

Electrochromic Iridium Oxides

PREPARATION AND PROPERTIES OF HYDROUS FILMS

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The recent development of potential cycling procedures for producing relatively thick hydrous noble metal oxide layers, plus the introduction of sputtering techniques for laying down such films on other substrates such as conducting glass, has added an important new dimension to the study of noble metal oxidation. Differences in composition, apparent density and redox behaviour between the hydrous and anhydrous layers are discussed here with particular reference to the iridium oxide system. Commercial applications of the electrochromic activity are also covered.

Interest in the anodic behaviour of platinum metals, especially ruthenium and iridium, has increased significantly in the past decade, largely due to the development of RuO₂-activated titanium anodes in the chlor-alkali industry (1) and the discovery of marked electrochromic behaviour in hydrous iridium oxide layers (2, 3). Platinum and gold still possess major advantages as substrates for the investigation of the initial stages of metal oxidation. Apart from the absence of dissolution, which can be significant for instance in the case of palladium, these two metals show a clear separation between the potential ranges for hydrogen adsorption and surface oxidation. The layers formed on the rarer noble metals, however, are generally more interesting as these surface oxides show intermediate transitions, for example Ir(III)/Ir(IV), which can give rise to marked electrocatalytic and electrochromic behaviour.

For any of these metals it is important to distinguish between two different types of oxides. First there are compact, anhydrous oxides such as PtO, Au₂O₃ and RuO₂ where the only ligands bonded to the cations in the bulk phase are bridging oxygen (-O-) species as in rutile. Secondly there are dispersed (or extended) hydrous oxides in which the surface layer is present in poorly crystallised, gel form.

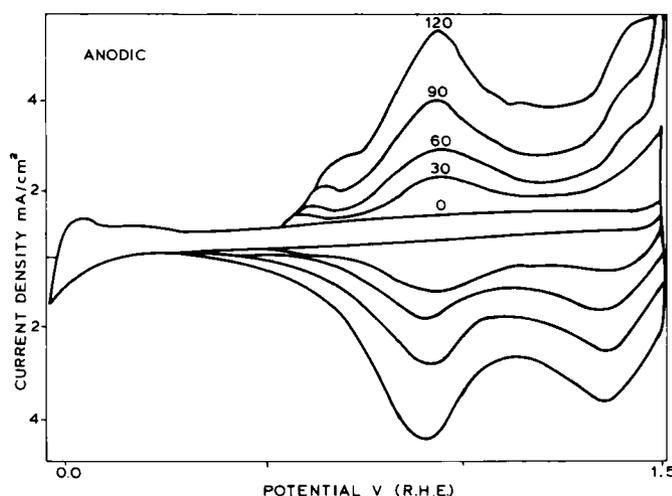
undergo an irreversible exothermic transition

These oxides can be observed for platinum and gold. The ligands involved may include OH and OH₂ species and there may be considerable quantities of water and electrolyte adsorbed and trapped within the layer. Most electrochemical studies of both platinum and gold oxides to date have been concerned with the formation and reactivity of the more anhydrous materials. The techniques for producing hydrous oxide films, especially on the rarer platinum metals, have only recently been developed. Their redox and electrochromic properties are rather novel and progress in these areas will be reviewed here with particular reference to hydrous iridium oxide.

Formation of Hydrous Oxide Layers

Although hydrous oxide films may be produced on gold (4, 5) and platinum (6) under severe anodic (d.c.) conditions, this method is apparently ineffective in the case of iridium. In fact the hydrous film grown on iridium on cycling dissolves at potentials above about 1.6 V with respect to the reference hydrogen electrode (R.H.E.) (2). The most widely used procedure for producing hydrous iridium oxide at the present time is the potential cycling technique, see Figure 1, described independently by Rand and Woods (7) and

Fig. 1 Cyclic voltammograms (-0.05 to 1.50 V (R.H.E.), 50 mV/s) recorded for an initially clean iridium electrode in 1.0 mol/dm³ sulphuric acid at 25°C at various stages of the oxide growth reaction. The latter was carried out by cycling (-0.05 to 1.50 V, 1 Hz). The figures in the diagram are the number of oxide growth cycles involved prior to recording the voltammogram



Buckley and Burke (2). Detailed investigation has shown that in 1.0 mol/dm³ sulphuric acid the optimum upper and lower limits for a triangular growth sweep at 10 Hz are about 1.60 and 0.01 V (R.H.E.), respectively (8). This procedure is also effective in dilute (9), but not in strong (8), base. As outlined recently for platinum, hydrous oxides are frequently more stable with regard to reduction than their anhydrous analogues, especially in base (10). However, their formation under d.c. conditions is unfavourable since, with the platinum atom largely embedded in the metal lattice, a full oxy ligand co-ordination state is not readily attainable. Instead, during the initial sweep the metal surface becomes coated with a layer of hydroxy species, which apparently are charged (11). These rapidly alter, via place-exchange type reactions, to form a largely anhydrous surface film which in the case of iridium scarcely extends beyond one or two monolayers. From the work with platinum it appears that the function of the lower limit in such cycling experiments is to disrupt the initial anhydrous film by extensive reduction (10). Renewed anodisation then results in oxidation not only of the displaced metal atoms formed on reduction but also some of the underlying metal. The outer region of the oxide thus produced is evidently more prone to hydration, giving a rather

disperse, stable material which is not readily reduced. Growth continues at the inner region, that is at the metal/(porous oxide + solution) interface, usually at a decreasing rate. Recent Rutherford back-scattering analysis indicates that with thick films produced in this manner the water content of the hydrous layer decreases across the film, that is on going from the oxide/solution to the oxide/metal interface (12). Hydrous oxide formation is therefore assumed to be inhibited by the accumulation of increasing quantities of poorly hydrated material at the latter boundary. The function of the upper limit is less clear; possibly vigorous anodisation is needed to drive oxygen species into the outer layer of the metal lattice, since on subsequent reduction this would enhance the degree of disturbance of the outer region of the metal.

Another approach for the generation of hydrous iridium oxide films involves the use of sputtering techniques (13, 14, 15). In the literature the two types of deposits are sometimes distinguished by the acronyms AIROF and SIROF, anodic and sputtered iridium oxide films, respectively; the former of course being produced by cycling. The sputtering conditions have been described in some detail recently by Kang and Shay (15). The most active deposits (blue SIROFs) were obtained by fast deposition

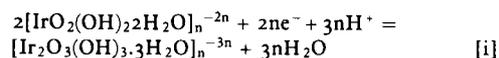
of iridium dioxide, in an argon/oxygen (80/20) atmosphere at a net pressure of approximately $33\ \mu\text{m}$ of mercury onto cooled substrates. Inadvertent traces of water in the deposition chamber were found to be highly beneficial, although high levels had a detrimental effect. The dispersed nature of the oxide is clear from the mean density values quoted for the various deposits. These range (in g/cm^3) from 11.68 for bulk anhydrous IrO_2 to 10 or 7.8 for sputtered films of low reactivity in the as-deposited and cycled condition, respectively (16), about 4.0 for active, blue, sputtered films (15) and, finally, about 2.0 for films grown by potential cycling (17). The two latter types of film are obviously highly hydrated in aqueous media and their redox and electrochromic properties are quite similar. The less active sputtered films, deposited in pure oxygen, evidently have a less porous structure. Generally they have a higher electrical conductivity (15) and are more resistant to dissolution under oxygen evolution conditions (18). However, they apparently require conditioning, that is potential cycling, during which they swell due to solvent uptake before displaying significant charge storage behaviour. Even then the peak potential for the main charge storage process is observed at a significantly lower potential as compared with active deposits (15). The active deposits also maintain their open-circuit potentials (and optical densities) in the oxidised or reduced state for longer times, that is to say they have a better memory than the inactive deposits (15). This is probably due to the greater degree of conversion of the material in the more dispersed form to the reduced or oxidised state in the first instance. Differential thermal and evolved gas analysis studies by Beni and co-workers (16, 19) have shown that the amorphous iridium oxide layers produced by sputtering techniques undergo an irreversible exothermic transition ($\Delta H \approx 106\ \text{kJ}/\text{mol}$), with little change in stoichiometry, at about 300°C . This was attributed to an amorphous/crystalline transition in the oxide and resulted in a loss of electrochromic properties. An endothermic reaction was noted at about 700°C and this was

accompanied by significant loss of water, hydrogen and oxygen. There was also some initial loss of water at lower temperature (about 120°C) under vacuum conditions.

Potential/pH and Electrochromic Behaviour

Although there are indications in cyclic voltammetry data recorded for iridium oxide layers of about four redox transitions in the oxide region (21), discussion will be restricted here to the major peak observed just below 1.0 V (R.H.E.) in acid. The initial claim by Buckley and Burke (2, 8) that the reaction involved here is an Ir(III)/Ir(IV) transition in a hydrated oxyhydroxide film appears to be borne out by the work of McIntyre and co-workers (17). There is, however, an unusual aspect of hydrous oxide electrochemistry involved here that is most clearly demonstrated by the pH-dependence of the reversible peak potential values. While it is widely accepted that the reversible potentials of oxide electrode systems vary by 59 mV per unit change in solution pH with respect to a pH-independent reference electrode, such as standard hydrogen or calomel electrode (22), the observed value for the main reversible charge storage peak for hydrous iridium oxide (8, 20, 23) is close to 88.5 mV, that is $3/2 (2.303\ \text{RT}/\text{F})\ \text{V}$, per unit change in pH. In terms of a hydrogen reference in the same solution, that is on the R.H.E. scale, the corresponding values are 0 and 29.5 mV/pH unit, respectively.

To explain this result, it has been assumed (20, 24), by analogy with earlier work on the hydrous gold oxide system (4, 5), that the redox behaviour in the iridium case is of the form:



In this scheme the main oxide component in the surface layer is regarded as a porous, cross-linked gel or polymer (the composition given above is largely nominal), the polymer strands bearing a negative charge with the counterion present in the aqueous phase which permeates throughout the porous oxide layer. The assumptions here are not unusual; transition metal ions in high oxidation states in aqueous

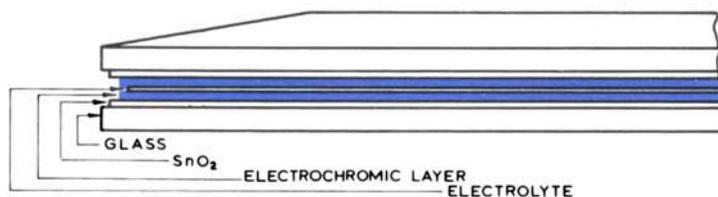
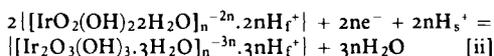
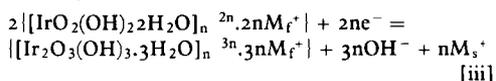


Fig. 2 This is a typical configuration for an electrochromic display device. The doped SnO_2 layer is used as a transparent conductor; the electrolyte may be a solid ionic conductor, ion-exchange resin or aqueous gel, and for display purposes it may be deliberately made opaque. The counter electrode may be a film of battery-type oxide or metal

media frequently exist in anionic form due to hydrolysis effects (25). The acidity and therefore ion-exchange capacity of the oxide increases on oxidation. This is reflected in the insertion of hydroxide ions, which in acid media are supplied by locally bound or trapped water molecules, when film oxidation occurs in accordance with Equation [i]. Since delocalised counterions (identified by the subscript "f") are already present in the film, it is convenient to distinguish between these and ions which must transfer between the film and bulk solution (the latter are identified by the subscripts "s"). The main charge storage reaction in the film may therefore be represented by Equation [ii] for acid:



and Equation [iii] for base:



The major difference between the hydrous and anhydrous oxides is that the open structure of the former enables interaction to occur between most of the oxyspecies in the film, not just those at the external surface as in the case of anhydrous material, and solution species, especially H^+ and OH^- ions. Such interaction influences not only the extent of charge storage capacity of the films but also the thermodynamic, that is the potential/pH, behaviour of the redox transition, as recently described elsewhere (5, 24).

There has been considerable controversy in

the literature recently as to the nature of the ion-insertion reaction in the charge storage process. Some authors assert that the process involved is proton insertion/removal (2, 12) while others have claimed that the hydroxide species is involved (26). In fact it appears from Equations [ii] and [iii] that hydroxide ion insertion/removal reactions are involved locally at cation sites within the film. However, these hydroxide ions are probably produced locally from water molecules within the film. In aqueous media local pH gradients probably induce proton migration, even OH^- ion movement in such systems is likely to involve proton switching via a Grotthus-type mechanism. There may also be water and alkali metal ion transfer between the film and the aqueous phase during the course of the redox reaction. Other important properties of these films which may be affected by the open, solvent-separated structure of the hydrous polymer layer include the fact that the reduced form of the layer is less conducting than the oxidised form (27)—it has been suggested that this is due to some degree of non-stoichiometry in the latter (20)—while in the lower region of the cyclic voltammogram the currents decrease only very slightly during the hydrous oxide growth reaction, as may be seen in Figure 1. It has been postulated with regard to the latter that monolayer, compact oxide formation/reduction processes, together with hydrogen adsorption/desorption processes, occur at the iridium surface (which scarcely alters in roughness value) beneath an ever

increasing thickness of hydrous material (28).

Finally, there is the electrochromic effect; the reduced form of the hydrous layer is transparent to visible radiation while the oxidised state is strongly absorbing, the layer in the latter case appearing deep blue. Since the electrochemical reactions (Equations [ii] and [iii]) giving rise to the change in oxidation state are quite rapid, considerable interest has developed recently with regard to potential applications of this effect.

Applications

Much effort has been devoted recently, mainly in Bell Laboratories, to the development of devices such as optical displays based on the colour changes associated with the main redox transition in hydrous iridium oxide layers and first reported by Buckley and Burke (2). In its simplest form an electrochromic cell may be regarded as a thin film battery with a significant colour difference between the charged and discharged states. Typical construction details are given in Figure 2. In an early publication in this area Gottesfeld and McIntyre (29) pointed out that the iridium oxide system possessed numerous advantages compared with WO_3 , the traditional electrochromic material. These are: (a) fast response, (b) strong absorption in the written state throughout the visible spectral region, (c) good open-circuit memory, (d) an operating range that avoids electrolyte decomposition and (e) the ability to grow and remove the oxide layer in situ within the electro-optic display cell. They also demonstrated that slow oxide dissolution in acid media could be avoided by operating at higher pH. In

0.5 mol/dm^3 sodium sulphate with $\text{pH} = 3.5$, negligible loss of film thickness or optical contrast was noted after more than 5×10^5 colouration/bleaching cycles at 0.5 Hz. In addition Beni and co-workers have pointed out that WO_3 films in acid degrade in the presence of water, and altering to non-aqueous solvents containing Li^+ or Na^+ salts increased the switching time from about 0.1 to 1.0 s (26); the corresponding value for the iridium-based devices is about 20 ms. The main advantages of electrochromic, as compared with liquid crystal, displays are the wide viewing angle and open-circuit memory; at present their major disadvantage is their large peak currents at fast switching rates (30).

The fabrication of a seven-segment, sputtered iridium oxide display device, and its incorporation into a simple, low-power, battery-operated driver circuit, have been described recently by Shay and co-workers (30). A further development in this area is the recent description of a matrix addressable system in which the display segments are not driven individually but are connected in rows and columns (31), the desired image being generated by controlling the potential of the individual rows or columns. A theoretical treatment of the application of electrochromics in this area has also been published and shows that in principle these electrochromic systems can be used in large complex active displays (32). Finally, the application of optical writing, where patterns are etched on electrochromic material by a laser beam, should not only enhance the possible use of these films in display devices but also lead to applications in optical data storage systems (33).

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Precision Temperature Measurements

EFFECTS OF AIR QUENCHING AND STRESSING ON PLATINUM:RHODIUM-PLATINUM THERMOCOUPLES

In 1979 the Ottawa laboratories of the Physics Division of the National Research Council of Canada issued the first two volumes of a report on the use of platinum:10 per cent rhodium-platinum thermocouples for measuring temperatures with a precision of at least 0.1°C (1).

A third volume has now been published, examining in considerable detail "the thermoelectric effects of mild quenching and deformation that might be experienced by the individual elements during the preparation and use of standard thermocouples" (2).

The earlier report specified that for precision use the couples (usually 186 cm long) should, before use, be electrically annealed in air at 1300°C for 1 to 10 hours and, after cooling in air, be annealed for 1 hour at 450°C to eliminate quenched-in vacancies and finally, after sheathing, be given a recovery and equilibrium anneal at 450°C overnight.

After this elaborate pre-treatment it is not easy to visualise why a competent experimenter intent on using the couple to measure

temperatures with a precision of $\pm 0.1^{\circ}\text{C}$, should air-quench either elements from temperatures between 800 and 1300°C or should stretch the wires to near their breaking point or twist the ends into tight spirals.

However, the present volume examines conscientiously in meticulous detail the effects of such mistreatments. It provides a tribute to the care and thoroughness with which this study of the factors affecting the readings of this thermocouple has been conducted. It may be reassuring to industrial users to note that the greatest damage recorded by any of these treatments amounts to no more than a reduction in temperature reading of 0.8°C .

J. C. C.

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