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Hydrous oxide species as inhibitors of oxygen reduction at platinum activated fuel cell cathodes

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The successful development of a methanol/air fuel cell requires optimum performance of the air/oxygen cathode at about 0.8 V vs RHE. Ideally the operating potential should be even more positive but oxygen gas reduction on platinum (the best electrocatalyst for this reaction to date at low pH) is generally severely inhibited above 0.8 V. It was demonstrated that in the region of interest the performance of platinum dispersed on carbon prepared by a thermal reduction technique was much superior to that of a similar material in which the platinum was dispersed on carbon by a wet chemical procedure. With the latter material the surface is apparently too reactive: surface platinum atoms of quite low lattice coordination number spontaneously oxidize to yield incipient hydrous oxide species that inhibit the oxygen gas reduction process to potentials below about 0.6 V vs RHE, at which point this oxide is unstable with regard to reduction. The superior performance of the slightly sintered material may be attributed to the lower tendency of the slightly less reactive surface to spontaneously form the inhibiting oxide.

1. Introduction

Despite its high cost and relative scarcity platinum still appears to be the electrocatalyst of choice for oxygen gas reduction in direct methanol/air fuel cells that operate with an acid electrolyte. The conditions involved at the cathode of such cells, for example operation at about 0.8 V vs RHE in 3.0 M H_2SO_4 at 60° C, are rather severe, as are the demands on the electrocatalyst; with platinum it is a matter of minimum amount, maximum activity and good long term stability. The question of stability will not be considered here: instead, it will be demonstrated that some procedures used to maximize the activity of small amounts of platinum in this area may be counterproductive.

For a wide ranging positive sweep the behaviour of platinum in aqueous media at low pH is generally interpreted [1] in terms of six distinguishable phenomena: hydrogen gas evolution (< 0 V), oxidation of adsorbed hydrogen (0 to ~ 0.35 V), double layer charging (0.35 to ~ 0.85 V), oxide film (or OH_{ads} and O_{ads}) formation (0.85 to ~ 1.55 V), oxygen gas evolution (> 1.55 V), and multilayer hydrous oxide formation ($> \sim 2.0$ V). The potential scale used here is reversible hydrogen in the same solution (RHE). A significant modification of this view of the behaviour of the Pt/aqueous solution interface was outlined recently [2]: it was suggested that with polycrystalline platinum, low lattice coordination, highly reactive, surface metal atoms oxidize to yield incipient (low coverage) hydrous oxide species at potentials prior to the onset of regular monolayer oxide formation. This appears to be a widespread phenomenon; it was suggested recently for both gold [3, 4] and palladium [5, 6] in aqueous media. A similar effect, anomalous oxidation of dry platinum clusters in the presence of oxygen gas, has also been described [7]; two further examples (totally independent of the present author's laboratory) of this premonolayer oxidation of platinum in hot acid solution will be discussed here later. The importance of this unusual oxidation is that the product frequently plays a major role in electrocatalytic processes [8]; with sluggish, inhibited or electrocatalytically demanding reactions the incipient hydrous oxide may either mediate oxidation or inhibit reduction processes.

In the present work it was demonstrated, as postulated earlier [9], that oxygen gas reduction on finely divided platinum deposits prepared by chemical reduction from aqueous media is inhibited at the potential region of interest in fuel cell systems, about 0.8 V vs RHE, due to formation of incipient hydrous oxide species that hinder access to active sites. Thermally prepared Pt/C electrodes were found to be more active in this region than those prepared by the wet techniques. Ac voltammetry provided evidence for a faradaic process in the double layer region in the case of platinum in acid. Hydrous oxide films may be produced on platinum in 3.0 M H_2SO_4 at 60° C and are quite stable on open circuit in the hot acid, i.e. such materials are not nebulous or transient species that can be ignored.

2. Experimental details

Platinum and gold electrodes were used in the form of wires (Johnson Matthey Chemicals Ltd., Puratronic Grade, 1.0 mm diam., about 1.5 cm exposed length) sealed directly into glass. Platinum-activated carbon electrodes were prepared both by wet chemical and

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hydrogen gas reduction techniques. In the former case 0.3 g of carbon powder (Norit BRX, surface area of about 1700 $m^2 g^{-1}$) was suspended in 100 ml of distilled water and the suspension was heated to 60° C; the required amount of H_2PtCl_6 was added and the pH adjusted to 7.0 by slow addition of 0.05 M Na_2CO_3. The suspension was refluxed for 2 h and allowed to cool; excess formaldehyde was then added to reduce the platinate salt and the suspension refluxed for 1 h. The platinum-activated carbon was recovered from the cooled suspension by filtration; it was then washed with distilled water and dried in air at 110° C. In the second case, the H_2PtCl_6, dissolved in a small quantity of water, was applied to an appropriate amount of carbon; the liquid was evaporated by gentle heating and the solid was then heated in a flow of hydrogen gas to 400° C in a furnace for 2 h to reduce the salt to the metal. For test purposes the carbon, usually activated by 3.0 mass % Pt, was suspended in water, a colloidal suspension of PTFE was added (to yield a final value of 30 mass % PTFE) and, following ultrasonic agitation, the C (3% Pt)/PTFE suspension was recovered by centrifuging and dried; this mixture was then used to fill the end of the electrode cavity in the type of Perspex electrode holder shown in Fig. 1. The rod had an outer diameter of 1.2 cm; the cavity dimensions were 0.95 cm diameter and 0.2 cm deep; a platinum wire (0.5 mm diam.), sealed to the Perspex close to the cavity, provided electrical contact between the electrode and the external circuit. The objective in this case was to study the current/voltage behaviour of the platinum-activated carbon; the oxygen gas reduction performance of the material was not optimized, for example the oxygen gas was passed through the solution and not fed in through a porous electrode arrangement; in this configuration the reduction process was confined largely to the relatively flat electrode/solution interface.

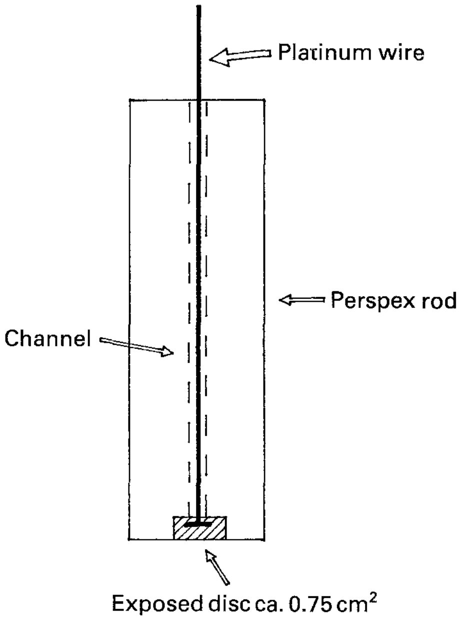


Fig. 1. Electrode holder designed for testing the electrocatalytic activity of platinum-activated carbon powder; the latter, mixed with 30 mass % PTFE, was packed into the cavity to form an exposed disc at the lower end of the Perspex rod where electrical contact was made to the platinum lead.

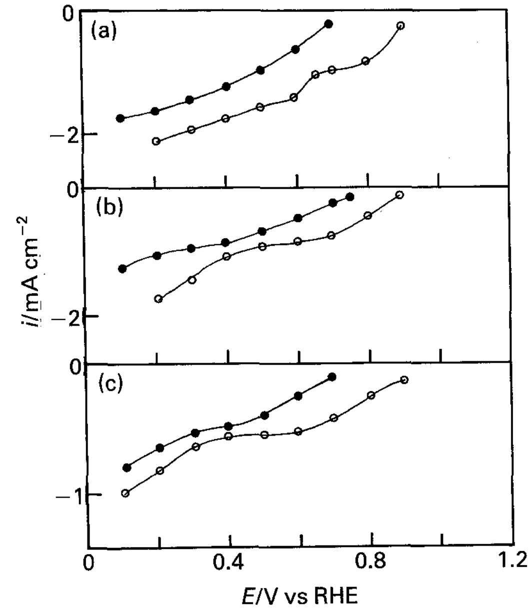


Fig. 2. Steady state i–E behaviour for carbon/30 mass % PTFE (●) and 3 mass % Pt-activated carbon/30 mass % PTFE (○) electrodes in oxygen-stirred (a) 1.0 M H_2SO_4 at 60° C, (b) 3.0 M H_2SO_4 at 60° C and (c) 3.0 M H_2SO_4 at 20° C. The platinum-activation was carried out using the wet chemical reduction technique.

The counter electrode was a platinum wire, 1.0 mm diam. and about 2.0 cm exposed length: in the case of platinized platinum wire working electrodes platinization involved cathodizing at 100 mA cm^{-2} for 5 min in a solution of 1 g of H_2PtCl_6 in 0.1 M HCl at room temperature. Potential values were recorded, and are reported, with respect to a reversible hydrogen electrode in the same solution. The electrochemical equipment was similar to that described earlier [9]; a.c. cyclic voltammetry involved imposing a small sine wave signal (20 mV peak to peak at 300 Hz) on the regular triangular sweep; the in-phase or faradaic response was extracted and amplified as before [10] using a lock-in amplifier (EG&G, Model 5208). All solutions were made up using triply distilled water and Analar grade chemicals.

For the oxygen reduction experiments, Figs 2 and 3, the electrode pretreatment in the solution involved holding the potential for 15 s at 1.2 V, 90 s at 0 V, 30 s at 0.4 V and then at the selected oxygen gas reduction potential. The current density values quoted in these diagrams are with respect to geometric surface area; the reduction potential values were varied in a random manner. As pointed out earlier [9], oxygen gas reduction rates at constant potential decayed initially with time: the values reported here are the steady state rates of reduction attained after a polarization period of about 25 min.

3. Results

3.1. *Oxygen gas reduction experiments*

Typical examples of steady-state responses for oxygen

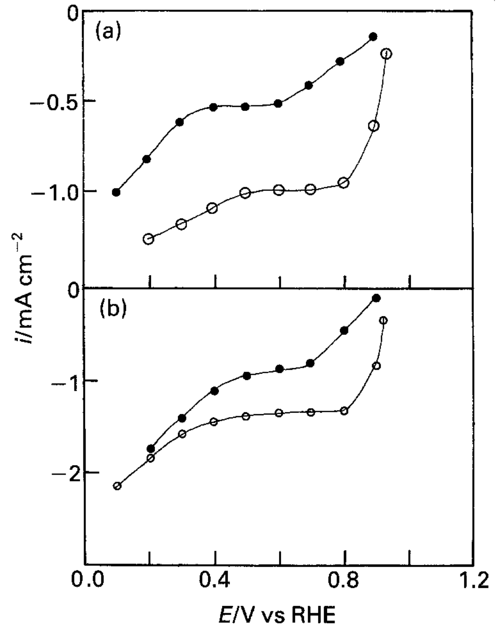


Fig. 3. Steady state current/voltage behaviour for 3 mass % platinum-activated carbon/30 mass % PTFE electrodes, prepared by wet chemical reduction (●) and thermal reduction (○) techniques, in oxygen-stirred 3.0 M H_2SO_4 at (a) 20° C and (b) 60° C.

gas reduction on both carbon and platinum-activated carbon electrodes are shown in Fig. 2 (platinum-activation in this case involved the wet chemical reduction technique). In all three cases shown here the rates of reduction, especially above 0.7 V, were significantly faster on the platinum-activated material. In the case of the 1.0 M H_2SO_4 at 60° C, Fig. 2(a), a significant increase in current density was observed at 0.6 V. With 3.0 M H_2SO_4 at 60° C, Fig. 2(b), the corresponding increase commenced at a lower potential, about 0.4 V, and extended over a larger range of potential. With 3.0 M H_2SO_4 at 20° C, Fig. 2(c), there was a significant increase in oxygen gas reduction rate again below 0.4 V.

In all cases (even with platinized platinum wire electrodes whose behaviour is not shown here) significant rates of oxygen gas reduction at platinum-activated electrodes in acid were observed at 0.9 V. However, with the type of activation involved in the case of Fig. 2 (platinum deposited by wet chemical reduction) the rate of increase in oxygen gas reduction current over the potential range 0.9 to 0.7 V was not dramatic. The increase in steady state reduction current at about 0.6 V, Fig. 2(a), was also observed in an experiment involving a platinized platinum wire in 1.0 M H_2SO_4 at 60° C: with a similar electrode in 3.0 M H_2SO_4 at 60° C the corresponding increase, as in Fig. 2(b), occurred over the region below about 0.45 V. In earlier work [9] with a platinized platinum rotating disc electrode, where superior hydrodynamic conditions prevailed, it was observed that in 3.0 M H_2SO_4 at 60° C the oxygen gas reduction current attained a diffusion limited rate only below about 0.6 V.

A significantly increased oxygen reduction performance was observed with Pt/C electrodes prepared by the thermal technique. This improved performance was most marked over the range 0.9 to 0.7 V, Fig. 3, which is the main region of interest from a fuel cell air cathode viewpoint. Attempts were made to improve the performance of Pt/C electrodes prepared by the wet technique, for example the carbon was first heated to 400° C in a hydrogen atmosphere for 30 min before depositing the platinum by chemical reduction in solution, or the carbon (with no prior heat treatment) was activated with platinum deposited by chemical reduction in solution and the active mass subsequently heated to 400° C in a hydrogen atmosphere for 30 min. Neither material gave the same level of activity with regard to oxygen gas reduction at 0.8 V when subsequently employed in Pt–C/PTFE electrodes as compared with Pt–C prepared by the hydrogen gas reduction technique.

3.2. *A.c. and d.c. voltammetry*

In a recent investigation of the a.c. response for gold electrodes in base, both in the absence and presence of dissolved reductants or oxidants [10], in-phase (i.e. faradaic) responses were observed at potentials prior to the onset of the monolayer oxide formation, i.e. within the so-called double layer region. Such behaviour was attributed to formation of incipient hydrous oxides and the role of the latter as mediators in oxidation processes and as inhibitors in reduction processes was outlined. A similar effect was observed in the present case with platinized platinum, Fig. 4. The large a.c. response in these diagrams at potentials below 0.4 V evidently reflects the high degree of reversibility of the adsorbed hydrogen formation

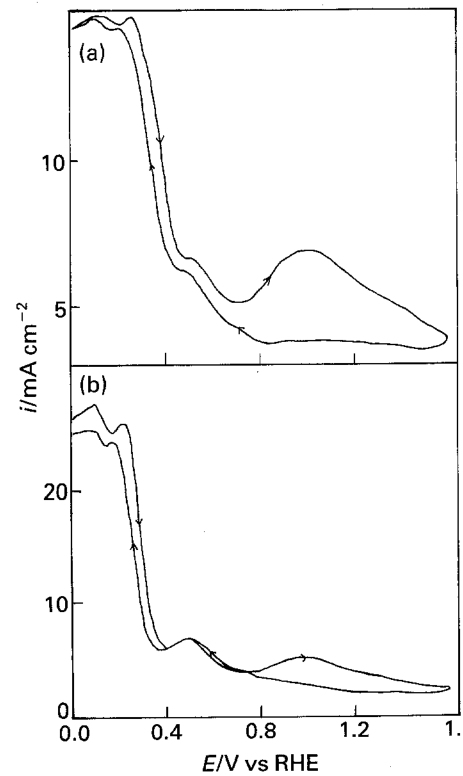


Fig. 4. In-phase a.c. cyclic voltammograms (0 to 1.60 V, 5 mV s^{-1}) for a platinized platinum electrode in oxygen-free 1.0 M H_2SO_4 at (a) 20° C and (b) 80° C.

and removal process, viz.

$$H^+(aq) + e^- = H_{ads} \qquad (1)$$

Above 0.7 V there was also a large response but only on the positive sweep; this supports the view [11] that the early stage of monolayer oxide formation, which was assumed to involve the process

$$H_2O = OH_{ads} + H^+(aq) + e^- \qquad (2)$$

occurs with a significant degree of reversibility. It has also been suggested [12] that the origin of this high initial reversibility is related to the hydrated character of the species formed at the early stages of the anodic process; the extent of hydration (and hence the reversibility as reflected in the a.c. response) decays with increasing OH_{ads} coverage above about 1.0 V and remains low on the subsequent negative sweep until the potential drops below 0.8 V. A minor increase in response was observed just below the latter value on the negative sweep; this change is assumed to be related to the monolayer oxide reduction process. However, the interesting feature with regard to the present work is the reversible peak at about 0.5 V. This feature is more clearly resolved at the higher temperature, Fig. 4(b); unlike the behaviour in the monolayer oxide formation/removal region, the a.c. current responses for this peak at about 0.5 V in the positive and negative sweep, Fig. 4(b), virtually coincided.

Some indications of faradaic processes in the double layer region of platinum can be seen also in d.c. cyclic voltammograms. The direct analogue recorder plot of a scan for a platinized platinum electrode in 3.0 M H_2SO_4 at 60° C, Fig. 5, showed a low level, but again highly reversible, response at about 0.45 V. Thick oxide films, produced on platinum by the potential cycling technique [13], showed a reduction peak, Fig. 6, at about 0.5 V; however, most of the oxide deposit was reduced in this case in the region of the second peak at about 0.15 V. It may be noted that the increase in current at the initial stages of these two peaks commenced at significantly more positive values, about 0.6 V and 0.4 V, respectively.

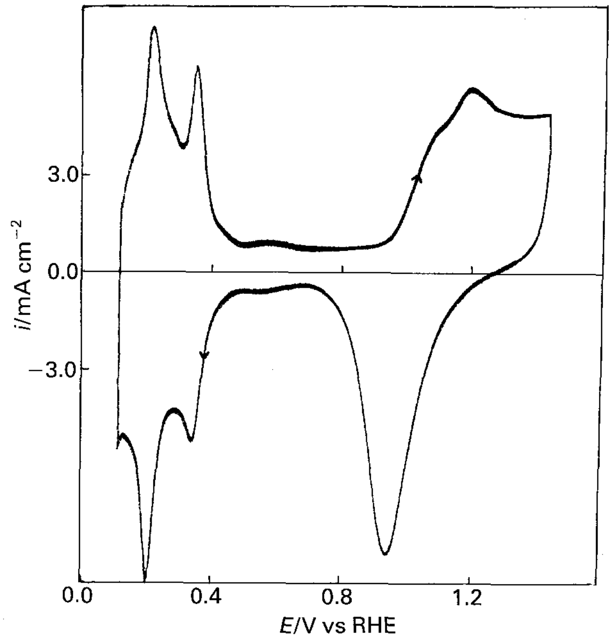


Fig. 5. D.c. cyclic voltammogram (direct recorder plot; 0 to 1.3 V, 50 mV s^{-1}) for a platinized platinum electrode in 3.0 M H_2SO_4 at 60° C.

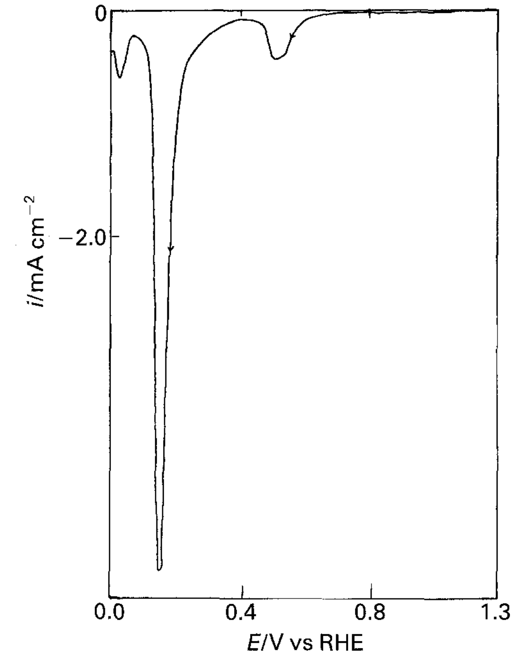


Fig. 6. Typical reduction profile (1.2 to 0 V, 5 mV s^{-1}) for a hydrous oxide coated (initially smooth) platinum electrode in 3.0 M H_2SO_4 at 60° C. The oxide was grown *in situ* by potential cycling (0.58 to 2.1 V, 80 V s^{-1} for 3 min). Allowing the cycled electrode to rest on open circuit for periods of up to 0.5 h in the hot electrolyte resulted in essentially no change in the subsequent reduction profile.

3.3. *Enhanced response associated with premonolayer oxidation*

The voltammetric response due to premonolayer oxidation of platinum is usually quite small and difficult to detect as it usually overlaps [14] with the much larger response due to oxidation of adsorbed hydrogen. However, as demonstrated recently [2], and illustrated here in Fig. 7(a), a much larger response may be observed for platinum in acid over the region 0.2 to 0.7 V following an unusual pretreatment of the electrode surface. Preliminary results in this laboratory, Fig. 7(b), showed that similar behaviour may be observed for gold in acid. Normally this metal commences oxidation at about 1.36 V [1]: however, when the gold was subjected to the same type of severe pretreatment as platinum a major premonolayer oxidation peak was observed (positive sweep) over the region 1.0 to 1.36 V. On the subsequent negative sweep an unusually broad reduction peak was observed over the range 1.0 to 0.3 V. As in the case of platinum [2], these new peaks for gold decayed significantly under repetitive cycling conditions.

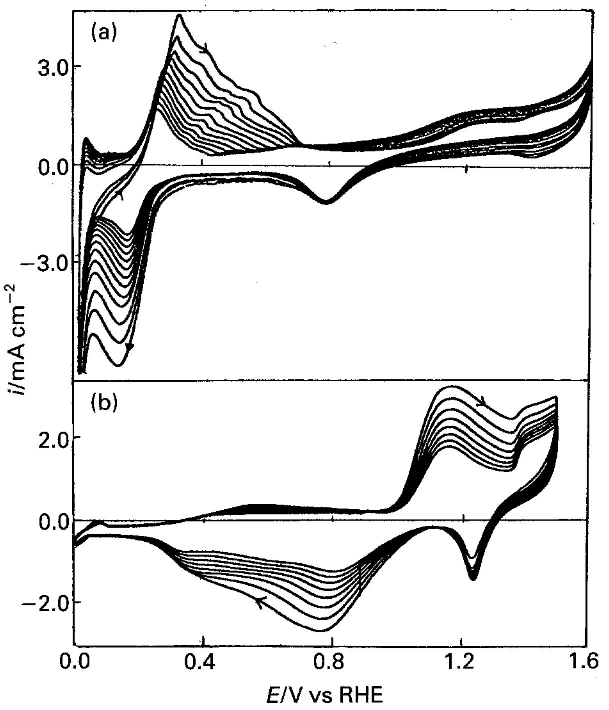
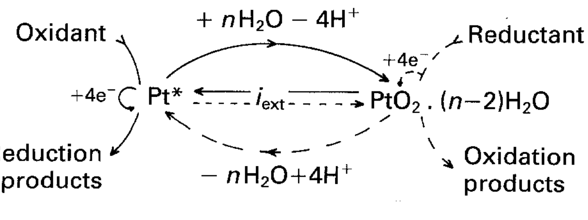


Fig. 7. Cyclic voltammograms (50 mV s^{-1}) recorded for (a) platinum in 3.0 M H_2SO_4 at 60° C and (b) gold in 2.0 M H_2SO_4 at 60° C. The smooth wire electrodes were pretreated in situ as follows: Pt, cycled, 0 to 1.9 V at 1 V s^{-1} for 6 h, with mild abrasion (~ 2 min) at half-hour intervals and a final rest period in air for 30 min; Au, cycled, 0 to 1.95 V at 1 V s^{-1} for 6 h, with mild abrasion at 2 h intervals and a final rest period in air for 1 h. The diagrams are direct recorder plots; the magnitude of the unusual peaks decayed, as reported earlier for Pt (2), on repetitive cycling.

4. Discussion

4.1. *Anomalous oxidation and its relevance to electrocatalysis*

The incipient hydrous oxide/adatom mediator model of electrocatalysis [8, 14] is summarized for platinum in Scheme 1. The basic interfacial cycle is between the adatom (Pt*) state and the low coverage hydrous oxide species $PtO_2.(n-2)H_2O$; although it is not shown here, this oxide is assumed to exist, or at least to react, as an acidic or anionic species. A more detailed account of the anomalous, or premonolayer, oxidation of platinum was published recently [2, 14]. Support for the validity of this premonolayer oxidation approach is provided by the independent work of both Clouser and coworkers [15] and Vogel and Baris [16]. Both groups observed small peaks due to faradaic oxidation processes in the double layer region of the positive sweep for platinum in concentrated H_3PO_4 solution at elevated temperature. The absence of a stirring rate dependence on the magnitude of the charge associated with these unusual peaks [15] eliminated the possible involvement of a trace impurity in the solution. Both groups attributed these low level responses to the oxidation of the products of reduction of H_3PO_4. However, this interpretation seems improbable; a similar premonolayer peak on the positive sweep appears [9] in voltammograms recorded for platinum in H_2SO_4 solution at elevated temperature (even Vogel and Baris [16] pointed out that the behaviour observed with platinum in H_3PO_4 was also noted when using 10% H_2SO_4 at 70° C). Furthermore, the need for prior treatment of the platinum surface at potentials negative to 0.4 V [15] in H_3PO_4 solution has also been demonstrated in the case of H_2SO_4 solution [17]. These premonolayer responses are clearly independent of the nature of the acid and are most likely due to oxidation of low lattice coordination surface metal atoms that are activated (apparently by interaction with adsorbed hydrogen) at low potentials.



Scheme 1

It is interesting to note also that earlier claims for a similar process in the case of gold in acid are supported by the recent quartz crystal microbalance data of Gordon and Johnson [18]. Premonolayer oxidation in this case was postulated earlier [3] to commence at about 0.8 V and to yield a low coverage, anionic, hydrous oxide product. Gordon and Johnson observed a mass increase for this interface, corresponding to about 32 water molecules per gold atom oxidized (assuming an Au(I) product) — the mass increase being virtually independent of the nature of the acid, at approximately the same potential. Our conclusion, as stated again recently for palladium [5, 6], is that premonolayer oxidation is a phenomenon of widespread occurrence.

The premonolayer oxidation product influences electrocatalytic processes by mediating oxidation reactions and inhibiting reduction processes; both a generalized scheme [8] and a kinetic treatment [19] for this mode of electrocatalysis have been published. Two points to note about the hydrous oxides are (a) the reduction potentials for the two main components involved (HO1 and HO2) shift to more positive potentials with increasing solution temperature [20], and (b) the adatom/incipient hydrous oxide transition may not occur at a distrete potential value (the electrochemical processes involving the adatom may be quite rapid, but the reduced state of the couple, of which the adatom is only an extreme form, is of variable activity due to variation in lattice coordination number).

4.2. *Inhibition of oxygen gas reduction on platinum*

With regard to oxygen gas reduction on platinized platinum it was established recently [9], using a rotating disc electrode system, that at the potential region of interest to the operation of a methanol/air fuel cell cathode, i.e. ~ 0.8 V, the initial rate of reduction was time dependent and the steady state value was independent of stirring (or controlled by reaction at the interface rather than by mass transfer) to potential values below 0.75 V. Since the electrode was initially oxide-free and the monolayer oxide (or OH_{ads}) material commenced deposition only at about 0.8 V it was difficult to see why a diffusion controlled, steady state limiting current for oxygen gas reduction required a potential as low as 0.6 V, Fig. 3 in [9] or, alternatively, Fig. 7 in the work of Clouser and coworkers [15]. However, it was noted that after holding the potential at 0.85 V for a significant period of time in oxygen-free 3.0 M H_2SO_4 at 60° C two minor reduction peaks were observed on a subsequent negative sweep prior to the deposition of adsorbed hydrogen. The first was attributed to reduction of monolayer oxide material and the second to reduction of some incipient hydrous oxide.

The formation of low coverage incipient hydrous oxide deposits on active platinum electrodes in the double layer region explains many aspects of the oxygen gas reduction process. The gradual accumulation of such material at the interface, which results in the loss, due to oxidation, of Pt^* active sites, explains for instance the slow decay in the rate of oxygen gas reduction on holding the potential at 0.8 V [9]. It is interesting to compare the behaviour of dichromate with oxygen with regard to reduction on platinum in acid. Although dichromate is a stronger oxidant, its reduction virtually ceases (positive sweep) at about 0.6 V [14]: evidently the process involved occurs only at highly active adatom sites which are largely converted at this potential to the incipient hydrous oxide state. Oxygen gas reduction on the other hand occurs, although at a slow rate, at potentials as high as 0.9 V; the process involved is evidently less inhibited (or less catalytically demanding). At 0.9 V (Fig. 2) the very active adatoms (Pt^*) are assumed to be converted to the hydrous oxide state; a significant portion of the less active surface platinum atoms may even be deactivated by OH_{ads} species; however, there are a sufficient number of such metal atoms remaining to react slowly with the dissolved oxygen gas, viz.

$$O_2 + 2H^+ + 2e^- = 2OH_{ads} \qquad (3)$$

$$2OH_{ads} + 2H^+ + 2e^- = 2H_2O \qquad (4)$$

This is a highly simplified reaction scheme: a much more complex version has been published in a recent review [21] of this topic. The main point is that major oxide film inhibition prevails at 0.9 V. As the potential is decreased below the latter value the rate of oxygen gas reduction on platinized platinum increases rapidly to an initial plateau value at about 0.7 V. There are three possible contributions to this increase:

(i) the overpotential (or driving force) for oxygen gas reduction increases as the potential becomes more negative;
(ii) monolayer oxide (or OH_{ads}) coverage – and hence the degree of inhibition – decreases;
(iii) hydrous oxide coverage also decreases.

The assumption here of two inhibiting species may seem rather complex but it is worth noting that Srinivasan and coworkers [22] have pointed out that studies of oxygen gas reduction on platinum in aqueous phosphoric acid yields three Tafel slope regions: (i) $E > 0.8$ V, 60 mV decade^{-1}; (ii) $0.6 < E < 0.8$ V, 120 mV decade^{-1}; (iii) $E < 0.6$ V, about 200 mV decade^{-1} (the current density in the latter region tended towards a limiting value). It may well be that in regions (i) and (ii) the main inhibiting species are OH_{ads} and incipient hydrous oxide species, respectively; the rate of reduction below 0.6 V is assumed to be limited by transport of dissolved oxygen to the active, inhibitor-free, electrode surface.

The oxygen gas reduction process, which for an active platinum surface, may be represented simply as follows, viz.

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad (5)$$

may be influenced by the incipient hydrous oxide species, over the range 0.8 to 0.6 V, in the following manner. The oxide (HO1) species is assumed to be produced at the interface via the following local cell reaction, viz.

$$O_2 + 4H^+ + 4e^- = 2H_2O \text{ (cathodic)} \qquad (6)$$

$$Pt^* + 6H_2O = Pt(OH)_6^{2-} + 6H^+ + 4e^- \text{ (anodic)} \qquad (7)$$

$$\overline{Pt^* + O_2 + 4H_2O = Pt(OH)_6^{2-} + 2H^+} \qquad (8)$$

At about 0.8 V, a value just prior to monolayer (OH_{ads}) oxide formation, the hydrous oxide species formed according to Equation 8 is relatively stable, the more active Pt^* sites are blocked and oxygen reduction (confined to less active sites that are unable to alter to the hydrous oxide state) is rather sluggish. As the potential is decreased the hydrous oxide coverage is progressively reduced by the reaction represented by the reverse of Equation 7; thus the rate of oxygen gas increases on decreasing the potential to attain a diffusion controlled limiting value at about 0.6 V where virtually all the HO1 oxide material has been removed from the surface.

With platinum-activated carbon electrodes in 3.0 M H_2SO_4 at 60° C, Fig. 2(b), there was no major increase in the rate of oxygen gas reduction at about 0.6 V. Instead there was a rather gradual increase in the reduction current as the potential was decreased below about 0.4 V. The alternative type of platinum hydrous oxide (HO2) is unstable in this region and evidently it is this second oxide that is more significant in the more concentrated acid solution (the same type of response as shown for Pt/C in Fig. 2(b) was observed with a platinized platinum wire electrode under similar conditions, i.e. the increase below 0.4 V is not due to the carbon). The influence of the acid concentration on the nature of the hydrous oxide species produced on platinum can be seen by comparing the oxide reduction response shown in Fig. 7 in the previous work [9] with that shown here in Fig. 6. In the earlier case the oxide film was produced by cycling the potential of the platinum in 1.0 M H_2SO_4 at 20° C and the dominant feature on the oxide reduction sweep was the response, just below 0.6 V, due to removal of the HO1 material. In the present case where the oxide was grown in 3.0 M H_2SO_4 at 60° C the dominant feature in the reduction sweep is the peak at about 0.2 V due to HO2 reduction. In all cases in the present work the platinum-activated carbon was more active than the carbon itself (Fig. 2); however, neither was as active (in terms of oxygen reduction current per unit geometric area) as platinized platinum wire electrodes.

One of the most interesting results from the methanol/air fuel cell viewpoint is the data shown in Fig. 3. It is clear that in this case the material produced by thermal reduction of the platinum salt in the presence of hydrogen gas is more active than a similar deposit produced by the wet chemical reduction procedure with regard to oxygen gas reduction, especially at the important region (from a fuel cell cathode viewpoint) about 0.8 V. It may be noted that both deposits approach the same level of activity at about 0.2 V at the higher temperature, Fig. 3(b). This may be expected as at this potential all hydrous oxide material, even HO2, is assumed to be reduced. The deposit prepared by the thermal technique is assumed to be somewhat more stable or less defective in character, i.e. the mean lattice coordination number of surface metal atoms is assumed to be larger in this case. With such a deposit the tendency to spontaneously form an incipient hydrous oxide deposit (HO2 above ~ 0.2 V or HO1 above ~ 0.45 V) is diminished, the coverage by the blocking species is evidently less and, therefore, the surface is significantly more active with regard to oxygen reduction. On this basis it is assumed that the ideal active site for oxygen gas reduction is a platinum surface atom of low coordination number; however, the latter should be high enough to inhibit conversion of this metal atom to the hydrous oxide state.

It has been checked elsewhere [20], by the type of experiment summarized in Fig. 6 (an oxide film was exposed to 3.0 M H_2SO_4 at 60° C for 0.5 h without any sign of deterioration), that this hydrous oxide material (at least in thick film form) is relatively stable. It has also been demonstrated using both potential sweep ([20] and Fig. 5) and a.c. (Fig. 4) techniques that there is spontaneous formation of such a species, at a very low coverage on the metal surface, even on brief exposure at the appropriate potential. The faradaic or in-phase a.c. response in the double layer region, Fig. 4, is highly reversible, i.e. some of the blocking species form at the interface almost instantaneously. The objective, from the fuel cell cathode viewpoint, seems to be the optimization of the thermally prepared platinum-activated carbon deposit. Such partially sintered materials may also be more resistant to deterioration due to ageing effects.

The data shown in Fig. 7(a) is an example of enhanced premonolayer activation of platinum; as discussed in more detail recently [2] it reflects the unusual redox behaviour of a very highly reactive platinum surface. The behaviour of active gold, Fig. 7(b), is rather similar; the large premonolayer peak (which gradually decays on repetitive scanning) on the positive sweep commences at about 1.0 V, a value postulated earlier (Section 3) for the gold adatom/incipient hydrous oxide transition in acid. This agreement between the onset potential for these anomalous peaks (~ 0.2 V for Pt and ~ 1.0 V for Au) – both values being predicted on the basis of earlier work [3, 10, 14] – supports the view that these enhanced premonolayer oxidation effects are a property of the noble metals, and not associated with a solution impurity.

4.3. *The influence of platinum particle size on the oxygen cathode performance*

It is known from the work of Blurton and coworkers [23], Bregoli [24], Sattler and Ross [25], and Stonehart and coworkers [26, 27] that the activity of platinum as an electrocatalyst for oxygen reduction in acid solution passes through a maximum with decrease in particle size or increase in specific surface area. Bregoli [24] pointed out that this had a beneficial practical effect in that the loss of activity due to particle recrystallization or sintering was partly compensated for by increased activity of the resultant larger crystallites. He also suggested that there was an additional, unknown (and possibly fundamental), parameter, which we assume is incipient hydrous oxide formation, in addition to particle size exerting a controlling influence on the activity of highly dispersed platinum.

Stonehart and coworkers [26, 27] explained this crystallite size effect in terms of interparticle interference effects. Basically, with well separated platinum particles on carbon, virtually all surface platinum atoms are available for reduction. However, when such particles are close together on the support, and each particle is surrounded by a solution diffusion zone (through which oxygen must diffuse to reach the platinum surface), the overlap of diffusion zones results in a lowering of the rate of oxygen transfer to any particular particle. Hence, for a given support, the observed rate of reduction (or the apparent activity) per unit real area of electrocatalyst decreases, below a certain particle size, with increasing specific surface area (or degree of dispersion) of the metal due to this diffusion zone overlap effect.

The hydrous oxide approach provides an alternative explanation of the particle size effect. Parmigiani and coworkers [7] have pointed out that the activity of supported platinum clusters as catalysts for oxidation reactions decreases with decreasing particle size (below a certain value, ~ 3.5 nm diam., for the latter), with an extrapolation to virtually zero activity for the monatomically dispersed metal, the latter trend was also noted [26] for the electrochemical reduction of oxygen on platinum. Our view is that minute particles of platinum on carbon, or highly reactive regions of an extended platinum surface, are inactive with regard to oxygen gas reduction above about 0.6 V as much of the active metal exists in this region in the hydrous oxide state, and the extent of this conversion is greater with the more highly dispersed metal deposits. Current results in this laboratory indicate that platinum hydrous oxide films are relatively stable on open circuit in hot, concentrated, aqueous H_2SO_4 or H_3PO_4 solutions. The present work indicates that hydrous oxide film deactivation is less marked with supported platinum deposits prepared by thermal, as compared with wet chemical, reduction techniques.

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