ , for  $t_{\text{ox}} = 10$  sec.

shows the time-dependence observed under these conditions. A limiting value of  $2.66 \pm 0.05$  is reached within 100 sec, staying constant up to 5,100 sec. Note that  $\phi_{\text{ox}}$ -values are corrected for  $iR$  drop between the Luggin probe and electrode surface. At an applied potential of 3.08 V where the current density was  $6.5 \text{ A cm}^{-2}$ , the  $iR$

drop was determined by a current interrupter technique to be 0.10 V. Oxygen evolution currents were in line with published polarization curves<sup>14</sup>. After all experiments were completed no platinum could be detected in the cell solution by the stannous chloride test.

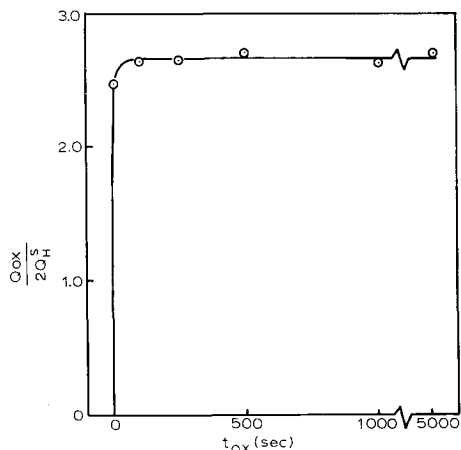


Fig. 4. Dependence of oxygen coverage on time of formation,  $t_{ox}$ , at  $\phi_{ox} = 2.98$  V.

A cathodic shift of 0.18 V in the "oxide" reduction peak found between  $\phi_{ox}$ -values of 1.3 and 2.1 V is of the same order as previous observations in this potential region<sup>5,15,16</sup>. At higher potentials, corresponding to the limiting value of  $Q_{ox}$ , this shift becomes much smaller, 0.02 V between  $\phi_{ox}$ -values of 2.3 and 3.0 V.

The above results were reproducible on this and other electrodes. However, under severe conditions of anodic polarization ( $\geq 1,000$  sec at 2.98 V) behaviour quite different from that described above was occasionally, but irreproducibly, observed.  $Q_{ox}$  increased, "oxide" reduction extended into the hydrogen region and the electrode area, as measured by  $Q_H$ <sup>5</sup> on subsequent cycles, was substantially higher than before anodization. The lack of reproducibility of this behaviour does not allow us to define the conditions under which it occurs. However, it is possibly related to earlier observations<sup>17,18</sup> of a less easily reduced "oxide" formed under extended anodic polarization.

For potentials up to 2 V, the present coverages are in good agreement with those of BECKER AND BREITER<sup>3</sup>, LAITINEN AND ENKE<sup>4</sup>, GILMAN<sup>7</sup> and BAGOTSKII AND VASIL'EV<sup>9</sup> none of whom extended their measurements to the potentials at which we observe a limiting coverage. Coverages reported by DAMJANOVIC *et al.*<sup>19</sup> cannot be compared with these data as real electrode areas were not given. Higher coverages at potentials up to 1.7 V have been reported by VISSCHER AND DEVANATHAN<sup>6</sup> and used in support of a phase oxide theory. Their conclusions are weakened by the facts that (a) the solution was saturated with molecular oxygen, and (b) electrode areas were determined by the unreliable double-layer capacity method, which depends on a choice of a value for capacity/true  $cm^2$ , given by various authors<sup>7,20,21</sup> as between 16 and 80  $\mu F/cm^2$ . Similar criticisms can be levelled at the high results of FLEISCHMANN *et al.*<sup>11</sup> who worked in solutions containing oxygen evolved at high

potentials and who failed to measure the true area of their etched electrodes. The shielded electrodes, and inefficient method of removing dissolved oxygen, also probably led to errors in the work of MAYELL AND LANGER<sup>10</sup> who reported very different results from those shown in Fig. 3. On smooth electrodes they found a maximum in  $Q_{ox}$  at 1.75 V, equivalent to  $Q_{ox}/2 Q_H^s \sim 4$ , while at higher potentials  $Q_{ox}$  fell to about one-quarter of this value. Inspection of Fig. 3 of ref. 10, shows that the smaller quantity of "oxide" formed at  $\phi_{ox} > 1.75$  V was in fact reduced at much lower potentials ( $\sim 0.45$  V) than the "oxide" formed at  $\phi_{ox} < 1.75$  V. This result contradicts all previous findings and the work of MAYELL AND LANGER must be considered suspect.

It is interesting to note that the inflection at  $\sim 1.6$  V in Fig. 3, also found by BECKER AND BREITER<sup>3</sup> and GILMAN<sup>7</sup>, occurs at an "oxide" coverage of approximately half the limiting value. A similar phenomenon occurs on the coverage-potential curve for adsorbed hydrogen<sup>22</sup>, corresponding to the well known double peak found on linear potential sweeps in the hydrogen region and supposedly due to heterogeneity of the platinum surface<sup>1,23,24</sup>. This suggests that a second anodic pseudocapacity peak would be found at about 1.9 V if it were not obscured by the faradaic current due to oxygen evolution.

Our results above 1.0 V support a model in which oxygen atoms are chemisorbed onto the platinum surface and can be accommodated up to a coverage corresponding to about 2.66 oxygen atoms/platinum atom. The fact that a limiting coverage, independent of potential and time, can be observed indicates that this is a monolayer of oxygen atoms. This model fits into the first group of theories for "oxide" films described above. There has been a general reluctance amongst electrochemists to accept the concept of a chemisorbed oxygen monolayer containing more than one adsorbed oxygen atom/metal atom, but there is no convincing reason why such a layer cannot occur. The average area occupied by platinum atoms in the metal surface is about  $7.5 \text{ \AA}^2$  while the radius of covalently bonded oxygen can vary from 0.58 to 0.75  $\text{ \AA}$  depending on the nature of the bond<sup>25</sup>. These figures indicate that the observed oxygen coverage is well within the limits placed by steric factors.

The experimental results claimed by SCHULDINER AND WARNER<sup>26</sup> to support the idea of dermasorption of oxygen are just as easily explained by the ability of the surface to adsorb more than one oxygen atom/platinum atom. Furthermore, if all oxygen atoms in excess of one/platinum atom do in fact diffuse into the platinum lattice, one would expect to see a dependence of both oxygen coverage and the kinetics of reduction on the time of anodization. The time-independence of  $Q_{ox}$  at high potentials is therefore positive evidence against dermasorption contributing significantly to  $Q_{ox}$ . The potential- and time-independence of  $Q_{ox}$  provide evidence against the theory that the "oxide" layer above 1.4 V can be given the attributes of a phase, since one would expect a phase oxide to grow well beyond the limiting  $Q_{ox}$ -value we found. However, the few instances where we observed higher values of  $Q_{ox}$  under severe polarization (see above) might be explained by formation of phase oxide which, because of breakage of platinum-platinum bonds, could also account for the associated roughening of the electrode. Note that the conditions under which this irreproducible behaviour was found are much more severe than those for which phase oxides have generally been postulated. Ellipsometric evidence for phase oxide at lower potentials<sup>8,27</sup> relies on the assumption that the optical properties of a

platinum surface with chemisorbed oxygen atoms are not greatly different from those of a surface on which water is physically adsorbed. This assumption is difficult to justify. Evidence obtained from the chemical dissolution of the "oxide" layer<sup>28</sup> cannot be interpreted unambiguously<sup>1</sup>.

#### SUMMARY

We observe that coverage by oxygen on a platinum electrode increases continuously with potential until a limiting value of about 2.66 oxygen atoms/platinum atom is reached. In previous work, either the measurements were not extended to sufficiently anodic potentials to reach this limit or the techniques used are open to criticism. The present result is therefore important in distinguishing between theories of the nature of the oxygen-containing film. It is concluded that above 1.0 V, oxygen atoms are chemisorbed onto the platinum surface and that the limiting coverage represents a monolayer.

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