

High Energy States of Gold and their Importance in Electrocatalytic Processes at Surfaces and Interfaces

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The ability of metals to store or trap considerable amounts of energy, and thus exist in a non-equilibrium or metastable state, is very well known in metallurgy; however, such behaviour, which is intimately connected with the defect character of metals, has been largely ignored in noble metal surface electrochemistry. Techniques for generating unusually high energy surface states for gold, and the unusual voltammetric responses of such states, are outlined. The surprisingly high (and complex) electrocatalytic activity of gold in aqueous media is attributed to the presence of a range of such non-equilibrium states as the vital entities at active sites on conventional gold surfaces. The possible relevance of these ideas to account for the remarkable catalytic activity of oxide-supported gold microparticles is briefly outlined.

From a technological viewpoint heterogeneous catalysis is one of the most important areas of chemistry; in new technology such processes are responsible for over 90% of chemical and petroleum products by value (1). It is widely accepted (1) that a vital objective in this area is to identify the nature and mode of operation of surface active sites; this task was designated recently by Roberts (2) as "the ultimate in catalytic research". The problems involved appear quite daunting as, despite extensive investigation involving a vast array of sophisticated techniques, the general impression (for the vast majority of catalytic processes) is that "catalytic sites remain unidentified" (3).

The active site theory of heterogeneous catalysis was proposed by Taylor (4) in 1925. Along with the suggestion that only a small percentage of surface atoms participate in such reactions, he pointed out that the sites in question "manifest an extraordinary sensitivity to heat treatment". He attributed the latter to the incomplete crystallization of the active site material, *ie* the latter (as discussed here later) usually exists in a metastable, non-equilibrium state. By inducing crystallization, the heat treatment eliminates the active sites and the resulting more stable material produced at the surface is relatively inactive. Taylor's suggestions are in agreement with current ideas in the surface science approach to surface catalysis, *eg* Somorjai (5) pointed out recently that, for the same surface, catalytic processes occur much more rapidly at defects (the metal atoms (Me_d) associated with defects are intrinsically active, *ie* $\mu(\text{Me}_d) > \mu^\circ(\text{Me})$), such as kinks and ledges, than on terraces; he also stressed that "rough [disordered or non-equilibrated] surfaces do chemistry", *ie* they are the most active from a catalytic viewpoint.

In the present article the main emphasis is on electrocatalysis, *ie* the catalysis of faradaic reactions, and in particular on the behaviour of gold in aqueous media. This work may be regarded as an extension of an earlier 2-part review (6, 7) of the electrocatalytic properties of the same metal. Attention is focused on such topics as metastable, non-equilibrium or defect states of metals, metal microcluster behaviour, hydrous oxides, and the interfacial cyclic redox mechanism of electrocatalysis. Chemisorption is generally regarded as a vital feature of surface catalysis but conventional (low energy) gold surfaces exhibit extremely poor chemisorbing properties. It was suggested recently (8) that with activated gold surfaces a novel, highly localized form of chemisorption occurs due to the marked electropositive character of highly active surface gold atoms. Such behaviour may well be responsible for the remarkable catalytic properties of oxide-supported gold microparticles (9, 10) and may also be the basis of oxygen transient species which are known (11) to play a vital role in many heterogeneously catalysed reactions.

Metastable States of Metals

Metastable states of solid metals are well known in metallurgy; the market value for such materials in the US is currently *ca* \$0.3 billion per annum (12). In the equilibrium state the vast majority of metal atoms occupy lattice sites, *ie* the solid metal is rather highly ordered. In the *metastable* state, which is intrinsically unstable, the high energy state being 'frozen-in', the solid may be totally amorphous, poorly crystalline or simply contain an unusual number of different types of defects. One of the obvious difficulties in working in this area is that the disordered state is essentially infinitely variable, difficult to generate in a controlled form and prone to decay with time. Also, the degree of disorder, or the distribution of excess energy, may be non-uniform within a sample, *eg* it may be much higher in the outer layers of the lattice.

Suryanarayana (12) has described rapid solidification (or thermal quenching) procedures for generating such active states. He also mentioned other techniques, *eg* metal vapour condensation, electrodeposition, electroless deposition, ion or electron bombardment, laser treatment, *etc*. In fact any pretreatment that involves doing significant work on (or inserting energy into) a metal is likely to leave the latter in a metastable state. Confirmation of the ability of metals to store energy is provided by calorimetry (13, 14). Typically as the temperature of an active, *eg* cold-worked, metal sample is increased in a linear manner three energy release regions are observed (see Figure 1). The first stage, recovery, involves such processes as loss of point defects, clusters and dislocations, and subgrain formation and growth; during this process the texture of the sample remains unaltered. The second stage, primary recrystallization, involves nucleation and growth of new, and more stable, grains. Finally, in the

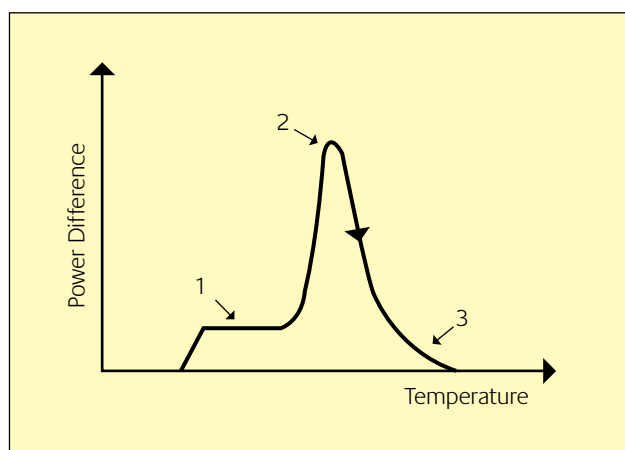


Figure 1

Schematic representation of a typical linear temperature increase annealing response for a sample of activated metal; typically three energy release stages, 1-3, are observed (13); these usually occur well above ambient temperature and their nature is outlined here in the text

third, recrystallization, stage grain growth is observed, *ie* large grains grow while smaller ones shrink and vanish.

It is evident from work in this area of metallurgy that the generation of the active state of a metal may be intentional or inadvertent. Intentional activation may involve cold-working (13) or thermal pretreatment (12) techniques. Inadvertent activation may occur when a metal sample is being prepared or pretreated, *eg* cleaned. A simple, but important (15), example of the latter is observed with electrodeposited copper; the objective of such work is to produce copper deposits, *eg* for current conduction purposes. However, the resulting films are usually structurally defective and calorimetric measurements (14) have demonstrated that they contain excess energy, or are metastable. It is interesting to note that in many cases much of the excess energy is released only at somewhat elevated temperatures (13), *ie* the spontaneous disappearance of a non-equilibrium state at ambient temperature is often extremely slow.

Being the most noble of metals, gold is often the material of choice in the microfabrication area where thin films of the metal are deposited, *eg* for use in sensors (16, 17), using slightly exotic techniques which may include a thermal pretreatment step. As pointed out recently (18) such deposits often display anomalous electrochemical responses, *ie* highly active surface metal atoms undergo oxidation at potentials well within the double layer region. Although such behaviour has been widely ignored in the noble metal area, it is in fact quite common, *eg* enhanced premonolayer oxidation effects were described recently for platinum and copper (19, 20).

The mechanism of retention of excess energy within a sample of metal may be viewed in different ways. Metal atoms close to defect sites, *eg* vacancies or grain boundaries, lack an appreciable portion of the lattice stabilization energy of fully stabilized bulk metal atoms and are therefore in an active state ($\mu_{Me_d} > \mu_{Me_e}$). Alternatively, if the grain size within the sample is extremely small (of nanoparticle dimensions) quantum confinement effects operate. The study of metal microclusters is a very active area of research (21 - 23) and electrochemical aspects of their behaviour were reviewed earlier by Henglein (22). As the number (*n*) of metal atoms per particle (M_n) becomes extremely low, non-linear behaviour is observed, *ie* the standard reduction potential (E°) and lattice stabilization energy of the atoms involved decrease dramatically at very low values of *n*. In the case of silver the shift in E° value on going from the bulk metal to a single atom is *ca* 2.6 V (22); $E^\circ(\text{Ag}_\infty/\text{Ag}^+(\text{aq})) = +0.8$ V (SHE), $E^\circ(\text{Ag}_1/\text{Ag}^+(\text{aq})) = -1.8$ V (SHE), $T = 298$ K. The behaviour of these minute particles is not simple (22) as (i) they are very reactive and tend to disappear rapidly due to agglomeration either with one another or with larger particles, and (ii) certain "magic number" configurations, *eg* Ag_2 and Ag_8 (which have closed shell electron configurations), are surprisingly stable.

The Anomalous Electrochemical Behaviour of Gold

The basic electrochemical response of a stable polycrystalline gold surface in aqueous solution, Figure 2, is very well known. As discussed earlier (6) monolayer (or α) oxide formation in acid solution commences in the positive sweep at ca. 1.36 V* and the resulting deposit undergoes reduction at ca 1.15 V in the negative sweep. With regard to these potential values the agreement with standard equilibrium potential (E°) data for gold (24) is reasonable (precise agreement is not expected; neither surface gold atoms or monolayer oxide films correspond to the standard state of the relevant bulk phase). Until recently it was generally assumed that over the range 0.0 to 1.35 V, positive sweep, no faradaic reaction occurs under the conditions shown in Figure 2, *ie* charge does not cross the interface, the extremely low flow of current or charge observed being due to capacitive, double layer charging, phenomena.

The anomalous behaviour of a gold/solution interface was discussed in some detail earlier (6). If the metal surface is disturbed or activated, *eg* by severe cathodization (which results in (25, 26) hydrogen embrittlement) or severe thermal pretreatment (8), gold atoms (or clusters of same) become poorly lattice stabilized and such atoms undergo oxidation at unusually low potentials within the double layer region. Dramatic examples of such behaviour are shown in Figures 3 and 4: as pointed out earlier (25) there is independent evidence for such behaviour in the case of cathodically pretreated gold (27) and gold single crystal surfaces. The latter are often thermally pretreated (a procedure (28) which may well have a detrimental effect on the order of single crystal surfaces) and these also frequently exhibit anomalous double layer (or premonolayer oxidation) responses (29).

* Unless specifically designated otherwise, all potential values in this review are given in terms of the RHE scale, *ie* with respect to a hydrogen reference electrode, $p(\text{H}_2) = 1.0 \text{ atm}$, in the same solution.

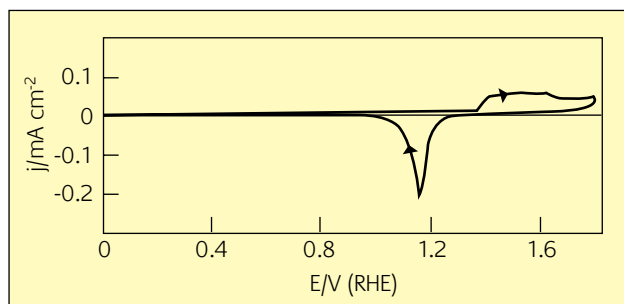


Figure 2
Cyclic voltammogram ($0.0 - 1.8 \text{ V}$, 50 mV s^{-1}) for a non-activated gold electrode surface in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C

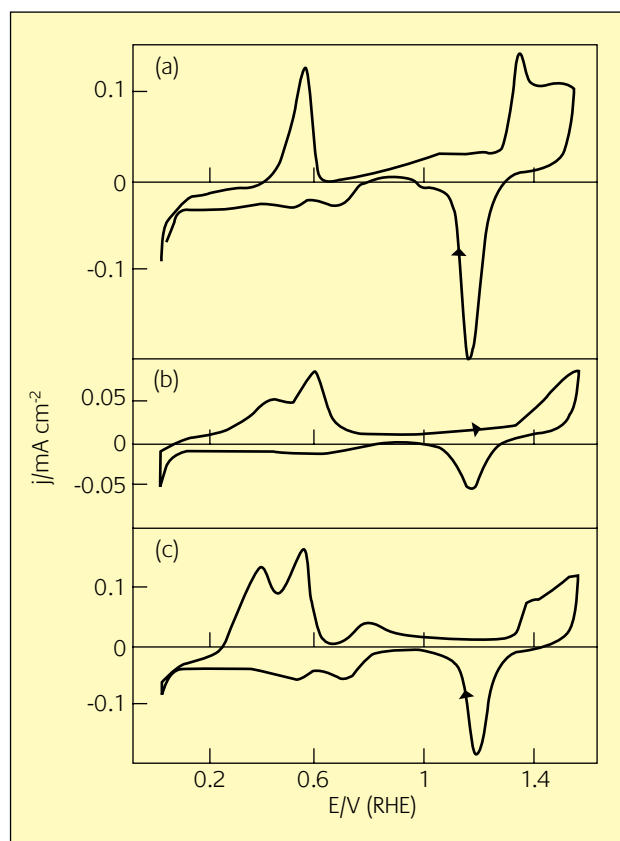


Figure 3
Cyclic voltammograms ($0.0 - 1.6 \text{ V}$, 50 mV s^{-1}) for a gold wire electrode in $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ at 18°C ; the gold wire was thermally pretreated (8) for 20 s in an Ar atmosphere at (a) 570°C , (b) 700°C and (c) 905°C

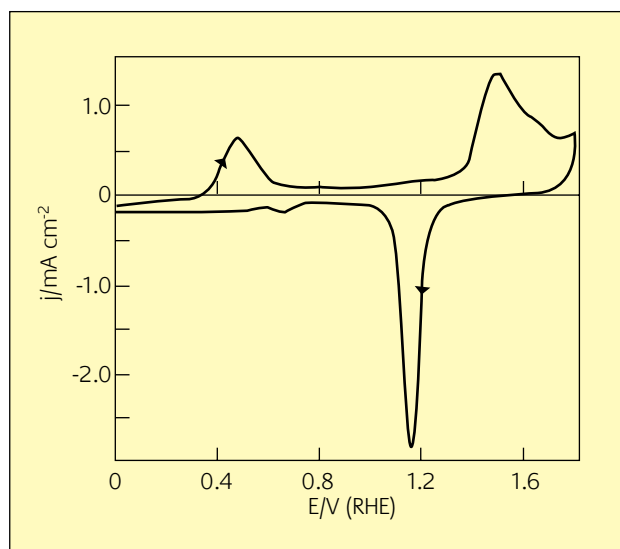


Figure 4
First cyclic voltammogram ($0.0 - 1.8 \text{ V}$, 50 mV s^{-1}) for gold in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C - the electrode pretreatment (25) involved in situ cathodization at -0.4 V for 1 hr. The magnitude of the anodic charge associated with the peak at 0.5 V (positive sweep) decreased gradually on repeated cycling - independent evidence for this feature is given in reference 27

Premonolayer oxidation behaviour is not confined to gold (20); a simple scheme to describe the more general behaviour of metal surfaces is depicted in Figure 5. A stable, low energy or equilibrated metal surface undergoes oxidation in aqueous media to yield a monolayer (α) oxide deposit (the response for this reaction is shown for gold in the positive sweep in Figure 2). However, when the metal surface is subjected to vigorous activation pretreatment the disrupted surface (or highly active atoms) is oxidized at low potentials, Figures 3 and 4, to form a β -oxide deposit. There are some complications to be borne in mind, viz:

- (i) Apparently stable surfaces almost invariably contain defects or active metal atoms (presumably at active sites) which give rise to low coverage, or incipient, β -oxide formation within the double layer region (the evidence for such behaviour (6) was discussed earlier).
- (ii) Hydrous (β) oxide deposits are low density, porous materials which do not protect or passivate the surface (30); hence α -oxide deposits may be produced readily on a gold surface which is already coated with a β -oxide film.

Thick β -oxide deposits may be produced at an α -oxide-coated gold surface by severe dc anodization (30); it is not clear whether the β -material is produced directly, eg from Au^{3+} ions migrating through the α -oxide deposit, or by direct slow conversion of α - to β -oxide.

It may be noted that enhanced premonolayer oxidation responses, Figures 3 and 4, do not occur in a reversible manner, the reduction response at low potentials in the negative sweep being quite sluggish. This may be due to the development (with films of appreciable coverage) of contact problems at the β -oxide/metal interface (25). Recent data, in the case of similar experiments with platinum (19), showed that a more reversible type of response was observed on reducing the sweep rate. Also (as will be described shortly) much more reversible premonolayer oxidation behaviour is

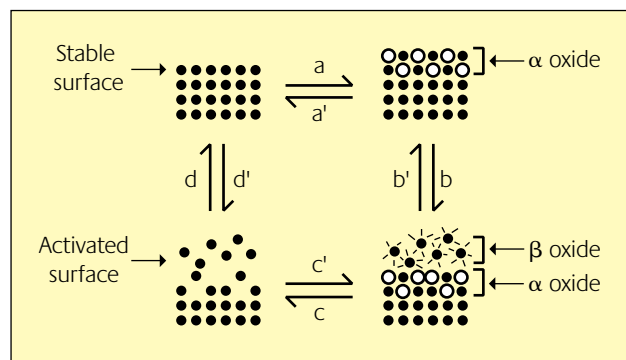


Figure 5

Schematic arrangement illustrating the participation of stable and activated states of metal surfaces in the formation of α - and β -oxide deposits at electrode/solution interfaces

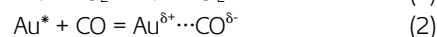
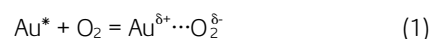
observed with gold in aqueous media when the extent of surface oxidation (or β -oxide coverage) is quite low; this is the type of condition that is assumed to prevail at active sites on a conventional gold surface.

Hydrous oxide deposits are usually amorphous; it was suggested earlier, solely on the basis of E/pH data (30), that an anionic species, $[\text{Au}_2(\text{OH})_9]^{3-}$, was involved. This is not unreasonable as structures of this type, eg $[\text{W}_2\text{Cl}_9]^{3-}$, $[\text{Mo}_2\text{Cl}_9]^{3-}$ and $[\text{Bi}_2\text{Br}_9]^{3-}$, are well known (31); the species involved are face-sharing octahedra and if the linking of opposite faces is continued then a strand of composition MX_3 is produced. Such a strand structure would explain the low density of hydrous oxide systems; it is interesting to note that Pourbaix (24) formulated hydrous gold oxide as $\text{Au}(\text{OH})_3$; this is in agreement with the strand formulation.

Surface and Interfacial Catalysis

The interpretation of the surface electrochemistry of gold is very challenging as the system displays the characteristics of a very weak chemisorber, eg for hydrogen (32), combined with excellent activity for quite a variety of electrocatalytic processes (7). This high activity is observed also in heterogeneous catalysis (9, 10) when the gold is present in the form of oxide-supported nanoparticles. A solution to this dilemma was suggested recently (8), based on the assumption that highly active gold atoms at a surface provide a route for chemisorption that is unavailable in the case of a stable, low energy gold surface.

Activating a gold surface involves lowering the lattice stabilization energy of surface atoms which, as a result, are converted to highly electropositive surface species (this is the basis of premonolayer oxidation behaviour). When such atoms (Au^*) come into contact with gaseous species an unusual mode of chemisorption, involving polar covalent bonding, is assumed to occur, viz:



Alternatively, if these active gold atoms are in contact with an aqueous phase they can undergo oxidation at unusually low potentials and coordinate oxy and/or hydroxy species. Since active surface atoms are protruding species they can coordinate an unusual number of ligands; thus the assumption that the product of premonolayer oxidation involves formation of β - rather than α -oxide species is not unreasonable.

The role of active surface metal atoms and their oxidation products, incipient hydrous oxide species, as mediators in electrocatalytic reduction and oxidation reactions,

respectively, has been discussed earlier (7) for gold (a generalized, schematic, version of this approach was published recently (33)). Two points are worth noting, viz:

(i) The mediator approach to electrocatalysis at metal surfaces is not confined to gold. The same approach has been applied to both copper in base (33) and platinum in acid (34). The copper case is particularly interesting from a chronological viewpoint; the electrocatalytic response within the double layer region, commencing at -0.1 V, was described (35) well before it was discovered (36) that it was possible to grow a multilayer hydrous oxide film on copper in base. The film in question also undergoes rapid reduction at $ca -0.1$ V which is an unusually low value from a thermodynamic viewpoint, *ie* anomalous behaviour is again observed. These results support the assumption that the same type of reaction (hydrous oxide/active state of copper, at -0.1 V) is involved in both multilayer hydrous oxide reduction and electrocatalysis at copper electrodes in base. In essence, the type of unusual behaviour described here for gold is replicated by other metal electrode systems.

(ii) It is assumed that the highly active surface states giving rise to the dramatic responses shown in Figures 3 and 4 exist, at extremely low coverages, at active sites on a conventional gold surface. The nature of these sites is discussed in the next section; attention will be focused here on the diversity of the electrocatalytic responses for gold. It was pointed out earlier (7) that with gold in acid solution the onset/termination potential for oxidation of many alcohols and some organic acids occurs at $ca 1.10$ V; the same type of behaviour was observed for ethylene glycol, ethanal and hydrazine oxidation, plus dichromate reduction (37), at $ca 0.85$ V; these values coincide reasonably well with multilayer hydrous oxide reduction peaks (see Figure 4(a) in reference 6) for this electrode system. In more recent work it was pointed out that there appears to be two other onset/termination regions for electrocatalytic processes on gold in acid, one (25) at $ca 0.5$ V (for processes such as carbon monoxide oxidation (38)) and another at $ca 0.3$ V (for reduction of species such as nitrobenzene (8)). It may be noted that marked premonolayer oxidation peaks occur at these two potential values in Figure 3(c).

These data highlight the complexity of electrocatalytic behaviour at metal surfaces. It is not just that unstable states of metals and ill-defined oxyspecies are involved; it also appears that for a given electrode system there is a selection or range of transitions. It may be noted that similar ideas were proposed earlier for platinum in acid (34) and the same type of behaviour was observed recently (39) with silver in base. In the case of the latter electrode monolayer oxide formation commences in the positive sweep at $ca 1.15$ V.

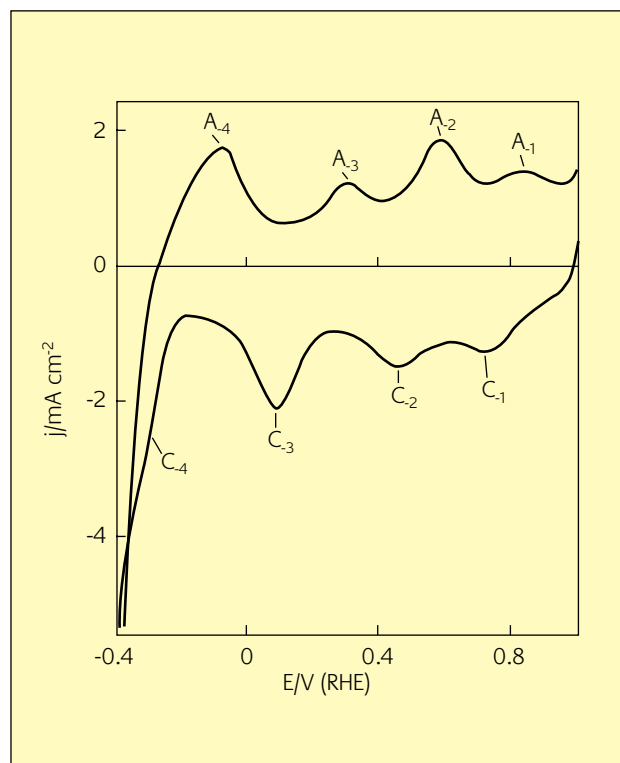


Figure 6

*Cyclic voltammogram ($-0.4 \rightarrow 1.0$ V at 100 mV s^{-1}) for a silver wire electrode in 0.5 mol dm^{-3} NaOH at 25°C following cathodic polarization at -0.7 V for 3 hr in the same solution; monolayer oxide formation for this system commences at $ca 1.15$ V, *ie* the responses shown here relate to the double layer region*

However, after cathodic activation of the silver surface four quasi-reversible redox transitions, Figure 6, were observed at the following mean potential values within the double layer region: A_1/C_1 , 0.77 V; A_2/C_2 , 0.50 V; A_3/C_3 , 0.20 V; A_4/C_4 , -0.20 V (these values are approximate). As in the case of gold in acid, each of these transitions appear to correspond to different low coverage mediator systems which participate in electrocatalysis of different types of reactions at the metal/solution interface. Clearly multiple active state configurations and transitions are a widespread feature of metal surfaces.

The discussion of electrocatalysis here is confined largely to gold in acid; however, it is worth noting that with gold in base carbon monoxide oxidation commences at an even lower potential, $ca 0.1$ V, than in acid, $ca 0.5$ V; the voltammetric responses, for the two different electrolyte solutions, are given (Figure 5) in the work of Kita and coworkers (40). The nature of the redox transition at $ca 0.1$ V for gold in base was discussed earlier (7).

Surface Active Site Behaviour

It is assumed here that the vital ingredient in most catalytic and electrocatalytic reactions at metal surfaces are low coordination, high energy, unusually electropositive metal atoms. Such atoms may well be transient species generated via thermal vibrations at extended surface defects. A very simple model of a metal surface is shown in Figure 7. The atoms are represented as cubes with six faces or coordination sites; assuming that the excess energy of an atom is directly proportional to the number of exposed (or unshared) faces, the variation of the atomic energy with site character is as follows: terrace adsorbed atom (TA, 1) > step adsorbed atom (SA, 2) > step corner atom (SC, 3) > step atom (S, 4) > terrace atom (T, 5) > bulk atom (B, 6); the figures in the brackets here are the number of shared or occupied coordination sites. It is obvious that this is a very simplified approach; rough surfaces are far more complex and among the factors that are ignored here are the involvement of species such as surface microclusters (which have quite unusual properties) and the possible involvement of subsurface oxygen (41); the fact that metal atoms participating in catalytic processes may exhibit dynamic behaviour (42), probably resulting in a change in lattice coordination number and energy, should also be borne in mind.

The most active (in thermodynamic terms), or electropositive, atom on the surface, as represented in Figure 7, is the terrace adsorbed atom. This is the type that undergoes oxidation at very low potentials but it is also the one most likely to disappear, *eg* the atom in question can migrate to a step site where its lattice coordination number increases and its energy

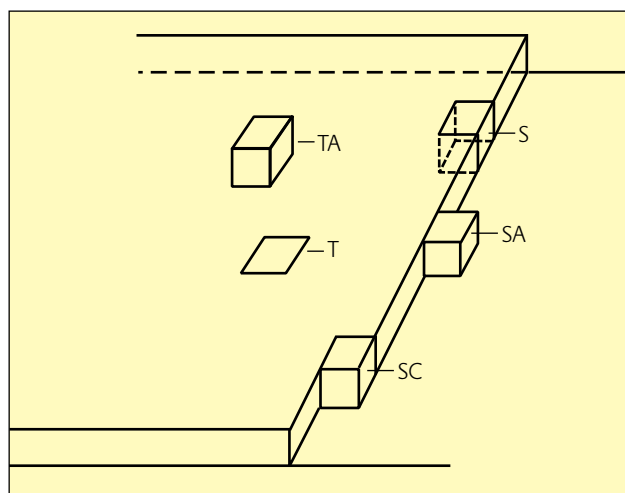


Figure 7

Variation of lattice coordination number (and hence energy) for different types of atoms at a slightly disordered metal surface: TA, terrace adsorbed atom; SA, step adsorbed atom; SC, step corner atom; S, step atom; T, terrace embedded atom; bulk atoms (B) are obviously not shown here

is reduced. Hence, the coverage of terrace adsorbed atoms is usually quite low and their presence is difficult to detect (it is well established (43) that mobile surface and even kink atoms are not easily imaged by STM techniques as they move away from the probe tip). However, terrace adsorbed atoms, on reaching a step or even a kink site are still relatively active and have a finite possibility of returning to their original, higher energy, state. Such behaviour, *ie* enhanced occupancy of the high energy state, may be favoured also during the course of a catalytic reaction if, as demonstrated by von Oertzen and coworkers (42) for CO oxidation on platinum, catalytic processes induce dynamic behaviour and displacement of surface metal atoms.

It is evident from Figure 7 that there are a range of different types of sites and metal atom energy values at the surface. This is one of the factors that would account for the different redox potential values observed for active state transitions (Figure 6) within the double layer region. However, caution is required here as the type of oxide produced on oxidation of the active site atom may also be variable (such variation may be due to incorporation of different amounts of solution anions (30) into the coordination sphere of the oxide product). A highly interesting feature of these electrocatalytic processes is that not only is there only a limited number (apparently four) mediator systems available at the interface but each of the electrocatalytic processes seems to select one specific mediating couple, *eg* with gold in acid CO oxidation commences at about 0.5 V (38, 40) whereas alcohol oxidation commences at *ca* 1.1 V (7). A similar type of mediator selectivity has been observed with silver in base (39); evidently the reaction being mediated influences the choice of mediator system, in a manner that is not yet understood.

The assumption that low coordination surface metal atoms are important in catalysis is not especially novel; this idea was proposed by Taylor (see Figure 1 in reference 4) and has been discussed more recently by Anderson (44) in connection with the behaviour of small metal particles. He drew attention to the fact that minute crystallites are seldom perfect, *eg* the outermost layer of atoms is likely to be incomplete. Low coordination surface atoms have two important characteristics or advantages from a catalytic viewpoint: (i) they can coordinate several species from the liquid or gaseous phase at the same site, thereby favouring reaction between the resulting ligand species and (ii) the energy and redox properties of such atoms are quite different from those of the bulk metal. An interesting point noted with platinum (45) is that activating a metal surface by severe pretreatment to an unusually high degree may have an adverse effect on its electrocatalytic activity; it was suggested that extensive activation may result in overoxidation of the surface, *ie* there may be few free metal

atoms available to react with the dissolved solution species or β -oxide films formed at high coverages may be reluctant to undergo reduction in a rapid, quasi-reversible, manner.

Oxide-Supported Gold Microparticles

The properties of oxide-supported gold microparticles were surveyed recently (from a heterogeneous catalysis, especially CO oxidation, viewpoint) by Bond and Thompson (46); two earlier articles by Thompson (47, 48) are also of considerable interest. The support may play a multifunctional role eg it may inhibit loss of gold atoms from the individual particles and retard particle agglomeration or growth, thereby maintaining the metal in an active, quantum confined, state. Also species present at the oxide surface, such as OH or OH⁻, may migrate onto the gold surface and participate in catalytic processes occurring at active sites on the latter.

Carbon monoxide oxidation on gold in aqueous solution commences and terminates (40) at *ca* 0.5 V in acid and 0.1 V in base, *ie* the type of mediator system involved is based on the presence of unusually high energy surface gold atoms. It is assumed that similar high energy atoms exist also, as low coverage transient species, at gold microparticle surfaces in the absence of the aqueous phase; in the presence of an oxidizing gaseous environment such atoms are assumed to exist largely in the oxidized state. Such oxide intermediates were also assumed to be involved in CO-oxidation on oxide supported gold microparticles by Bond and Thompson (46) who outlined a detailed mechanism for the reaction in question. This topic, the role of short-lived oxygen (or oxide) transients and precursor states in surface catalytic processes, has been discussed in a more general manner by Roberts (11). We regard these non-equilibrium oxide species as reactive, low coverage, active site entities which participate in surface catalysis in a cyclic redox manner; a simple version of the latter approach, in the case of heterogeneously catalysed gas phase reactions, is the well known Mars-van Krevelen mechanism (49) for the catalytic oxidation of organics on oxide catalysts. Further research in the supported gold microparticle area is obviously highly desirable as the unusual catalytic activity of these systems may find considerable commercial applications.

Conclusions

1. The basic assumption here is that electrocatalysis at metal/aqueous solution interfaces often involves unusually active (in the thermodynamic sense) surface metal atoms which exist virtually outside, or only weakly attached to, the stable lattice. Such atoms are regarded as low

coverage, thermodynamically forbidden, species which undergo rapid reaction in a quasi-reversible manner to produce the vital electrocatalytic mediators at the interface. The role of chemisorption is not discounted; indeed with a metal such as gold localized interaction at the active site atom, see Equation 2, may be quite important.

2. Thermodynamically forbidden (or metastable) states are well established in metallurgy. The investigation of such states is obviously difficult as they are neither well defined nor stable (the lack of progress, or knowledge, with regard to our understanding of rough, disordered surfaces was pointed out recently by Somorjai (5)); furthermore, for any one metal, such states exhibit a complex, poorly understood, range of voltammetric responses (an account of active state responses for platinum in acid solution has just been published (50)). However, there is an excellent correlation, which is not confined to gold, between such premonolayer active state responses and those observed for both multilayer hydrous oxide reduction and electrocatalysis (33).
3. It is assumed that the ideas proposed here with regard to electrocatalysis are relevant also to the unusual catalytic activity of oxide-supported gold microparticles. It is assumed that with regard to both areas of catalysis it is the active state, rather than the conventional, behaviour of gold surface atoms that is of greatest relevance.

About the Authors

Laurence Declan Burke is a graduate of University College Cork who was introduced to noble metal electrochemistry, as a PhD student, by FA Lewis at Queens University Belfast in 1961. Since returning to Cork in 1965 he has supervised over 30 PhD students in this area and has published and lectured extensively.

Andrea Judith Ahern received a BSc Degree in Chemistry from University College Cork in 1997 and then joined Professor Burke's research group studying the electrochemistry of noble metals and the role of active states of metal surfaces and hydrous oxides in electrocatalysis. Recently she has been investigating the area of sulphur/polysulphide electrochemistry which is of interest in large scale energy storage; this work is financed by the UK company Innogy Technology Ventures Limited. Currently she is completing her PhD thesis.

Anthony Peter O'Mullane is a graduate of University College Cork (BSc 1997) and was awarded a PhD in March 2001 on the basis of a thesis entitled 'The Electrochemistry of the Superactive Surface States of Gold'. He is currently working on Solar Cell Materials as a postdoctoral fellow in the Technical University Darmstadt, under the supervision of Prof Dr Heinz von Seggern.

References

- 1 W.M.H. Sachtler, *Ber. Bunsenges. Phys. Chem.*, 1995, **99**, 1295
- 2 M.W. Roberts, *Cat. Lett.*, 2000, **67**, 39
- 3 B.C. Gates, 'Catalytic Chemistry', John Wiley and Sons, 1992, p. 352
- 4 H.S. Taylor, *Proc. Roy. Soc. Lond. A*, 1925, **108**, 105
- 5 G.A. Somorjai, *Chem. Rev.*, 1996, **96**, 1223
- 6 L.D. Burke and P.F. Nugent, *Gold Bull.*, 1997, **30**, 43
- 7 L.D. Burke and P.F. Nugent, *Gold Bull.*, 1998, **31**, 39
- 8 L.D. Burke, L.M. Hurley, V.E. Lodge and M.B. Mooney, *J. Solid State Electrochem.*, 2001, **5**, 250
- 9 M. Haruta, M. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, **115**, 301
- 10 G.C. Bond and D.T. Thompson, *Catal. Rev. - Sci. Eng.*, 1999, **41**, 319
- 11 M.W. Roberts, *Chem. Soc. Rev.*, 1996, **25**, 437
- 12 C. Suryanarayana, in 'Materials Science and Technology - A Comprehensive Treatment', Vol. 15, ed. R.W. Cahn, P. Haasen and E.J. Kramer, VCH Weinheim, 1991, pp. 57-110
- 13 R.E. Reed-Hill and R. Abbaschian, 'Physical Metallurgy Principles', 3rd ed., PWS-Kent Publishing Co., Boston, 1992, pp. 227-242
- 14 H.M. Clarebrough, M.E. Hargreaves and G.W. West, *Proc. Roy. Soc. Lond. A*, 1955, **232**, 252
- 15 P.C. Andricacos, *The Electrochem. Soc. Interface*, 1999, **8**, 32
- 16 D.H. Craston, C.P. Jones, D.E. Williams and N. El Murr, *Talanta*, 1991, **38**, 17
- 17 M. Bisenberger, C. Bräuhle and N. Hampf, *Sensors and Actuators B*, 1995, **28**, 181
- 18 L.D. Burke and A.P. O'Mullane, in 'Chemical and Biological Sensors and Analytical Methods', ed. M. Butler, P. Vanysek and N. Yamazoc, PV 2001-18, The Electrochem. Soc., Pennington, NJ., 2001, pp. 320-328
- 19 L.D. Burke and L.M. Hurley, *J. Solid State Electrochem.*, 2000, **4**, 353
- 20 L.D. Burke, J.A. Collins, M.A. Horgan, L.M. Hurley and A.P. O'Mullane, *Electrochim. Acta*, 2000, **45**, 4127
- 21 G. Schmid and G.L. Hornyak, In 'Current Opinion in Solid State and Materials Science', Vol. 2, No. 2, ed. A.K. Cheetham, H. Inokucki and J.M. Thomas, Current Chemistry Ltd., London, 1997, pp. 204-212
- 22 A. Henglein, *Ber. Bunsenges. Phys. Chem.*, 1995, **99**, 903
- 23 H. Natter, M. Schmelzer, S. Janssen and R. Hempelmann, *Ber. Bunsenges. Phys. Chem.*, 1997, **100**, 1706
- 24 M. Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solutions', Pergamon, Oxford, 1966, pp. 399-405
- 25 L.D. Burke and A.P. O'Mullane, *J. Solid State Electrochem.*, 2000, **4**, 285
- 26 L.D. Burke, A.P. O'Mullane, V.E. Lodge and M.B. Mooney, *J. Solid State Electrochem.*, 2001, **5**, 319
- 27 Y. Ling, J.C. Elkenbracht, W.F. Flanagan and B.D. Lichter, *J. Electrochem. Soc.*, 1997, **21**, 151
- 28 L.A. Kibler, A. Cuesta, M. Kleinert and D.M. Kolb, *J. Electroanal. Chem.*, 2000, **484**, 73
- 29 T. Sawaguchi, Y. Sato and F. Mizutani, *Phys. Chem. Chem. Phys.*, 2001, **3**, 3399
- 30 L.D. Burke and M.E.G. Lyons, in 'Modern Aspects of Electrochemistry', No. 18, ed. R.E. White, J.O'M. Bockris and B.E. Conway, Plenum Press, New York, 1986, p.169
- 31 U. Müller, 'Structural Inorganic Chemistry', 2nd ed., Wiley and Sons, Chichester, 1992, p.167
- 32 R. Woods, in 'Electroanalytical Chemistry', Vol. 9, ed. A.J. Bard, Marcel Dekker, New York, 1976, p. 1
- 33 L.D. Burke, J.A. Collins and M.A. Murphy, *J. Solid State Electrochem.*, 1999, **4**, 34
- 34 L.D. Burke and L.M. Hurley, *Electrochim. Acta*, 1999, **44**, 3451
- 35 L.D. Burke, G.M. Bruton and J.A. Collins, *Electrochim. Acta*, 1998, **44**, 1467
- 36 L.D. Burke and M.A. Murphy, *J. Solid State Electrochem.*, 2001, **5**, 43
- 37 L.D. Burke and P.F. Nugent, *Electrochim. Acta*, 1997, **42**, 399
- 38 S.-G. Sun, W.-B. Cai, L.-J. Wan and M. Osawa, *J. Phys. Chem. B*, 1999, **103**, 2460
- 39 A.J. Ahern, L.C. Nagle and L.D. Burke, *J. Solid State Electrochem.*, in the press
- 40 H. Kita, H. Nakajima and K. Hayashi, *J. Electroanal. Chem.*, 1985, **190**, 141
- 41 E.R. Savinova, P. Kraft, B. Pettinger and K. Doblhofer, *J. Electroanal. Chem.*, 1997, **430**, 47
- 42 A. von Oertzen, H.H. Rotermund, A.S. Mikhailov and G. Ertl, *J. Phys. Chem. B*, 2000, **104**, 3155
- 43 T.P. Moffat, in 'Electroanalytical Chemistry', Vol. 21, ed. A.J. Bard and I. Rubinstein, Marcel Dekker, New York, 1999, p. 253
- 44 J.R. Anderson, 'Structure of Metallic Catalysts', Academic Press, New York, 1975, p. 244
- 45 L.D. Burke and J.K. Casey, *Bull. Electrochem.*, 1992, **8**, 601
- 46 G.C. Bond and D.T. Thompson, *Gold Bull.*, 2000, **33**, 41
- 47 D.T. Thompson, *Gold Bull.*, 1998, **31**, 111
- 48 D.T. Thompson, *Gold Bull.*, 1999, **32**, 12
- 49 P. Mars and D.W. van Krevelen, *Chem. Eng. Sci.*, 1954, **4**, 41
- 50 L.D. Burke and A.J. Ahern, *J. Solid State Electrochem.*, 2001, **5**, 553