



Superactivation of metal electrode surfaces and its relevance to CO_{ads} oxidation at fuel cell anodes[†]

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Received 27 June 2000; accepted in revised form 15 August 2000

Key words: CO_{ads} oxidation, electrocatalysis, fuel cells, gold, platinum, superactivation

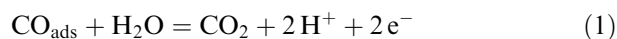
Abstract

The inhibiting effect of CO_{ads} on platinum-based anodes is a major problem in the development of ambient temperature, polyelectrolyte membrane-type fuel cells. One of the unusual features of the response for the oxidative removal of the species in question is that the response observed for this reaction in the positive sweep is highly dependent on the CO admission potential, for example, when the CO_{ads} is formed in the H_{ads} region it undergoes oxidation at unusually low potentials. Such behaviour is attributed here to hydrogen activation of the platinum surface, with the result that oxide mediators (and CO_{ads} oxidation) occurs at an earlier stage of the positive sweep. It is also demonstrated, for both platinum and gold in acid solution, that dramatic premonolayer oxidation responses may be observed following suitable preactivation of the electrode surfaces. It is suggested that the defect state of a solid electrode surface is an important variable whose investigation may yield improved fuel cell anode performance.

1. Introduction

One of the major problems in the development of a viable polymer electrolyte fuel cell (PEFC) for transport applications is the deactivation of platinum-activated anodes by CO_{ads} [1]. The latter species arises either as a side-product in the direct oxidation of methanol [2] or is produced by adsorption of CO or CO₂ gas which are usually present [3], as contaminants, in on-board generated hydrogen in indirect methanol/air fuel cells. The presence of CO_{ads} causes unacceptably large anode polarization losses which severely reduce the cell efficiency and power output.

At a superficial level the oxidative removal of CO_{ads}, that is,



seems to be a rather simple reaction. However experimental investigations by many groups [1–18] reveal that this is not the case. One of the complications in this reaction, for which a novel explanation will be provided in the present work, is that the anodic response for CO_{ads} oxidation on platinum in acid solution is highly depen-

dent on the conditions under which the CO is adsorbed or CO_{ads} is formed. For example according to Bellows and coworkers [3] when CO is adsorbed on platinum, in 0.5 mol dm⁻³ H₂SO₄ at 25 °C, at 0.45 V vs RHE it is oxidatively removed in a positive sweep at about 0.9 V. However when the CO is adsorbed in the same system at 0.10 V CO_{ads} oxidation commences at about 0.40 V, a small anodic peak is observed in the positive sweep at 0.5 V and this is followed by a second, larger, anodic response at about 0.7 V. A similar variation of the anodic response, with admission potential, for the oxidation of CO at the interface in question is also evident in the work of Kunimatsu et al. [4], Gutierrez and Caram [8] and Kita et al. [18].

Two interesting questions are raised by the CO oxidation work to date. These are: (i) ‘Why does the CO admission potential affect the oxidation response (or why does the oxidation of CO_{ads} commence at a lower potential when the CO_{ads} is formed in the H_{ads} region of platinum)?’ and (ii) ‘How is the oxygen transferred from the water molecule to CO_{ads}, see Equation 1, (or is there an involvement of a surface oxide species in the latter reaction)?’. The involvement of low coverage premonolayer oxides in noble metal electrocatalysis has been suggested by one of the present authors [19, 20] for several years and generalized versions of this approach have been published recently [21–23]. A similar opinion has been expressed by other authors, for example, Zhang and Weaver [14] have suggested that some form

[†]Paper presented at the workshop on ‘‘Electrocatalysis in direct and indirect methanol fuel cells’’ held at Portoroz, Slovenia, September 1999.

of oxygen or oxide film component may act as a coreactant in the oxidation of CO adsorbed on platinum. This is the type of approach adopted in the present work: no attempt is made here to identify, or specify, the type of oxide involved (it was suggested recently [23, 24] that the species in question are hydrous metal oxide entities).

The objective of the present work is to demonstrate, for both platinum and gold, that the oxidation behaviour of a metal surface is a function of the electrode pretreatment and that in some instances, following for example severe thermal or cathodic (or hydrogen) pretreatment, extensive electrode oxidation can occur at anomalously low potentials. This work provides the basis of a novel interpretation of the effect of admission potential on the CO_{ads} oxidation reaction. As suggested earlier [23, 24] the effective oxidant for such a reaction in the double layer region is the premonolayer oxide whose presence is favoured or enhanced by hydrogen activation of the metal surface; there is independent evidence for this type of activation in the case of iron [25], the process involved is assumed to be a form of hydrogen embrittlement. Basically, when CO_{ads} is formed at $E > \sim 0.35$ V the platinum surface is inactive and subsequent CO oxidation is sluggish; however, when the CO_{ads} is formed at $E < \sim 0.35$ V the platinum surface is hydrogen activated, oxide mediators are formed more readily at the interface and hence CO_{ads} oxidation occurs at lower potentials.

2. Experimental details

To demonstrate the general nature of the variability of solid metal electrode surface activity or redox behaviour two different noble metals, platinum and gold, and two different methods for surface activation, thermal and cathodic pretreatment, were employed. The thermal pretreatment was described earlier in some detail in the case of platinum [24]. A loop of wire was heated electrically in an inert gas atmosphere (either Ar or 5% H_2 in N_2 ; switching from one type of gas to the other made little difference to the nature of the subsequent active state response) and allowed to cool rapidly. Then, without allowing the metal surface to contact the atmosphere, the deoxygenated electrolyte was added to the cell and some quite unusual cyclic voltammograms were recorded. The only changes made, relative to the earlier work with platinum [24], were that the cell temperature was elevated to about 75 °C and much of the work was carried out using HClO_4 , rather than H_2SO_4 , electrolyte (the nature of the acid seemed to have very little effect on the anomalous cyclic voltammetry response). The same equipment and techniques were used in the case of gold; in both cases the wires (Johnson Matthey, Puratronic grade) were about 20 cm long and 0.5 mm diameter. Since the melting point of gold is significantly lower than for platinum, the pretreatment temperature use for the former

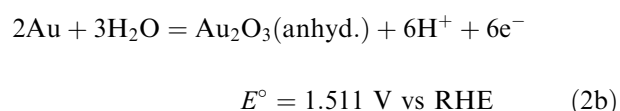
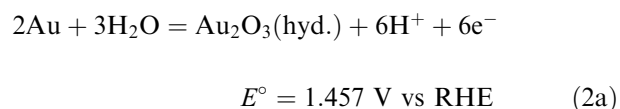
(~ 850 °C) was considerably lower than that for the latter (~ 1300 °C). Solutions were made up using high purity, Analar grade chemicals and triply distilled water; all solutions were purged with oxygen-free nitrogen gas before, and sometimes during, use.

Cathodic activation of the metal surface involved subjecting the metal to prolonged periods of cathodization in the hydrogen gas evolution region. It is assumed that under such conditions hydrogen atoms are forced into both interstitial and defect sites (e.g., vacancies) in the outer layers of the lattice with the result (as demonstrated for other systems [25, 26]) that some metal atoms are forced to the surface. For such work it was necessary to use a carbon rod anode; it was observed for instance with gold that when both electrodes, cathode and anode, were of the same metal prolonged severe electrolysis in acid solution resulted in slight dissolution of the anode. The product was probably an auric acid [27], H_3AuO_3 -based species which was then reduced to gold atoms at the cathode. This effect gave rise to large increases in monolayer oxide reduction charge, surface area or roughness factor for the cathode. Such an increase was avoided when using a carbon anode. The type of equipment, cathode dimensions and other features of the electrochemical pretreatment of noble metals have been described earlier [28, 29]; earlier work (including some from other laboratories) on the cathodic activation or anomalous behaviour of both gold [29, 30] and platinum [28, 31–34] in acid solution is worth noting. All potential values are quoted here with respect to hydrogen ($p = 1.0$ atm) in the same solution, that is, in terms of the RHE scale.

3. Results

3.1. Surface activation of gold

The standard potential for the oxidation of gold in aqueous solution at 25 °C has been estimated by Pourbaix [27], on the basis of standard chemical potential (μ°) data, and the results may be summarized as follows:



In the first case the product is a hydrated oxide or a hydroxide, $\text{Au}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Au}(\text{OH})_3$, whereas in the second the product is the anhydrous oxide, Au_2O_3 . According to the conventional view of gold in aqueous acid solution at 25 °C, based on cyclic voltammetry responses [35], the onset of oxidation of the metal occurs

at a somewhat lower value of about 1.36 V; the small discrepancy involved here is understandable as metal atoms at the surface are slightly active, compared with the bulk, as they are less highly coordinated, or have a lower lattice stabilization energy, than similar atoms within the bulk metal (Pourbaix's values in Equation 2(a) and 2(b) relate only to bulk species).

The differences referred to above are quite small; however, oxidation potential responses for gold in aqueous acid solution may be observed at much lower potentials when the gold surface is highly activated. Examples are shown in Figure 1 of repetitive sweeps recorded for thermally pretreated gold in aqueous HClO₄ solution. The elevation of the solution temperature to 50 °C is of no great significance, the conventional monolayer oxide formation/removal reaction response is still evident in this case at about 1.3 V. The most dramatic feature in Figure 1(a) is the appearance of a major anodic doublet, extending from about 0.2 to 0.6 V, that is, well within the double layer region for this electrode system. This unusual oxidation response is attributed to the oxidation of highly active gold atoms at the electrode/solution interface.

It appears that two different states of highly active gold are involved, the first giving an anodic response (E_p) at ~0.4 V and the second at ~0.5 V. The first peak disappeared more rapidly on repeated cycling, this feature being absent in the fourth cycle (dashed line in Figure 1(c)). This missing feature could be at least partially restored by subjecting the electrode to *in situ*

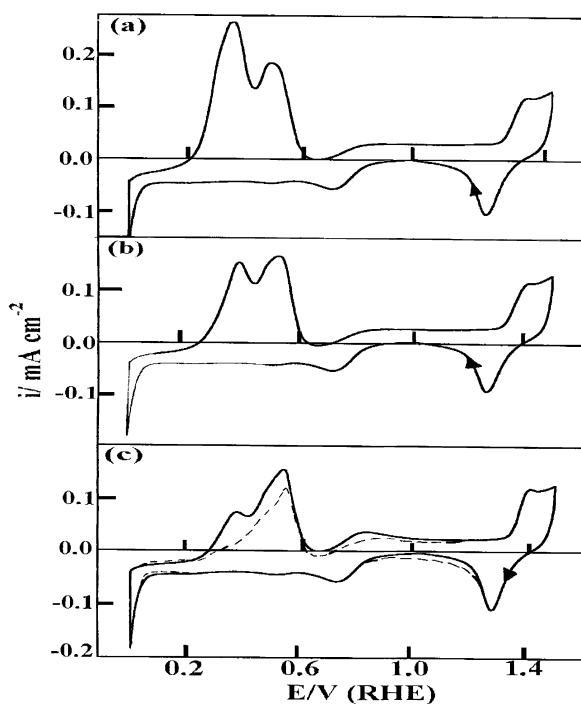


Fig. 1. Cyclic voltammograms (0.00–1.50 V, 50 mV s⁻¹) for a thermally pretreated (905 °C for 20 s in argon atmosphere) in 1 mol dm⁻³ HClO₄ solution at 50 °C: (a) first cycle, (b) second cycle, (c) third (full line) and fourth (dashed line) cycles.

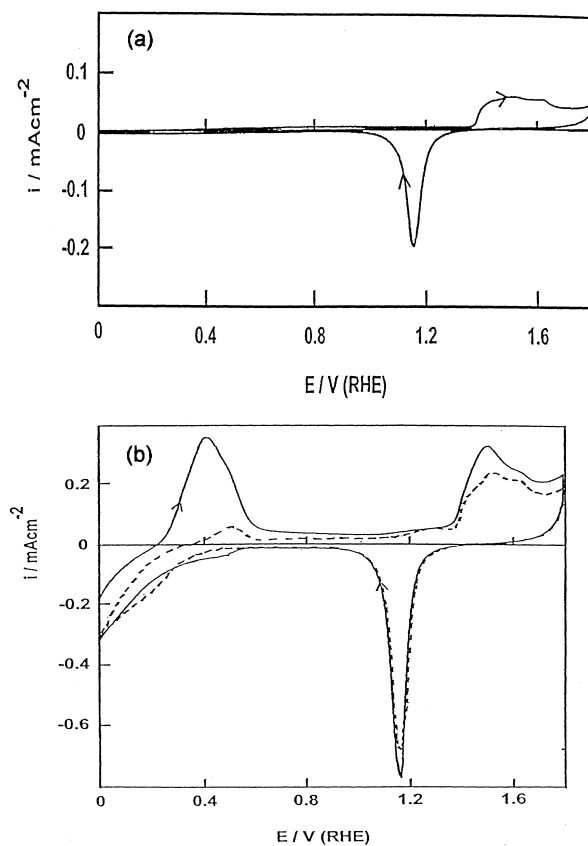


Fig. 2. Cyclic voltammograms (0.00–1.80 V, 50 mV s⁻¹) for a gold wire electrode in 1.0 mol dm⁻³ H₂SO₄ at 25 °C: (a) no preactivation (conventional gold response); (b) same electrode, preactivated by polarizing at -0.6 V for 20 min; the first (full line) and second (dashed line) cycles are shown in this case.

cathodic polarization, for example, holding its potential at -0.1 V for 50 min.

As outlined in Figure 2(b) a similar anodic response (in some instances a doublet) was observed at low potentials, well within the double layer region, after the electrode was subjected to prolonged cathodic polarization within the hydrogen gas evolution region. The validity of the response shown in Figure 2(b) can scarcely be in doubt as it merely reproduces an earlier, independent, result by Ling and coworkers (Appendix in [30]). In their discussion of this unusual double layer feature, Ling and coworkers dismissed the possible role of an impurity species and attributed the anodic feature at about 0.5 V in the positive sweep to the formation of some type of surface oxyspecies. A more detailed account of this cathodic activation of gold in acid solution was published recently [29].

One remarkable feature of the anodic response at low potentials for thermally or cathodically activated gold is the absence of an equally clearcut cathodic response on the subsequent negative sweep (the same general behaviour pattern, as reported here later, was observed with platinum). Cathodic reduction did occur in the case of gold below about 0.6 V (Figure 1) but the rate was quite sluggish (similar behaviour is evident in the work of

Ling et al. [30]). There are a number of possible explanations, for example, there may be poor contact between the oxide product and the metal surface, the resulting resistance to reduction increasing with decreasing potential as the inner region of the oxide deposit undergoes progressive reduction. Another possibility is hysteresis-type behaviour (e.g., the oxide or hydroxide species generated anodically at about 0.5 V may coordinate anionic (ClO_4^- or HSO_4^-) species in a post-electrochemical step), resulting in the formation of a species that (obviously for kinetic reasons) is quite reluctant to undergo reduction.

Finally, it is worth noting that the potentials of the anomalous peaks in the double layer region for gold in acid solution are of some relevance to the electrocatalytic behaviour of this system. The response observed for gold in acid solution in the presence of peroxide is shown in Figure 3. Cathodic reduction commences (negative sweep) and terminates (positive sweep) just below 0.6 V; this is the region where, according to the responses shown in Figure 1, the main anodic transition in the double layer region (i.e., the oxidation of the highly active gold atoms) is completed. According to this view of electrocatalysis, which has been discussed in considerable detail recently [22, 23], the highly active gold atoms are the mediators for peroxide reduction and this reaction cannot occur above about 0.6 V as the highly active gold atom state is no longer available in this region. Several other species (e.g., dissolved oxygen gas and nitrobenzene) behave in a quite similar manner, in other words, they yield a reduction response at gold in acid solution only at $E < \sim 0.6$ V.

Assuming that highly active gold atoms exist at active sites on a conventional gold surface, and that such atoms undergo oxidation in acid solution in the range 0.2–0.6 V (Figure 1), then one would expect [23] to

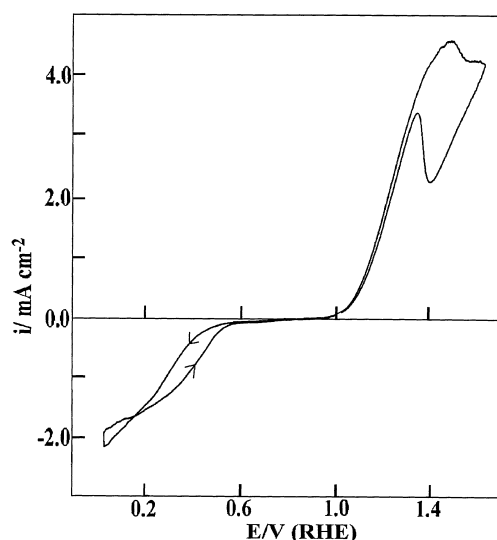
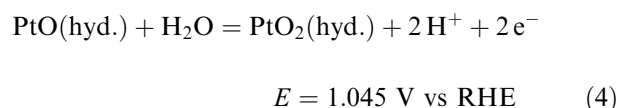
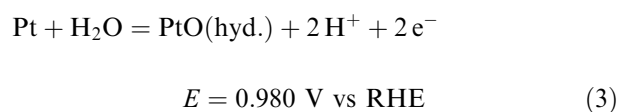


Fig. 3. Cyclic voltammogram (0.00–1.60 V, 50 mV s^{-1}) for a thermally pretreated (905°C for 20 s in an argon atmosphere) gold wire electrode in a solution containing $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 0.15 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ at 70°C .

observe oxidation of some reductants to commence in this region. Such behaviour was reported independently by Sun et al. [36]. They observed that the oxidation of carbon monoxide on gold film electrodes in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ solution commenced (positive sweep) and terminated (negative sweep) at about 0.1 V vs SCE (i.e., at ~ 0.4 V vs RHE). These results for gold in acid are in excellent agreement with the recently outlined [22, 23] IHOAM model of electrocatalysis.

3.2. Surface activation of platinum

Pourbaix's data [27] for oxide formation on platinum in aqueous media at 25°C may be summarized as follows:



A somewhat unstable higher oxide, PtO_3 , may be produced at about 2.0 V. Anhydrous platinum oxides were not considered by Pourbaix. As discussed here earlier for gold, direct electrochemical oxidation of a platinum surface in aqueous acid solution also commences at a slightly lower value, about 0.85 V [35], than expected on the basis of Equation 3; the E° value in the latter again refers to bulk, not surface, species.

The effect of activation of platinum by thermal pretreatment was discussed in considerable detail in a recent publication from this laboratory [24]. It was suggested, on the basis of the observed unusual redox behaviour, that (at the simplest level) three active states of the metal surface are involved, which give rise to three distinct anodic features (positive sweep, acid solution), one at ~ 0.75 V (b), another at ~ 0.45 V (c) and a third at ~ 0.25 V (d). The notation used here is derived from [24] and there is a further state, (a), which refers to high coordination (or low energy) surface metal atoms. It is important to note here that both the number of surface active states and their redox potential values are subject to some uncertainty; the area in question (active, nonequilibrium surface states of noble metals) has received surprisingly little attention in electrochemistry (the work of Heusler and Lang [37] in this respect is noteworthy).

In the previous work with thermally activated platinum in acid solution at room temperature [24] anodic responses for states (b) and (c) were readily observed. An anodic response at about 0.25 V, indicating significant occupancy of the highest energy state, (d), was observed only when the thermally activated electrodes were subjected to additional activation using cathodic polarization. In the current work it was observed, Figure 4, that a major anodic response at about 0.2 V

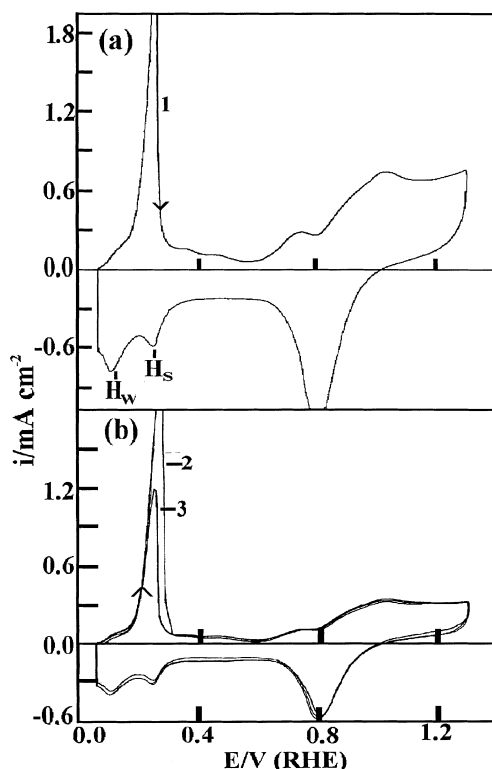


Fig. 4. Cyclic voltammograms (0.05–1.50 V, 50 mV s⁻¹) for a thermally pretreated (1310 °C for 25 s in a 5% H₂ in N₂ atmosphere) platinum wire electrode in 1.0 mol dm⁻³ H₂SO₄ at 80 °C; the first three successive cycles are shown here.

was readily observed for thermally activated platinum in aqueous acid solution without the need for cathodic pretreatment when the cell temperature was raised to about 80 °C. This result strongly supports an earlier, controversial claim from this laboratory [20] that it is possible to generate oxyspecies on a platinum electrode in acid solution at unusually low potentials. The type of premonolayer oxidation responses shown in Figure 4 for platinum is rather similar in a number of respects (though obviously simpler, as only one sharp anodic peak appears at low potential with Pt) to that shown here for activated gold, Figure 1. For example, in both cases this anodic feature decays in height or intensity on repetitive cycling and the cathodic counterpart in the negative sweep is quite sluggish (as will be described in more detail shortly [38], this cathodic feature becomes much more obvious when the sweep rate is reduced to 10 mV s⁻¹). For both metals there is a correlation between the premonolayer response behaviour and electrocatalysis. This is illustrated here in Figure 3 for gold. With regard to platinum in acid it was pointed out earlier [39] that both hydrazine oxidation (positive sweep) and dichromate reduction (negative sweep) commence and terminate on Pt in acid solution at about 0.2 V. These are two totally different processes whose electrocatalytic character is demonstrated by the fact that their responses are highly dependent on the nature of the electrode material [39]. The fact that both commenced at about 0.2 V clearly demonstrated that a

change that is vital with respect to electrocatalysis occurs at the Pt/solution interface at this potential value. Independent evidence to support this view is provided by the recent work of Lu et al. [40] who observed that formic acid oxidation on polycrystalline platinum in aqueous acid solution also terminated at about 0.2 V (the HCOOH oxidation in the positive sweep is inhibited by CO_{ads} species; the latter is oxidatively removed at the upper limit of the sweep; hence the negative sweep is a better reflection of the response for HCOOH oxidation on CO_{ads}-free Pt).

The activation of platinum in acid solution under cathodic conditions, which was the subject of two previous publications [28, 31] from this laboratory in which the topic was discussed in some detail, occurred less readily than in the case of gold. This may reflect two effects: (a) the hydrogen overpotential is lower with platinum and thus the activity of the surface intermediate (H_{ads}) is probably lower; (b) displaced active surface platinum atoms probably bind more strongly to the underlying metal lattice than in the case of gold (the latter metal, in bulk form, being an extremely weak chemisorber compared with platinum). Some typical responses for platinum in acid solution recorded after prolonged cathodization at low potentials are shown in (b) and (c) in Figure 5. Normally the anodic peaks in the double layer region would be attributed to the oxidation of impurities deposited on the surface during the course

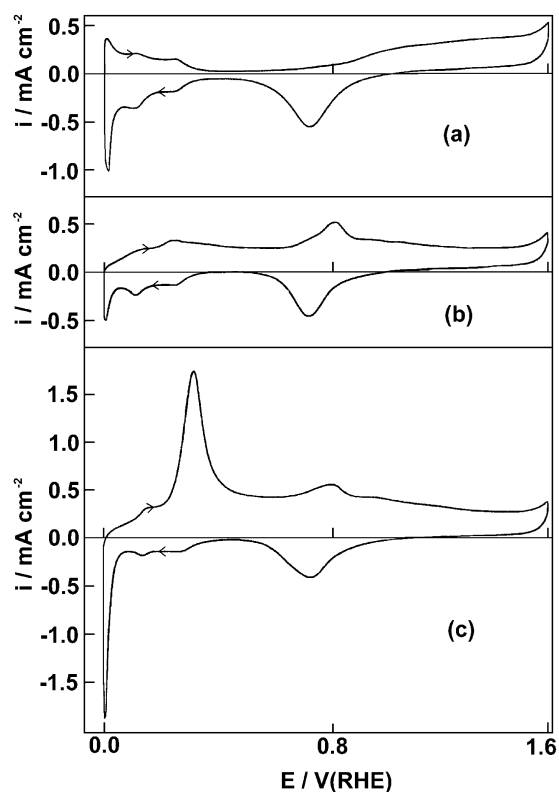


Fig. 5. Cyclic voltammograms (0.00–1.60 V, 50 mV s⁻¹) for polycrystalline platinum in 1.0 mol dm⁻³ H₂SO₄ at 25 °C: (a) no pretreatment; (b) and (c), electrode precathodized at 0.3 A cm⁻² for 21 h and 39 h, respectively.

of the long cathodic pretreatment step. The counterarguments to this view are as follows:

- (i) Other authors [32–34] who have also observed anodic peaks in the double layer region have dismissed the involvement of impurity species (their interpretation is discussed here briefly later).
- (ii) Anodic peaks at about the same potential values have been observed with thermally pretreated platinum electrodes (see Figure 4 here and the earlier work described in [24]) which were not subjected to cathodic pretreatment.
- (iii) There is clear evidence (as outlined both here earlier and in ref. no. [20]) that a dramatic change, from an electrocatalytic viewpoint, occurs at the Pt/aqueous acid interface at about 0.2 V, that is, the anodic peak commencing at the latter value in Figure 4(c) is an enhanced version of a characteristic property of this interface.

The discrepancy in the charge values between the positive and negative sweeps in Figure 5(b) and (c), is also evident in the responses for both thermally pretreated gold (Figure 1) and platinum (Figure 4) and precathodized gold (Figure 2). Although the possibility of some dissolution of the active metal cannot be discounted, current work in this laboratory suggests that much of the oxide generated in the positive sweep is produced in a form that is reluctant to undergo reduction in the negative sweep.

4. Discussion

Since detailed discussions of premonolayer oxidation and its role in electrocatalysis at metal electrode surfaces [22, 23], and surface activation by thermal [24] and cathodic [29] pretreatment, were published recently, these topics will not be discussed in detail here. The activation pretreatments are basically means of inserting energy into the electrode to intensively disrupt and thus highly activate the outer layers of the metal [23]. The resulting high energy (superactive) surface states are quite unstable from a thermodynamic viewpoint but are frozen-in (in the case of Pt an enhanced premonolayer oxidation response was still quite evident [38] after allowing a thermally pretreated electrode to rest for five days prior to investigating its redox behaviour). As pointed out earlier for platinum [24] there appear, both from a redox and electrocatalytic viewpoint, to be at least three different mediator species involved in electrocatalysis at the Pt/aqueous acid solution interface. Other basic assumptions in our model of electrocatalysis are that these high energy metal atom states exist at low coverage active sites on a conventional metal surface and that the particular state or couple involved as a mediator in an electrocatalytic reaction is influenced by the process that is being catalysed.

Many features of the IHOAM model of electrocatalysis are not particularly novel. In his seminal paper on active sites on metal surfaces Taylor [41] postulated that

metastable, i.e. active, surface atomic arrangements were involved. He noted for instance that thermal annealing, which resulted in the decay of labile surface states, usually resulted in a severe loss in catalytic activity. The thermal pretreatment used in the present work was quite severe and was followed by rapid quenching; this evidently favoured the formation and retention of the active surface state. Taylor [41] also postulated the presence of various types of sites of different energy levels, which catalyse different reactions on the same surface.

The electronic properties of a metal surface are also quite variable, that is, they are influenced quite significantly by surface structure. This was demonstrated by Besocke and Wagner [42] who observed that the work function of a W(1 1 0) surface dropped by 0.6 eV at room temperature when 0.5 of a monolayer of W atoms was evaporated in a nonordered arrangement onto the surface. Lowering the degree of order of the metal atoms in the outer layer of the metal evidently facilitates electron loss from this region, that is, a labile surface state of unusual electropositive character is created (or frozen-in) and this is the basis of the enhanced premonolayer oxidation phenomena observed in the present work.

The low level of understanding of catalysis at metal surfaces in general was highlighted recently by the work of Haruta et al. [43, 44] who observed that oxide-supported gold microparticles are active with regard to the oxidation of CO gas to temperatures as low as -70 °C. Since gold is generally regarded as a very weak chemisorber [35] and a rather unreactive metal, its unusual reactivity in Haruta's case is assumed to be due to a particle size effect. This unexpectedly high activity of gold is not confined to oxide-supported gold microparticles as conventional gold electrodes display a surprisingly high electrocatalytic activity for quite a wide variety of anodic reactions [22]. The connection between the two areas, heterogeneous catalysis using supported metal catalysis and electrocatalysis, seems to be that gold microparticle behaviour is involved in both cases (in the case of gold electrodes the surface active sites are assumed to be minute particles, if not indeed mobile adatoms [29], of the metal). The main function of the oxide support in Haruta's work is assumed to be that it maintains the gold particles as discrete species and in a texture or form that is unusually electropositive (this favours the binding of oxygen; the unusual electropositive character of minute metal microparticles has been discussed previously by Heinglein [45]).

The nature of active sites at metal surfaces is generally regarded as being poorly understood [46]. They are regarded here as being associated with surface defects (i.e., ledges, kinks, microclusters, on any type of irregularity) at the surface which can act as a source or sink for metal adatoms or microclusters. The pretreatments used in the present work are assumed to enhance the level of such defects (direct evidence for surface cluster generation due to hydrogen pretreatment

of metal surfaces is given by various authors [25, 26]). The highly active entities are assumed to be low coordination surface metal atoms present, or originating, at such defects. We do not regard active site atoms as being static; they are assumed to be capable of promotion to a mobile state on the surface due to thermal vibrations and it was pointed out recently [29] that surface gold atoms that undergo oxidation at about 0.3 V, Figure 1, probably have a very low lattice stabilisation energy, that is, such atoms are probably outside (or on, rather than in) the metal lattice.

In the case of gold electrodes in acid solution there appear (as with Pt) to be at least three different interfacial mediator systems involved in electrocatalytic processes. Many organic compounds (e.g., alcohols, acids and most reactive nitrogen-containing compounds) commence oxidation in solutions of low pH [22] at 1.05 V. However, quite a number of other compounds (e.g., hydrazine, propargyl alcohol, pyrocatechol, ethanol, glycol aldehyde and phenylenediamine [22]) commence oxidation under similar conditions at 0.85 V. Finally, as already pointed out here, both peroxide reduction and carbon monoxide oxidation commence and terminate at 0.5 V (nitrotriazole, nitrobenzene and oxygen [22] are further examples of substances whose reduction commences on gold in acid at about the latter value). What is remarkable about these three potential values is that they coincide rather well with the potential maximum values reported for the reduction of the three components in multilayer hydrous oxide films formed on gold in acid solution (Figure 1 in [47]). It seems that in both cases there are three different types of active metal atom/hydrous oxide transitions involved both in electrocatalysis and hydrous oxide reduction reactions. A more explicit correlation between premonolayer oxidation, multilayer hydrous oxide behaviour and electrocatalysis was presented recently [23], in diagrammatic form, for copper in base.

With regard to CO_{ads} oxidation on platinum in acid solution it appears that when the gas is admitted to the system at $E > 0.3$ V the surface is relatively inactive, few of the surface metal atoms are at the higher energy levels and the surface is further deactivated due to the formation of the CO_{ads} layer. Under such conditions the oxidation only commences at high potentials (above 0.6 V; reported responses for this reaction [3, 4] differ significantly). The oxide mediators involved in the reaction are those formed at the less active surface states of platinum, (Figure 14(a) and (b) in [24]). When the CO is admitted at $E < 0.3$ V, it appears that some initial adsorption of hydrogen, prior to CO entry, results in activation of the surface, that is, it induces a low level occupancy of states (c) and (d). This means that the surface oxide mediators are formed, and CO_{ads} oxidation commences, at a lower potential [3, 4]. It is interesting to note that at least two groups [4, 5] have established that CO_2 is formed from CO_{ads} just above 0.2 V; evidently the high energy platinum state (d) is involved. However, the response in this region is quite

low (the occupancy of state (d) being low for energetic reasons). A much larger anodic response was observed by both groups just above 0.45 V; this is the region where surface state (c), which is expected to have a higher occupancy than (d), is assumed to be involved. It is clear, therefore, that the present model explains (i) the ability of platinum to transfer oxygen from H_2O to CO_{ads} , Equation 1, at unusually low potentials, (ii) the dependence of the CO_{ads} oxidation response on the CO admission potential (a low value for the latter favouring a high energy state for Pt surface atoms and thus mediator generation at lower potentials), and (iii) the appearance of two anodic peaks, a minor peak above 0.2 V and a major peak above 0.45 V, in the CO_{ads} oxidation sweep.

The importance of different types of active sites on platinum in acid solution is clear from the work of Gutierrez and Caram [8] on the oxidation of dissolved CO. When the CO admission potential was above 0.3 V very little oxidation was observed in the positive sweep prior to about 0.9 V; an unusually sharp anodic peak was observed at about 0.9 V which may be attributed to oxidation of a monolayer of CO_{ads} . When the CO admission potential was reduced to 0.07 V oxidation commenced at about 0.2 V, two anodic peaks were observed in the double layer region but the sharp anodic peak again appeared at about 0.9 V. In this second case most of the surface (i.e., the inactive regions) remained covered with CO_{ads} until 0.9 V but the active sites (in this case for oxidation of dissolved CO) were effective for oxidation at low potentials. This work supports Taylor's well known view [41] of surface catalysis, that is, only a small percentage of surface metal atoms (those present at low coverage active sites) are involved in catalytic processes.

There is independent evidence of unusual behaviour for platinum in acid at about 0.2 V (CO_2 formation from CO_{ads} [4, 5] and hydrazine oxidation [39] occurs just above, while dichromate reduction [39] is observed just below, the latter value). According to quartz crystal microbalance measurements by Lamy and coworkers [17] there is a reversible increase in mass of the electrode over the range 0.2–0.4 V. While this was attributed to adsorption of both anions and water molecules, it may also include a contribution due to conversion of highly active platinum atoms to oxide species [24]. The formation of adsorbed anions is not discounted here but the effect is not regarded as dominant (especially at active sites) since such adsorbed anions do not inhibit electrocatalytic processes (e.g., hydrazine [48] or formic acid [40] oxidation) above 0.2 V; also the present work (e.g., Figure 4) demonstrates that oxyspecies may be formed at the interface in this region. It is also interesting to note that when very low levels of CO are present in the system, two small increases in mass, one commencing at about 0.3 V and another at about 0.5 V (Figure 4(b) in [17]) were observed; since these values correspond approximately to the CO_{ads} oxidation peak maxima reported by Kunitatsu et al. [4], these two

mass changes may correspond to mediator generation effects.

Kita et al. [18] have also carried out some interesting CO admission experiments. They again demonstrated for instance that surface activation (prior to CO admission) occurred only when the potential was held well within the H_{ads} region. Also, when the CO was admitted while maintaining the potential of the Pt electrode at 0.05 V an anodic current spike appeared; evidently the H_{ads} , displaced from the surface by the incoming CO, was oxidatively removed. More interestingly, when the potential was held at 0.50 V for 2 min the introduction of CO resulted in the appearance of a similar, but cathodic (and smaller) spike. It is assumed here that holding the potential at 0.5 V resulted in the generation of some premonolayer oxide species which then tended to be replaced by the incoming CO, thereby triggering a cathodic response (most of the oxide being removed electrochemically).

It is frequently assumed [11–13] that anodic oxidation of CO and CO_{ads} on platinum in acid solution involves the participation of oxygen species such as adsorbed hydroxy radicals (OH_{ads}); the involvement of the latter in the oxidation of dissolved organics, e.g. ethylene, at this electrode system was assumed earlier by Bockris et al. [49]. The difficulty with such a view is that the OH radical is a highly electronegative species, the standard potential for its formation from water being 2.85 V [50]. The most likely species to undergo oxidation at low potentials (e.g., 0.4 V) are active surface metal atoms which may then coordinate hydroxide ions or water molecules to form some type of mediating metal hydroxy or oxy species. The remarkable correlation between the potential for hydrous oxide film reduction and the onset potential for electrocatalysis (of both oxidation and reduction processes), outlined originally for the noble metals [20], was extended recently to nonnoble metal systems (e.g., copper in base [23]). Obviously when some of the earlier mechanisms were proposed [49] the behaviour of hydrous oxides was largely unexplored; however, the correlations between electrocatalysis and hydrous oxide electrochemistry are now so obvious that the role of the latter in the former can scarcely be ignored.

Much of the fundamental work in electrocatalysis in recent years has been carried out with single crystal electrode surfaces. However, the limitations of this approach need to be borne in mind, for example, (i) ideally most of these surfaces contain no irregularities or highly active sites and are probably quite different in character from typical finely dispersed Pt-on-carbon fuel cell anode systems, (ii) in practice, most of these monocrystalline surfaces have plenty of imperfections [51] (this aspect of single crystal surface is currently receiving considerable attention [52]), and may acquire more when in use [53], and such uncharacterized surface features may function as active sites (i.e., dominate the electrocatalytic behaviour), (iii) it appears that high resolution microscopy techniques, such as STM cannot

easily image highly active, mobile surface metal atoms at room temperature [54]. It is interesting that in their investigation of NO decomposition on a Ru single crystal surface Ertl et al. [55] concluded that the important species from a catalytic viewpoint were low coordination, or protruding, single atom sites; these are the type of labile surface species proposed here as the basis of active site behaviour in electrocatalysis.

Previously reports of anodic peaks in the double region, in the positive sweep, for platinum in acid (usually H_3PO_4) [32–34] have been discussed in terms of the redox responses of the decomposition products of the acid. However, since similar anomalous behaviour has been observed in this and other [32] laboratories for platinum in different acids (H_3PO_4 , H_2SO_4 and HClO_4), and also, as described here, for at least one other metal, there can be little doubt but that it is the metal itself (i.e., the oxidation of active surface states of the latter) that is responsible for these anodic effects. It is worth noting also that several other groups [30, 33] who have observed these unusual redox responses have also dismissed the possible involvement of impurities.

It is well known [5, 12] that the performance of mixed metal (e.g., Pt/Ru) electrocatalysts exceeds that of pure Pt with regard to CO or CH_3OH oxidation in acid solution. It appears that the basic function of the second metal is to enhance the oxygen transfer capability of the anode. However, it is far from clear as to how this is achieved. There are several possibilities, for example, Ru (which is oxidized more readily than Pt [56]) may transfer an oxyligand either directly to the carbon species (which is assumed to be coordinated to Pt) or to the active Pt atom which in turn transfers it rapidly to the C_1 species coordinated at the same site. Alternatively, oxidation of the Ru atoms at low potentials in the surface layer may enhance the reactivity of nearby Pt atoms at the surface, that is, reduce their coordination number and lattice stabilization energy, thereby causing such platinum atoms to undergo oxidation, to yield an oxidation mediator, at lower potentials.

In most work on mixed metal electrocatalysts to date attention is devoted primarily to the effect of composition (i.e., the ratio of the two or more metals present) on anodic activity. However, there is another variable in these systems whose investigation may yield substantially improved performance. This is the surface texture of the metal, for example, it may be possible to improve the performance of Pt or Pt/Ru fuel cell anode catalysts by suitably adjusting or modifying the type, ratio, distribution or density of the surface active sites.

The large variability of metal atom activity (or reactivity) at solid electrode surfaces rarely receives much attention in electrochemistry. In this context it is worth noting that gold surfaces may also be activated by mechanical pretreatment [54], following which they display quite unusual chemical reactivity, for example, they chemisorb some organic species in a dissociative manner; as in the present work, such behaviour was

attributed to the generation of surface irregularities which behaved as active sites.

The basic assumption in the present work is that there is an area of electrochemistry, involving the active states of solid electrode surfaces, that is of major importance in electrocatalysis but is largely unexplored at the present time. The properties of these active states, as demonstrated here, are quite different from those of conventional metal surfaces. An illustration of such unusual behaviour in the case of catalysis by gold (in addition to the work of Haruta et al. [43]) is the observation [57] that a tribologically activated gold surface chemisorbs unsaturated organics in a dissociative manner (this is a remarkable reaction for a metal which normally does not chemisorb hydrogen).

The importance of the disorder of metal surfaces with regard to catalysis was acknowledged recently in Somarjai's statement [58] that 'rough surfaces do chemistry'. The problem with such states is that they are extremely difficult to control and investigate, and are therefore poorly understood [58]. A degree of caution is required when investigating active states as it is easy to concentrate on what may well be spectator entities, i.e. rather static, low energy species or sites which are not directly involved in surface or interfacial catalysis. The vital entities in many cases seem to be high energy surface atoms or clusters of same, partially stabilized by adsorption; the ability of these labile atoms to undergo oxidation, and trigger electrocatalysis, within the double layer region (Figure 3) merely reflects their high energy state. With regard to investigating such surface states, electrochemistry has advantages, for example, it may be used not only to produce such states (Figure 2) but also to determine their energy and occupancy values (in terms of peak potential and peak charge, respectively); also electrochemistry is a very convenient method for monitoring electrocatalytic processes (Figure 3) mediated by these active surface species (this is a useful, although indirect, method of obtaining information concerning active sites). Obviously there is a need for alternative, more sophisticated, procedures, but the low coverage and instability of active sites, plus the presence of major amounts of less active surface features (which may be irrelevant from a catalytic viewpoint), are a severe complication in this area.

It appears that in the case of the superactive state of platinum the ability to adsorb hydrogen in acid solution is often rather low [28, 31]. With such electrodes a significant fraction of the surface is assumed to be covered or masked by active, highly electropositive metal atoms which not only yield the marked premonolayer oxidation responses but also inhibit hydrogen atom adsorption (the hydrogen is unable to transfer or share electrons with the unusually electropositive metal atom). One result of such behaviour is that the conventional technique for measuring true surface area (in terms of the hydrogen adsorption/desorption charge [35]) may not be applicable when the platinum surface is in the superactive state.

A final aspect of the superactive state and the mechanism of CO oxidation is whether or not subsurface oxygen is involved. It was postulated recently by van Oertzen et al. [59] that such oxygen plays an important role in the catalysis of gas phase oxidation of CO at a Pt (1 1 0) surface. The presence of subsurface oxygen in a superactive surface state is not improbable as the outer layers of metal atoms are not in a very compact form (an essential requirement for superactivity is a low lattice stabilization energy [29]). Note also the presence of cathodic currents at low potentials in the first positive sweep in Figure 1 and Figure 2(b); as discussed recently [29] such behaviour is difficult to explain and further work is required in this area.

5. Conclusions

- (i) It has been demonstrated in the present work that the redox activity of metal surfaces is a highly variable parameter which may be dramatically altered by appropriate pretreatment. For example the surfaces of both gold and platinum may be activated to such a level that they undergo oxidation at a potential that is lower than that quoted for oxidation of conventional copper, $E^\circ(\text{Cu}/\text{Cu}_2\text{O}) = 0.47 \text{ V}$ [27], in aqueous media. Such anomalous behaviour is already known [45] from studies of ultrasmall metal microparticle behaviour.
- (ii) The well known variability of the anodic response for CO_{ads} oxidation on platinum in aqueous acid solution, and in particular the dependence of this response on the CO admission potential, is attributed to variations in the metal surface activity. As demonstrated earlier for gold [29, 30] and iron [25] the presence of hydrogen activates the metal surface, resulting in the formation of interfacial oxyspecies which are assumed to mediate the oxidation of adsorbed or dissolved reductants (CO_{ads} , CO_{aq} etc.) at unusually low potentials. All the results reported here are in agreement with previous ideas expressed in relation to premonolayer oxidation and electrocatalytic processes [21–24] occurring at metal/aqueous solution interfaces.

References

1. R. Parsons and T. VanderNoot, *J. Electroanal. Chem.* **257** (1988) 9.
2. B. Beden, J.M. Leger and C. Lamy, in J.O'M. Bockris, B.E. Conway and R.E. White (Eds), 'Modern Aspects of Electrochemistry', Vol. 22, (Plenum Press, New York, 1992), pp. 97–264.
3. R.J. Bellows, E.P. Marucchi-Soos and D.T. Buckley, *Ind. Eng. Chem.* **35** (1996) 1235.
4. K. Kunitatsu, H. Seki, W.G. Golden, J.G. Gordon and M.R. Philpott, *Langmuir* **2** (1986) 464.
5. R. Ianniello, V.M. Schmidt, U. Stimming, J. Stumper and A. Wallau, *Electrochim. Acta* **39** (1994) 1863.

6. T. Frelink, W. Visscher, A.P. Cox and J.A.R. van Veen, *Ber. Bunsenges. Phys. Chem.* **100** (1996) 599.
7. G. Estiu, S. Maluendes, E.A. Castro and A.J. Arvia, *J. Electroanal. Chem.* **283** (1990) 303.
8. C. Gutierrez and J.A. Caram, *J. Electroanal. Chem.* **308** (1991) 321.
9. K.A. Friedrich, K.-P. Geyzers, U. Linke, U. Stimming and J. Stumper, *J. Electroanal. Chem.* **402** (1996) 123.
10. S.J. Lee, S. Mukerjee, E.A. Ticianelli and J. McBreen, *Electrochim. Acta* **44** (1999) 3283.
11. N.M. Markovic, T.J. Schmidt, B.N. Grgur, H.A. Gasteiger, R.J. Behm and P.N. Ross, *J. Phys. Chem. B* **103** (1999) 8568.
12. H.A. Gasteiger, N. Markovic, P.N. Ross and E.J. Cairns, *J. Phys. Chem.* **98** (1994) 617.
13. N.M. Markovic, C.A. Lucas, B.N. Grgur and P.N. Ross, *J. Phys. Chem. B* **103** (1999) 9616.
14. Y. Zhang and M.J. Weaver, *J. Electroanal. Chem.* **354** (1993) 173.
15. A. Czerwinski and J. Sobkowski, *J. Electroanal. Chem.* **91** (1978) 47.
16. J. Sobkowski and A. Czerwinski, *J. Phys. Chem.* **89** (1985) 365.
17. M. Hachkar, T. Napporn, J.-M. Leger, B. Beden and C. Lamy, *Electrochim. Acta* **41** (1996) 2721.
18. H. Kita, K. Shimazu and K. Kunimatsu, *J. Electroanal. Chem.* **241** (1988) 163.
19. L.D. Burke and V.J. Cunnane, *J. Electroanal. Chem.* **210** (1986) 69.
20. L.D. Burke, *Electrochim. Acta* **39** (1994) 1841.
21. L.D. Burke, G.M. Bruton and J.A. Collins, *Electrochim. Acta* **44** (1998) 1467.
22. L.D. Burke and P.F. Nugent, *Gold Bull.* **31** (1998) 39.
23. L.D. Burke, J.A. Collins and M.A. Murphy, *J. Solid State Electrochem.* **4** (1999) 34.
24. L.D. Burke and L.M. Hurley, *Electrochim. Acta* **44** (1999) 3451.
25. J. Flis, T. Zakroczymski, V. Kleshnyal, T. Kobiela and T. Dus, *Electrochim. Acta* **44** (1999) 3989.
26. P.D. Cobden, B.E. Nieuwenhuys, V.V. Gorodetskii and V.N. Parmon, *Platinum Metals Rev.* **42** (1998) 141.
27. M. Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solutions' (Pergamon Press, Oxford, 1966).
28. L.D. Burke and D.T. Buckley, *Russ. J. Electrochem.* **31** (1995) 1037.
29. L.D. Burke and A.P. O'Mullane, *J. Solid State Electrochem.* **4** (2000) 285.
30. Y. Ling, J.C. Elkenbracht, W.F. Flanagan and D. Lichter, *J. Electrochem. Soc.* **21** (1997) 151.
31. L.D. Burke, D.T. Buckley and J.A. Morrissey, in B.E. Conway and G. Jerkiewicz (Eds), 'Electrochemistry and Materials Science of Cathodic Hydrogen Absorption and Adsorption, PV 94-21' (The Electrochemical Society, Pennington, NJ, 1999), pp. 232–244.
32. W.M. Vogel and J.M. Baris, *Electrochim. Acta* **23** (1978) 463.
33. S.J. Clouser, J.C. Huang and E. Yeager, *J. Appl. Electrochem.* **23** (1993) 463.
34. N. Sugishima, J.T. Hinatsu and F.R. Foulkes, *J. Electrochem. Soc.* **141** (1994) 3325.
35. R. Woods, in A.J. Bard (Ed), 'Electroanalytical Chemistry' Vol. 9 (Marcel Dekker, New York, 1976), pp. 1–182.
36. S.-G. Sun, W.-B. Cai, L.-J. Wan and M. Osawa, *J. Phys. Chem. B* **103** (1999) 2460.
37. K.E. Heusler and G. Lang, *Electrochim. Acta* **42** (1997) 747.
38. L.D. Burke and L.M. Hurley, *J. Solid State Electrochem.*, submitted.
39. L.D. Burke and P.F. Nugent, *Electrochim. Acta* **42** (1997) 399.
40. G.-Q. Lu, A. Crown and A. Wieckowski, *J. Phys. Chem. B* **103** (1999) 9700.
41. H.S. Taylor, *Proc. R. Soc. Lond. A* **108** (1925) 105.
42. K. Besocke and H. Wagner, *Phys. Rev. B* **8** (1973) 4597.
43. M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.* **115** (1989) 301.
44. G.C. Bond and D.T. Thompson, *Catal. Rev. – Sc. Eng.* **41** (1999) 319–388.
45. A. Henglein, *Ber. Bunsenges. Phys. Chem.* **99** (1995) 903.
46. B.C. Gates, 'Catalytic Chemistry' (Wiley, New York, 1992), p. 352.
47. L.D. Burke and P.F. Nugent, *J. Electroanal. Chem.* **444** (1998) 19.
48. L.D. Burke and K.J. O'Dwyer, *Electrochim. Acta* **34** (1989) 1659.
49. J.O'M. Bockris, H. Wrobleva, E. Gileadi and B.J. Piersma, *Trans. Faraday Soc.* **61** (1965) 2531.
50. G. Milazzo and S. Caroli, 'Tables of Standard Electrode Potentials' (Wiley, New York, 1978), p. 229.
51. D.M. Kolb and M.A. Schneeweiss, *Interface* **8** (1999) 26.
52. L.A. Kibler, A. Cuesta, M. Kleinert and D.M. Kolb, *J. Electroanal. Chem.* **484** (2000) 73.
53. K.M. Robinson, I. K. Robinson and W.E. O'Grady, *Electrochim. Acta* **37** (1992) 2169.
54. T.P. Moffat, in A.J. Bard and I. Rubenstein (Eds), 'Electroanalytical Chemistry', Vol. 21 (Marcel Dekker, New York, 1999), p. 253.
55. T. Zambelli, J. Wintterlin, J. Trost and G. Ertl, *Science* **273** (1996) 1688.
56. L.D. Burke, in S. Trasatti (Ed), 'Electrodes of Conductive Metallic Oxides, Part A' (Elsevier, Amsterdam, 1980), pp. 141–181.
57. S. Mori and Y. Shitare, *Appl. Surf. Sci.* **78** (1994) 269.
58. G.A. Somarjai, *Chem. Rev.* **96** (1996) 1223.
59. A. van Oertzen, H.R. Rotermund, A.S. Mikailov and G. Ertl, *J. Phys. Chem.* **104** (2000) 3155.