

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/323823332>

ELECTROANALYTICAL CHEMISTRY AND INTERFACIAL ELECTROCHEMISTRY 269 Elsevier Sequoia S.A., Lausanne-Printed in The Netherlands LIMITING OXY....

Article · March 2018

CITATIONS

0

READS

665

3 authors, including:



David Rand

The Commonwealth Scientific and Industrial Research Organ...

195 PUBLICATIONS **5,914** CITATIONS

[SEE PROFILE](#)



Ronald Woods

Griffith University

213 PUBLICATIONS **8,337** CITATIONS

[SEE PROFILE](#)

LIMITING OXYGEN COVERAGE ON PLATINIZED PLATINUM; RELEVANCE TO DETERMINATION OF REAL PLATINUM AREA BY HYDROGEN ADSORPTION

T. BIEGLER, D. A. J. RAND AND R. WOODS

CSIRO, Division of Mineral Chemistry, Port Melbourne, Victoria 3207 (Australia)

(Received 11th August 1970)

INTRODUCTION

When a smooth platinum electrode is anodized, the oxygen coverage increases with both time and potential until a well-defined limit is attained^{1,2}. This phenomenon indicates that the oxygen is chemisorbed, the limit representing monolayer coverage. Other models which consider the surface oxygen layer to be a phase oxide (*e.g.* ref. 3) or to involve dermasorbed oxygen⁴ are not consistent with a limiting coverage. However, severe conditions of anodic polarization can produce what appears to be a distinct platinum oxide phase^{1,5-7} which has clearly different properties from the chemisorbed oxygen layer, in both the conditions of its formation and its electrochemical behaviour.

Comparison of oxygen and hydrogen adsorption led to the conclusion that the oxygen monolayer contained about 2.7 oxygen atoms/surface platinum atom¹. In order to ascertain whether this stoichiometry depends on platinum surface structure or degree of dispersion, it was decided to investigate oxygen coverages on platinized platinum. Establishment of the stoichiometry rests critically on the ability to determine the true hydrogen monolayer charge and it will be shown that this requires a reassessment of the conventions used to separate hydrogen adsorption from the hydrogen evolution reaction.

EXPERIMENTAL

Experiments were carried out at 25° in 1 M H₂SO₄ prepared from doubly distilled water and B.D.H. Aristar reagent, and degassed with purified nitrogen. A mercury/mercurous sulphate, 1 M H₂SO₄ reference electrode was used, the potential of which was 0.68 V *vs.* the reversible hydrogen electrode (RHE) in 1 M H₂SO₄. All potentials refer to the RHE. Potentials were controlled with a Wenking 68TS1 potentiostat programmed with a potential step bias unit and a sweep generator* designed and constructed in these laboratories. Voltammograms were recorded on a Moseley 7035A X-Y recorder.

The platinized electrode was prepared by electrodeposition on to 30-gauge platinum wire. Platinization was carried out for 3 min at 0.05 V in 2% chloroplatinic

* Complete circuit details are available from M. Zuiderwyk at the above address.

acid, 1 M HCl solution. The electrode was rinsed, soaked overnight in distilled water and then aged by triangular potential cycling in 1 M H₂SO₄ (0–1.5 V, 20 mV s⁻¹, 500 cycles). This aging procedure resulted in an electrode whose roughness did not change significantly during the course of adsorption measurements. The roughness factor measured using monolayer hydrogen adsorption (*v.i.*) was 35.

The adsorbed oxygen layer was formed by holding the electrode at an anodic potential ϕ_{ox} for a period t_{ox} . The amount of oxygen adsorbed, Q_{ox} , was determined by applying a linear potential scan from ϕ_{ox} (Fig. 1A). Reduction of dissolved molecular oxygen interferes with the measurement of Q_{ox} . Therefore, when significant amounts of molecular oxygen were evolved at ϕ_{ox} , the potential was lowered to 1.48 V for a period t_d before the cathodic sweep was started (Fig. 1B). During this time the solution was

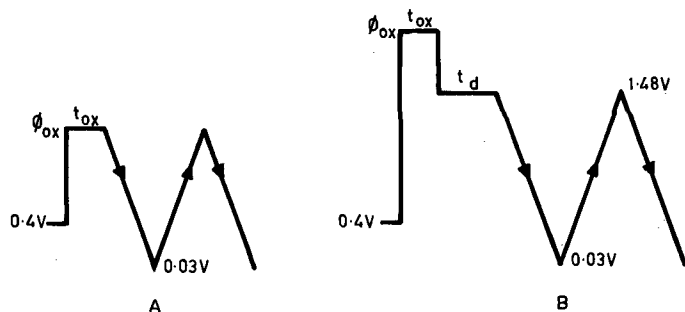


Fig. 1. Potential programs used to generate and determine the adsorbed oxygen layer.

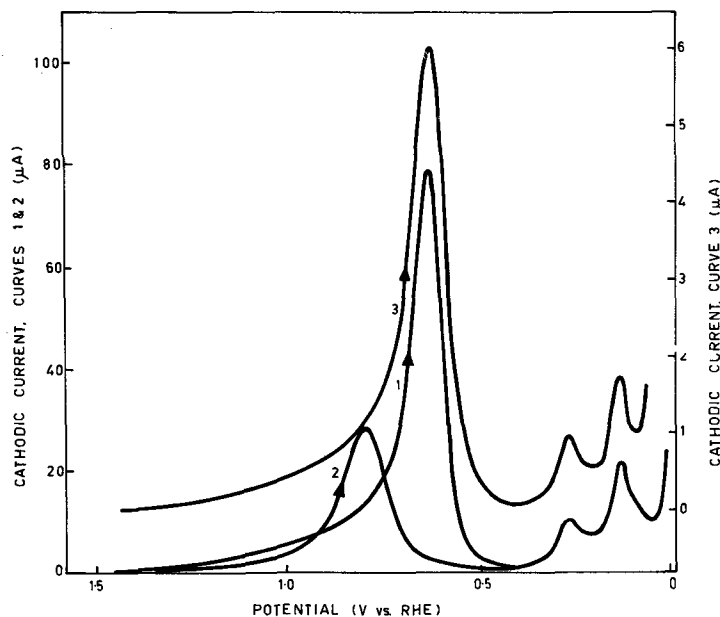


Fig. 2. Cathodic voltammograms for platinumized platinum (1 and 2) and smooth platinum (3). Sweep rate 20 mV s⁻¹. (1) and (3) After holding at $\phi_{ox} = 2.46$ V for $t_{ox} = 10$ s; (2) cathodic sweep of the triangular cycle following (1).

purged with nitrogen. Because of the well-known hysteresis in the oxygen adsorption and desorption process, Q_{ox} does not decrease during t_d and all the oxygen adsorbed at ϕ_{ox} is reduced during the cathodic sweep¹. The time t_d was 100 s except for $\phi_{ox} \geq 2.6$ V when the larger quantity of oxygen evolved necessitated an increase in t_d to 300 s.

The large currents due to oxygen evolution at high ϕ_{ox} caused an appreciable iR drop between the Luggin probe and electrode surface. The iR drop was measured with a current interrupter technique and was 0.28 V at the highest potential applied, 3.08 V. Values of ϕ_{ox} are corrected for iR drop.

Typical voltammograms for platinized platinum are shown in Fig. 2 (curves 1 and 2) and compared with a corresponding curve for smooth platinum. The oxygen desorption peak is followed by the two peaks due to adsorption of hydrogen; extending the sweep into the hydrogen region gives a measure of the real electrode area. The sweep was reversed at 0.03 V and a triangular potential cycle applied (see Fig. 1). The cathodic part of this cycle is shown as curve 2 in Fig. 2. Comparison between the hydrogen regions of the two cathodic scans (curves 1 and 2) shows whether oxygen desorption is complete before hydrogen adsorption commences.

The charges due to adsorbed oxygen, Q_{ox} , and hydrogen, Q_H , were obtained by integration of the corresponding peaks in the voltammogram. The current minimum in the double layer region of the second sweep was taken as a measure of the double layer capacitance, assumed constant, and used as a base-line for integration (*cf.* Fig. 2, ref. 1).

RESULTS AND DISCUSSION

Oxygen coverage

The dependence of Q_{ox} on ϕ_{ox} for t_{ox} of 10 and 100 s is shown in Fig. 3. Here Q_{ox} is expressed as a ratio of $2Q_{H,a}$, where $Q_{H,a}$ is the quantity of charge passed in adsorbing hydrogen up to the potential of the current minimum which follows the second hydrogen peak. This potential, ϕ_{min} , was 0.04 V (Fig. 2) for the platinized platinum electrode investigated.

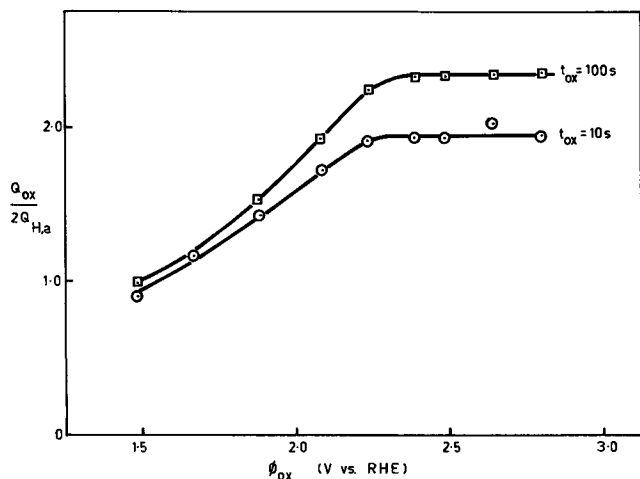


Fig. 3. Dependence of oxygen coverage on anodization potential ϕ_{ox} for platinized platinum.

Oxygen coverage increases with potential and at about 2.3 V (Fig. 3) $Q_{\text{ox}}/2Q_{\text{H,a}}$ reaches a limiting value of 1.95 and 2.35 for t_{ox} of 10 and 100 s respectively. For the same reasons as discussed for smooth platinum¹, we conclude from this behaviour that the anodic film under these conditions is best described in terms of chemisorbed oxygen atoms. At longer anodization times, the voltammograms for the reduction of the oxygen layer formed at $\phi_{\text{ox}} \geq 2.3$ V show marked differences from the typical curve of Fig. 2. The current in the hydrogen region is greater than that attributable to hydrogen adsorption alone and produces a distinct peak at about 0.1 V (Fig. 4). Un-

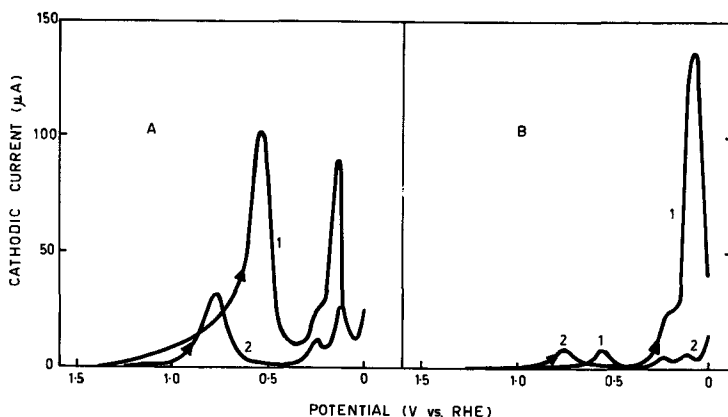


Fig. 4. Cathodic voltammograms for platinumized platinum under severe conditions of anodization. A(1) $\phi_{\text{ox}} = 2.36$ V, $t_{\text{ox}} = 1000$ s; B(1) $\phi_{\text{ox}} = 2.80$ V, $t_{\text{ox}} = 5000$ s. A (2), B (2) cathodic sweep of the following triangular cycle. Sweep rate 20 mV s^{-1} .

der the most severe conditions of anodization the "normal" oxygen reduction peak is substantially diminished and the peak at 0.1 V dominates (Fig. 4B); this phenomenon is accompanied by a four-fold decrease in surface roughness of the electrode as revealed by the diminished current of the following triangular sweep (*cf.* A(2) and B(2)). Such behaviour is clearly analogous to that associated with the formation and reduction of an oxide phase on smooth platinum electrodes^{1,5-7}. Thus a distinction between chemisorbed oxygen and phase oxide on platinumized platinum can be made in the same way as for smooth platinum¹. A similar distinction is also apparent for rhodium, palladium and gold electrodes⁸.

It can be seen from Fig. 3 that the coverage of chemisorbed oxygen shows some time-dependence even in the region where it is independent of potential. With smooth platinum, the coverage in this region reaches a limit at $t_{\text{ox}} = 100$ s (Fig. 4, ref. 1). With platinumized platinum, phase oxide develops more readily and proper separation of the charge contribution due to chemisorbed oxygen is not possible for t_{ox} much above 100 s. However, by analogy with the behaviour of smooth platinum, it is inferred that the potential-independent value of Q_{ox} for $t_{\text{ox}} = 100$ s is the limiting chemisorbed oxygen coverage $Q_{\text{ox,s}}$ which represents a monolayer. Consequently, the monolayer coverage for platinumized platinum, expressed as $Q_{\text{ox,s}}/2Q_{\text{H,a}}$, is 2.35 which is significantly lower than the value of 2.66 found for smooth platinum.

Oxygen monolayer stoichiometry

The method of expressing oxygen coverage as a ratio of monolayer hydrogen coverage is intended to yield values independent of surface roughness and to provide a

measure of the oxygen to platinum surface atom stoichiometry. In order to equate $Q_{\text{ox},s}/2Q_{\text{H},a}$ with this stoichiometry it must be assumed that (i) $Q_{\text{H},a}$ is the monolayer hydrogen coverage and (ii) this monolayer contains one hydrogen atom per platinum surface atom; these assumptions have been discussed in detail by Gilman⁹. The method used here to determine $Q_{\text{H},a}$ follows essentially the procedure advocated by Gilman^{9,10} to obtain the monolayer hydrogen charge*. As was pointed out⁹, this procedure involves an arbitrary choice of ϕ_{min} as an "end-point" for integration of the charge due to hydrogen adsorption. This choice implies that any charge required to complete the hydrogen monolayer at potentials cathodic to ϕ_{min} is compensated by the inclusion of a contribution from hydrogen evolution at potentials anodic to ϕ_{min} (Fig. 5A). Several observations bring the accuracy of this assumption into question.

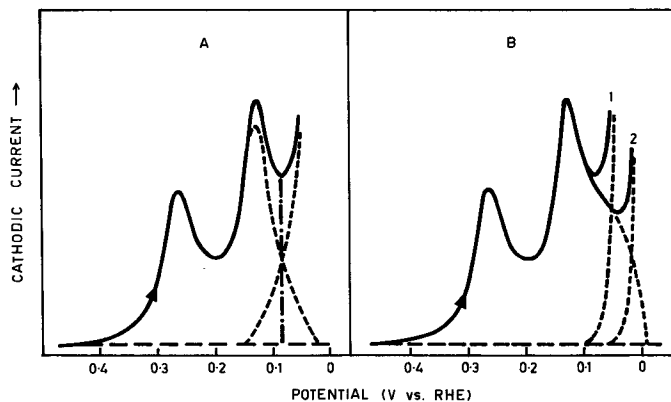


Fig. 5. Schematic cathodic voltammograms in the hydrogen region. (—) Total current, (---) double layer charging current, (·····) extrapolated hydrogen adsorption and evolution currents, (---) limit for integration of $Q_{\text{H},a}$. (A) basis for justifying ϕ_{min} as integration limit (cf. Gilman⁹), (B) extrapolations for (1) smooth and (2) platinized platinum based on experimental evidence discussed in text.

1. The potential ϕ_{min} was found to be 40 mV more cathodic for platinized platinum than for smooth electrodes, whereas the hydrogen peaks always occurred at the same potentials (Fig. 2). This means that the integration to obtain $Q_{\text{H},a}$ is extended 40 mV further for the platinized electrode. It is therefore unlikely that $Q_{\text{H},a}$ can be the saturated hydrogen coverage for both kinds of electrode. It seems more reasonable to integrate the hydrogen charge to a fixed potential, particularly since the position of the hydrogen peaks remains constant. Furthermore, when such a fixed potential is used the resulting values of $Q_{\text{ox},s}/2Q_{\text{H}}$ become the same for both electrodes. For example, if Q_{H} for the platinized electrode is integrated to 0.08 V, the end-point used previously¹ for smooth platinum, $Q_{\text{ox},s}/2Q_{\text{H}}$ becomes 2.70, which is in good agreement with the corresponding value of 2.66 for smooth platinum. On this basis we conclude that the stoichiometry of the oxygen layer on the two kinds of electrode is in presence of a contribution from the mass transport controlled hydrogen evolution fact the same. However, in view of the observation that the hydrogen region for pla-

* Note that the extrapolations used by Gilman to separate the hydrogen adsorption and evolution currents (Fig. 6, ref. 9) do not fulfil the requirement that the sum of the partial currents should equal the experimental current.

tinized platinum extends appreciably beyond 0.08 V, integration to this potential is likely to underestimate the true hydrogen monolayer charge and hence overestimate the oxygen stoichiometry. Before we can reach a conclusion regarding the true stoichiometry, it is first necessary to examine the other evidence concerning the accuracy of the determination of hydrogen monolayer charge.

2. The hydrogen evolution current is mass transport controlled¹¹ and it should therefore be possible to judge the adequacy of the extrapolation of this current in Fig. 5A by varying mass transport conditions. Experiments involving stirring require stringent conditions of solution purity in order to avoid effects of accelerated impurity adsorption. A 1 M H₂SO₄ solution of the necessary purity has been obtained by removing adsorbable impurities with a large platinized "scavenger" electrode (real area 1.5×10^4 cm²) held potentiostatically in the stirred solution for 30 h at 0.5 V. Confirmation of purity was obtained by holding a platinum wire electrode at a potential in the double layer region and then recording anodic or cathodic sweeps from this potential. Long adsorption times were needed to produce detectable changes in either sweep; from the decrease in the hydrogen region the rate of surface contamination in quiescent solution was estimated to be 2% in 1000 s.

The effect of stirring on cyclic voltammograms between 0.06 and 1.54 V for a smooth platinum electrode was then examined in the purified solution. As expected from the low residual impurity level, there was a complete absence of stirring effects except within a narrow region at the cathodic end of the triangular scan (Fig. 6). Below 0.10 V, stirring increased the cathodic current and decreased the anodic current on the reverse sweep. The stirring dependence in this narrow region must be attributed to the presence of a contribution from the mass transport controlled hydrogen evolution

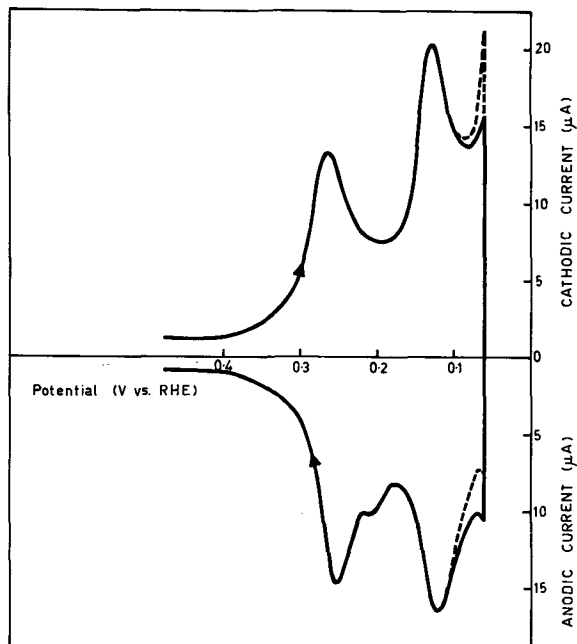


Fig. 6. Hydrogen region of a cyclic voltammogram for smooth platinum between 0.06 and 1.54V. Sweep rate 45 mV s^{-1} . (—) Quiescent solution, (---) stirred vigorously with high purity helium.

reaction. We therefore conclude that the contribution from this reaction is insignificant compared with the hydrogen adsorption current above 0.10 V. Accordingly, the extrapolated hydrogen evolution current on smooth platinum should intersect the potential axis at 0.10 V as shown in Fig. 5B.

The same extrapolation of hydrogen evolution current cannot be applied directly to platinized platinum electrodes because of the shift in ϕ_{\min} . This shift is a consequence of the mass transport control of the hydrogen evolution reaction, diffusion of molecular hydrogen away from the interface being restricted by the porous nature of the electrode. Hence the concentration gradient at the interface is smaller than with a smooth electrode and the hydrogen evolution current at the platinized electrode is not increased in proportion with its real surface area. On the other hand, the hydrogen adsorption current is proportional to real area so that its relative contribution at a given potential is greater on the rough surface. Consequently, ϕ_{\min} shifts to lower potentials. It follows that the extrapolated hydrogen evolution current on the platinized electrode should be displaced cathodically by an amount equal to the shift in ϕ_{\min} , *i.e.* by 40 mV as shown in Fig. 5B. In keeping with this extrapolation, no stirring effects were discernible above 0.06 V with platinized platinum.

3. The sweep technique cannot provide information about the hydrogen adsorption current at potentials below ϕ_{\min} . However, a.c. capacity measurements do allow investigation in this region and assumption of an appropriate equivalent circuit enables separation of the pseudocapacitance of the hydrogen adsorption reaction. The pseudocapacity curve determined by this procedure¹²⁻¹⁴ reveals the presence of a distinct shoulder at potentials cathodic to 0.08 V; from this shoulder the capacity falls to zero at -0.01 V. Furthermore, it can be seen from Fig. 2 that on platinized platinum the hydrogen adsorption current, which is proportional to pseudocapacity, shows part of this shoulder before it is obscured by hydrogen evolution. Hence the correct extrapolation of the adsorption current to cathodic potentials must include the shoulder and therefore have the form shown in Fig. 5B.

Comparison between Fig. 5A and 5B reveals that the extrapolations in Fig. 5A overestimate the hydrogen evolution current and underestimate the hydrogen adsorption current in the region where both processes contribute to the overall current. Accordingly, the compensation implied by these extrapolations and those in Fig. 6 of Gilman⁹ cannot be valid and the hydrogen charge integrated to ϕ_{\min} is significantly less than $Q_{H,s}$. In fact, the difference amounts to virtually all of the charge required to complete the hydrogen monolayer between ϕ_{\min} and -0.01 V.

The above arguments allow us to re-examine the question of the oxygen monolayer stoichiometry. As mentioned previously, the ratio $Q_{ox,s}/2Q_H$ was found to be 2.66 and 2.70 for smooth and platinized electrodes respectively when Q_H was integrated to 0.08 V. The fractional hydrogen coverage at 0.08 V is obtained from Fig. 5B by comparing the integral to 0.08 V with the saturation hydrogen coverage, $Q_{H,s}$, *i.e.* the integral of the complete extrapolated adsorption curve. The resulting coverage of 0.77 is in excellent agreement with interpolated values 0.77 and 0.78 obtained from the coverage-potential plots of Breiter^{12,13} and Honz and Nĕmec¹⁴ respectively. It follows that $Q_{ox,s}/2Q_{H,s}$ is 2.05 and 2.08 for the two electrodes studied.

These values lead to a simple picture of the chemisorbed oxygen layer since the ratio of the numbers of oxygen and hydrogen atoms in their monolayers is, within experimental error, an integer for both smooth and platinized platinum. As there is

good evidence that the hydrogen monolayer contains one hydrogen atom per surface platinum atom⁹, we must conclude that the oxygen monolayer contains 2 oxygen atoms per surface platinum atom. This integral stoichiometry of the oxygen monolayer vindicates the earlier conclusion¹ that the oxygen-containing film on platinum is best described in terms of a chemisorbed layer of oxygen atoms.

Area determinations by hydrogen adsorption

Measurements of hydrogen adsorption are widely used in determining real platinum surface areas. The conclusions reached above have established a basis for deriving the hydrogen monolayer charge from experimental linear sweep voltammograms and for solving the problem caused by the overlap between hydrogen adsorption and evolution reactions. This problem is common to all d.c. transient methods used in studying hydrogen adsorption and cannot be circumvented by simply varying details of the technique employed. For example, differentiation of galvanostatic charging curves may assist identification of inflection points but cannot provide directly the separation of contributions from simultaneous processes claimed by Gilroy and Conway¹⁵. This follows immediately from the fact that such differentiated curves give $d\phi/dq$ vs. time (ϕ is the potential, q is the charge) whereas linear sweep voltammograms give $dq/d\phi$ vs. time, *i.e.* one curve is proportional to the reciprocal of the other.

The available evidence shows that direct integration of $Q_{H,s}$ from experimental voltammograms is difficult. It is preferable to measure the charge to a potential for which the corresponding fractional hydrogen coverage is less than unity and to divide the charge so obtained by this coverage. The choice of an appropriate potential must be a compromise between measuring as large an adsorption charge as possible and avoiding a significant contribution from molecular hydrogen. For the potential sweep technique, ϕ_{\min} meets these requirements; on smooth platinum ϕ_{\min} is 0.08 V and the corresponding fractional coverage is 0.77. The coverage for other values of ϕ_{\min} (*e.g.* for platinized electrodes) can be obtained from the isotherms given by Breiter^{12,13} or Honz and Němec¹⁴. The agreement between the results of these authors is excellent, especially at potentials below 0.10 V. However, relatively few points were used¹²⁻¹⁴ to provide the capacity-potential curves from which these coverages were obtained and on which the extrapolation of the hydrogen adsorption current in Fig. 5B is based. Redetermination of the isotherm involving more capacity measurements would therefore seem desirable. It should be noted that the a.c. method requires determination and analysis of the frequency dependence of the electrode impedance and therefore does not lend itself to routine $Q_{H,s}$ measurements.

To obtain the real platinum surface area from values of $Q_{H,s}$, assumptions must be made about the distribution of crystal faces exposed and which atoms in these faces are accessible to hydrogen adsorption. The charge associated with a monolayer of hydrogen has been commonly taken as 210 $\mu\text{C}/\text{real cm}^2$, a value justified on the basis of predominance of the (100) plane¹⁶ or of equal distribution of the three low index planes⁹. Note that the calculated monolayer charge is 208 $\mu\text{C}/\text{real cm}^2$ for the (100) plane, 241 $\mu\text{C}/\text{real cm}^2$ for the (111) plane and 147 or 295 $\mu\text{C}/\text{real cm}^2$ for the (110) plane depending on whether surface atoms are defined¹⁷ as those with coordination 7 or those with coordination 11 as well as 7. The charge averaged over these three planes is 199 or 248 $\mu\text{C}/\text{real cm}^2$ depending on which value is used for the (110) plane.

The problem of defining surface atoms becomes more serious when one considers higher index planes likely to be present on a polycrystalline surface. Moreover, LEED investigations have shown that surface atoms may reside in structures which need not correspond to those calculated from the bulk unit cell¹⁸.

In view of the nature of the assumptions involved, the choice of a particular value for $Q_{H,s}/\text{real cm}^2$ must be arbitrary. Nevertheless, it is convenient to refer results to some standard of real area, particularly with rough electrodes, and since $210 \mu\text{C}/\text{real cm}^2$ has been commonly accepted, there is no reason to discard it as the conventional standard. Use of this value amounts to comparing the number of platinum atoms adsorbing hydrogen with the number of surface atoms in 1 cm^2 of the platinum (100) plane, viz. 1.30×10^{15} . Since chemisorptive and electrocatalytic properties are expected to depend on the number of available surface sites, activities referred to real areas defined in this way have a clear physical significance in that they relate to a fixed number of platinum sites. On the other hand, the concept of roughness factor ($Q_{H,s}(\mu\text{C})/210 \times \text{geometric area}$) for nominally smooth electrodes is less clear since, according to this definition, different perfect crystal planes have different roughness factors.

SUMMARY

A limiting oxygen coverage is found on platinized platinum electrodes and identified as a monolayer of chemisorbed oxygen atoms. Evidence is presented to support a realistic separation of hydrogen adsorption and evolution currents on linear sweep voltammograms in order to determine the hydrogen monolayer charge. Comparison with the hydrogen monolayer charge shows the stoichiometry of the oxygen monolayer to be 2 oxygen atoms/surface platinum atom for both smooth and platinized platinum electrodes. The problems involved in interpreting hydrogen adsorption measurements in terms of real electrode areas are discussed.

REFERENCES

- 1 T. BIEGLER AND R. WOODS, *J. Electroanal. Chem.*, 20 (1969) 73.
- 2 R. WOODS, *J. Electroanal. Chem.*, 21 (1969) 457.
- 3 A. DAMJANOVIC, in J. O'M. BOCKRIS AND B. E. CONWAY (Eds.), *Modern Aspects of Electrochemistry*, Vol. 5, Plenum, New York, 1969, p. 369.
- 4 S. SCHULDINER AND T. B. WARNER, *J. Electrochem. Soc.*, 112 (1965) 212.
- 5 S. SHIBATA, *Bull. Chem. Soc. Japan*, 36 (1963) 525.
- 6 A. KOZAWA, *J. Electroanal. Chem.*, 8 (1964) 20.
- 7 S. D. JAMES, *J. Electrochem. Soc.*, 116 (1969) 1681.
- 8 D. A. J. RAND AND R. WOODS, to be published.
- 9 S. GILMAN, in A. J. BARD (Ed.), *Electroanalytical Chemistry*, Vol. 2, Arnold, London, 1967, p. 111.
- 10 S. GILMAN, *J. Electroanal. Chem.*, 7 (1964) 382.
- 11 F. LUDWIG AND E. YEAGER, *Extended Abstract No. 172*, Electrochemical Society, Spring Meeting, Dallas, 1967.
- 12 M. BREITER, H. KAMMERMAIER AND C. A. KNORR, *Z. Elektrochem.*, 60 (1956) 37.
- 13 M. BREITER, in E. YEAGER (Ed.), *Transactions of the Symposium on Electrode Processes*, Philadelphia, 1959, John Wiley & Sons, New York, 1961, p. 307.
- 14 J. HONZ AND L. NĚMEC, *Collection Czech. Chem. Commun.*, 34 (1969) 2030.
- 15 D. GILROY AND B. E. CONWAY, *Can. J. Chem.*, 46 (1968) 875.
- 16 S. B. BRUMMER, *J. Phys. Chem.*, 69 (1965) 562.
- 17 J. F. NICHOLAS, *An Atlas of Models of Crystal Surfaces*, Gordon and Breach, New York, 1965.
- 18 G. A. SOMORJAI, *Ann. Rev. Phys. Chem.*, 19 (1968) 251.