

## Metastability and electrocatalytic activity of ruthenium dioxide cathodes used in water electrolysis cells

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Received 28 July 2004; accepted in revised form 29 March 2005

*Key words:* electrocatalysis, hydrogen evolution, ruthenium dioxide, surface mediators, water electrolysis

### Abstract

Ruthenium dioxide-coated titanium electrodes when used as cathodes in water electrolysis cells are metastable systems which display high catalytic activity and unexpected stability. At the potentials involved the oxide films clearly should undergo reduction; the barrier to the latter process seems to arise due to hydroxylation of the outer layers of the thermally prepared oxide; the reduction of hydrous oxide films in general is inhibited by the intervention (as the primary reduction product) of a high energy state of the metal. The catalysis of the hydrogen gas evolution reaction at the oxide/solution interface is attributed to the involvement of a metastable cyclic redox mediator system involving multivalent  $\text{Ru}(\text{OH})_x$  surface species.

### 1. Introduction

The role of high energy, non-equilibrium, atoms as a vital component in electrocatalysis at solid metal electrode surfaces was discussed in a number of recent publications from this laboratory [1–3]. The basic idea is that for solids there are two limiting surface states, referred to as the Equilibrated Metal Surface (EMS) and the Metastable Metal Surface (MMS); these correspond to low energy and high energy surface metal atoms, respectively. At real metal surfaces both types of atoms coexist, usually with the EMS state predominating. However, the MMS state is assumed to play a vital role in surface catalysis as it is often the basis of low coverage active site behaviour.

The MMS state is assumed to be rather indefinite as its coverage and energy level are variable. It is well established that (a) the surface energy of a solid cannot be measured [4], (b) certain high energy surface species, e.g. mobile adatoms, cannot be detected (even by STM) [5], (c) different high energy surface states, e.g., in the form of step adsorbed, step embedded and kink atoms (each with a different lattice stabilization energy and different oxidation potential), can exist. It appears also, as discussed for gold [1], that for the same surface EMS and MMS states behave differently with regard to oxidation, the former yielding a monolayer ( $\alpha$ , rather anhydrous) oxide and the latter yielding a hydrous (or  $\beta$ ) oxide. A notable feature of electrocatalysis on the Gp 11 metals [6] is that the reaction involved usually commences well within the double layer region, reflecting the

high activity (or low oxidation potential) of MMS state atoms. Various accounts of this approach, referred to as the Incipient Hydrous Oxide/Adatom Mediator (IHOAM) model of electrocatalysis, have been published [7, 8].

The objective of the present work is to extend this approach to Metastable Metal Oxide Electrodes (MMOE). These are oxides that exist, and indeed some show very promising applications, at potentials which are far below their standard reduction potential ( $E^0$ ) values. The MMOE state is quite common: it should be noted that most metals can form two types of oxide, anhydrous (or  $\alpha$ ) and hydrous (or  $\beta$ ) [9]; the pronounced metastability of interest here seems to be confined largely to the  $\beta$  oxides. According to Pourbaix's data [10], the lowest oxide reduction potentials for gold, copper, platinum, iridium and ruthenium (in aqueous media at 298 K) are ca. 1.4, 0.46, 0.98, 0.93 and 0.75 V (RHE), respectively. Gold [3] and copper [11] in base and platinum [12] in acid exhibit sharp  $\beta$  oxide reduction responses at ca.  $-0.2$ ,  $-0.1$ , and  $0.0$  V, respectively (it may be noted that Au and Pt exhibit a range of  $\beta$  oxide reduction peaks; the potential values quoted here are for those that show maximum departure from the  $E^0$  value). Platinum  $\beta$  oxide films in base cannot be reduced totally even on prolonged cathodization at  $E < 0.0$  V (RHE) [13], while iridium  $\beta$  oxide films show virtually no sign of oxide reduction under similar conditions,  $E < 0.0$  V, in either acid or base [14]. Ruthenium is a less clear-cut case; as compared with iridium, ruthenium  $\beta$  oxide – if it exists as a separate phase – exhibits little bulk charge

storage behaviour [9], but the inability to reduce thermally prepared RuO<sub>2</sub> films under cathodic conditions at  $E < 0.0$  V (RHE) is not in doubt (this aspect of RuO<sub>2</sub> electrochemistry is the subject of the present investigation).

Hydrous oxide films are usually quite reactive [9], e.g. many of them display highly reversible, bulk redox, electrochromic responses. The major barrier (or overpotential) to their cathodic reduction is assumed to be the formation, as the initial product, of very poorly lattice stabilized (and hence very active) metal atoms. Potential applications of MMOE systems at the present time include

- (a) Use of noble metal oxide, e.g. RuO<sub>2</sub> and IrO<sub>2</sub>, coatings (on titanium) as cathodes for hydrogen gas production in water electrolysis cells [15–25].
- (b) Use of RuO<sub>2</sub> deposits as charge storage electrodes in supercapacitor battery systems [26–29]; the oxide in question is thermodynamically unstable with respect to Ru metal under cathodic conditions at  $E < \text{ca. } 0.7$  V (RHE). Intermediate surface redox transitions, e.g. Ru(VI)/Ru(IV), Ru(IV)/Ru(III) and possibly Ru(III)/Ru(II), are assumed to occur readily (this is the main basis of the charge storage capacity of RuO<sub>2</sub> surfaces), but reduction to Ru(O), for reasons discussed here later, is highly inhibited.
- (c) Iridium oxides are thermodynamically unstable in aqueous media with respect to reduction below 0.93 V (RHE) [10]. However, multilayer hydrous iridium oxide films in base exhibit a quasi-reversible bulk charge storage, Ir(IV)/Ir(III), transition at ca. 0.65 V (RHE) [9]. This is a MMOE system with potential for use in the electrochromic device area.

The present work did not involve a detailed investigation of the hydrogen evolution reaction at RuO<sub>2</sub> cathodes. Its objectives were (i) to rationalize why, despite their thermodynamic instability at low potentials, RuO<sub>2</sub> deposits do not undergo reduction to the metal under hydrogen evolution conditions, (ii) to explain why RuO<sub>2</sub> is active only for hydrogen evolution (and not hydrogen oxidation or H<sub>2</sub>/H<sub>3</sub>O<sup>+</sup> equilibration), and (iii) to relate the high activity of RuO<sub>2</sub> cathodes to the marked charge storage (or pseudocapacitance) behaviour [26] of such electrodes. Much of the previous work on hydrogen evolution at RuO<sub>2</sub> cathodes was carried out using acid electrolytes; hence the present work was confined to base (some earlier work in base [18, 22, 30–33], often involving use of mixed oxide electrodes, may be noted).

## 2. Experimental details

The experiments were carried out using a Metrohm cell (Type EA 880R-20) containing a central RuO<sub>2</sub>-coated titanium working electrode and either a graphite or IrO<sub>2</sub>-coated titanium counter electrode. The reference

electrode was saturated calomel which was contained in a separate vessel connected to the main cell via a Luggin capillary whose tip was positioned ca. 1.0 mm from the surface of the working electrode. Both vessels were suspended in a water bath whose temperature was controlled at  $25 \pm 0.1$  °C. The cell solution was deoxygenated before use by a flow of nitrogen gas which was allowed to pass for a period of at least 10 min. All current density values are given with respect to geometric surface area and all subsequent potential values (unless designated otherwise) are given in terms of the SCE scale. The present work was confined to base; the trends seem to be the same in both acid and base and the same interpretation is assumed to be applicable in both cases.

The RuO<sub>2</sub>-coated working electrodes used in this work were prepared by conventional methods [19, 34]. Titanium wire was degreased with acetone, etched for 10 min in aqua regia at 40 °C and washed with triply distilled water. RuCl<sub>3</sub> × H<sub>2</sub>O (Aldrich) was dissolved in 25% HCl and the solution (0.1 g per 10 cm<sup>3</sup>) evaporated almost to dryness. The resulting material was taken up in a small volume of isopropanol to form a paste which was painted on to the titanium surface. The film was dried at 50 °C for 10 min and then heated in air for 10 min at a preselected temperature within the range 450–550 °C. This coating process was repeated; a total of four applications were used in the present case and the final heat treatment was carried out for a period of 4 h. The electrode was sealed into the end of a glass tube using Araldite, leaving an exposed RuO<sub>2</sub>-coated titanium wire of length ca. 3 cm.

The electrochemical equipment used to record cyclic voltammograms was described earlier [35]; Tafel plots for hydrogen gas evolution were recorded, without correction for *i*R error, using a digitized potentiostat (CH Instruments, model 660B). The electrolyte involved was 1.0 mol dm<sup>-3</sup> NaOH (Sigma) and the base was dissolved in triply distilled water.

## 3. Results and discussion

### 3.1. The barrier to RuO<sub>2</sub> film reduction

The effect of prolonged cathodization on the cyclic voltammetry response for RuO<sub>2</sub>-coated electrodes is shown in Figure 1. For fresh electrode the *j*/*E* response was rather featureless, with the exception of the pair of peaks at ca. 0.4 V; this feature, at ca. 1.4 V (RHE), was attributed earlier [36] to a ruthenate/perruthenate, Ru(VI)/Ru(VII), transition in protruding oxyruthenium surface groups. The charge involved in the extended sweeps is relatively uniform over the entire potential range and is attributed to a combination of double layer charging and surface redox (pseudocapacitive [27]) transitions. For fresh uncathodized RuO<sub>2</sub> electrodes the voltammetric charge or interfacial capacitance is proportional to the (BET estimated) surface

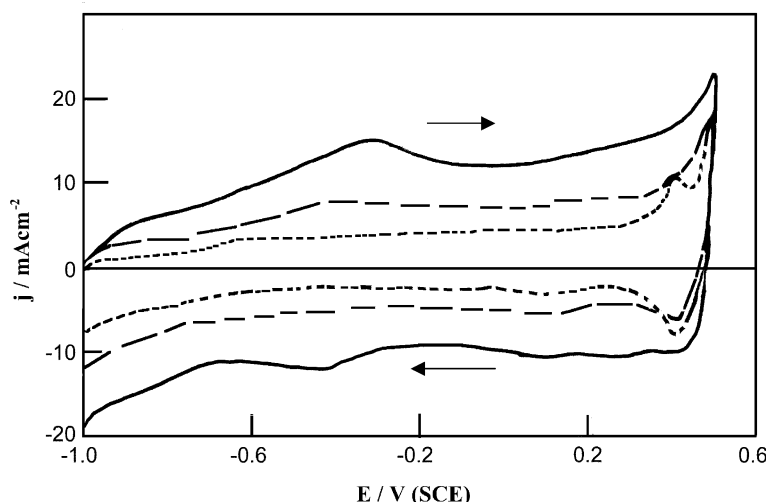


Fig. 1. Cyclic voltammograms ( $-1.0$  to  $0.5$  V (SCE),  $20$  mV s<sup>-1</sup>) for a RuO<sub>2</sub>/Ti electrode (annealed at  $550$  °C) in deoxygenated  $1.0$  mol dm<sup>-3</sup> NaOH at  $25$  °C: (.....), fresh electrode; (- - -) and (—), recorded after 3 and 7 days of cathodization at  $-1.25$  V, respectively (these are the steady state responses; as outlined in Figure 2 the first response recorded after cathodization was abnormal).

area of the oxide film [34]. Another interesting feature of the voltammogram for the fresh electrode is the increase in cathodic current in the negative sweep below  $-0.6$  V. Indeed over the range  $-0.7$  to  $-1.0$  V for all three cycles in Figure 1 the cathodic charge in the negative sweep exceeded the anodic charge in the positive sweep. Evidently there is a certain amount of oxide reduction (though not to the metal) in the negative sweep at  $E < -0.7$  V. It was observed also that saturating the electrolyte with hydrogen gas did not significantly alter the cyclic voltammetric response as recorded earlier for the same electrode in H<sub>2</sub>-free deoxygenated solution. Evidently ruthenium dioxide surfaces have little electrocatalytic activity for hydrogen gas oxidation.

Subjecting the electrode to prolonged cathodization in the hydrogen gas evolution region resulted, as reported independently [16, 17], in an increase in the net charge associated with the cyclic voltammogram, Figure 1, plus the appearance of an ill-defined, broad redox response at ca.  $-0.4$  V (SCE) or ca.  $0.6$  V (RHE). Under these conditions the peaks at ca.  $0.4$  V (SCE), which were quite clear in the first cycle, virtually disappeared but a new feature of rather low magnitude appeared at ca.  $0.1$  V (SCE) or ca.  $1.10$  V (RHE); this latter response is most clearly seen in the negative sweep in Figure 2, its anodic counterpart in the positive sweep being rather broad. The peak at ca.  $0.6$  V (RHE) for RuO<sub>2</sub> in base is assumed, on the basis of earlier work [36], to be due to an Ru(III)/Ru(IV), or Ru<sub>2</sub>O<sub>3</sub>/RuO<sub>2</sub>-type, transition

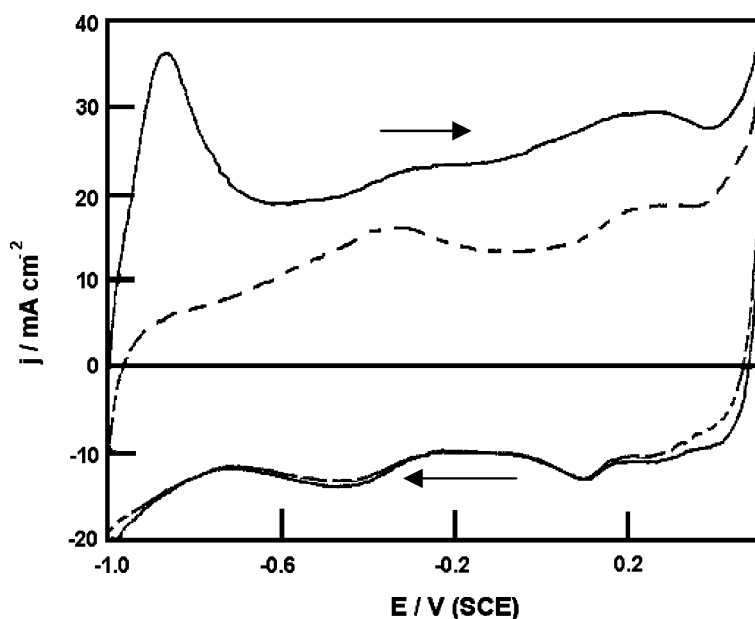


Fig. 2. First (—) and second (- - -) cyclic voltammogram ( $-1.0$  to  $0.5$  V,  $20$  mV s<sup>-1</sup>) recorded for a RuO<sub>2</sub>-coated Ti electrode (annealed at  $550$  °C) in  $1.0$  mol dm<sup>-3</sup> NaOH at  $25$  °C after 7 days of cathodization at  $-1.25$  V.

while that at ca. 1.10 V (RHE) is attributed to an Ru(IV)/Ru(VI), or RuO<sub>2</sub>/RuO<sub>4</sub><sup>2-</sup>-type, transition. The agreement between the transition potentials observed in the present work and the values quoted earlier [36], ca. 0.4–0.5 V (RHE) and 0.9–1.15 V (RHE), is reasonable, especially considering that the species involved are redox groups (or protruding oxy-species) attached to an oxide lattice whose outer layers are partially hydrated. The material present in the RuO<sub>2</sub> film is assumed to have a linked polyhedral, rutile-type [37], structure. In such a compact, 3-dimensionally bonded system bulk charge storage is unlikely; redox transitions are assumed to be confined largely to surface oxyruthenium groups. When such groups protrude from the surface reversible behaviour in the form of redox peaks is observed. However, most surface groups in these thermally prepared oxides are well embedded in the outer layer of the lattice and their limited redox transitions (which are the origin of the pseudocapacitative response) occur over the entire potential range.

The increase in the charge for the cyclic voltammogram as a result of the cathodization of RuO<sub>2</sub> film is attributed to an extension of the redox active zone either into the outer region of the RuO<sub>2</sub> lattice or to regions of the surface that were initially redox inactive. Below ca. –0.4 V the main active oxygroup on the electrode surface is assumed to be Ru<sub>2</sub>O<sub>3</sub> (possibly with, as discussed latter, a trace of RuO). The formulations given here are nominal as it is most likely that at the oxide/solution interface terminal O ligands are hydroxylated, viz.



Hence even through the bulk film is RuO<sub>2</sub>, the electro-active species at the surface are at least partially hydroxylated and are prone to undergo rapid redox transitions.

The increase in the hydroxylation or hydration at the interface is assumed to be due to partial reduction of oxygen, or oxy-species, at the RuO<sub>2</sub> surface; this is assumed to remove some of the bridging oxygen species between the RuO<sub>6</sub> octahedra, thereby enhancing the

hydroxide coverage and charge capacity of the surface. Evidence for partial oxide reduction under prolonged cathodic polarization conditions is presented in Figure 2. The first positive sweep recorded after cathodization in the hydrogen gas evolution region showed an unusually large anodic peak at ca. –0.9 V and a high anodic current response over the remainder of the positive sweep. The subsequent negative sweep and later cycles were normal in that they showed little change in current response on repeated cycling. The excess anodic current in the first positive sweep in Figure 2 is attributed to reoxidation of the surface; the process involved may be regarded as reinsertion of oxygen or reoxidation of partially reduced oxyruthenium species. Two points are worth noting with regard to extended cathodization in the hydrogen evolution region: (i) the outer surface of the oxide is permanently altered (its steady state interfacial charge storage value is increased, Figure 1); (ii) the oxide surface involved in the hydrogen gas evolution is in a significantly reduced state (although such reduction is reversed by a single positive sweep, Figure 2).

Data from a more extended series of cathodization experiments are summarized in Figure 3. Over a period of 6 days of almost continuous cathodization (interrupted only for brief periods to record cyclic voltammograms) the interfacial charge capacity value increased linearly with cathodization time. For the first 2 days the rate of hydrogen gas evolution at a constant overpotential increased in a similar manner but then attained a constant time-independent value. It seems that the increase in interfacial charge after the initial 2-day period is due to changes in oxide species which are unable to participate in (or enhance) the hydrogen evolution reaction. These catalytically inactive species may be subsurface, i.e. there may be an increase in the thickness of the hydroxylated layer, or they may be produced in less accessible regions, e.g. in small pores at the surface.

Pourbaix's thermodynamic data [10] show that no oxide of ruthenium is stable at potentials well above the

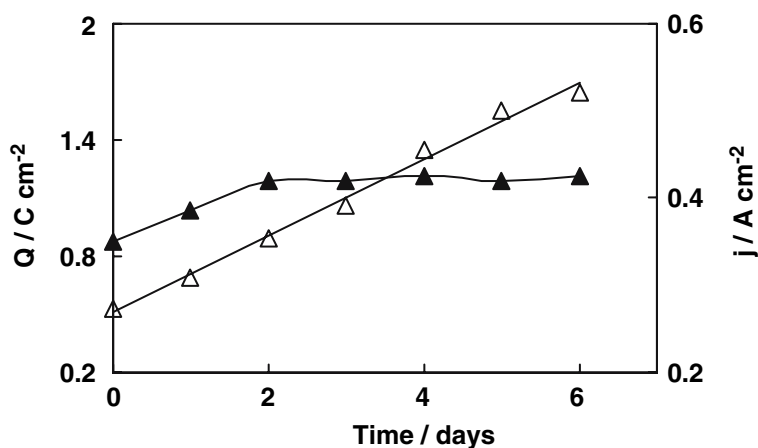
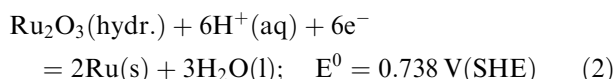
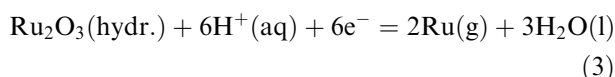


Fig. 3. Variation of (a) the apparent hydrogen evolution current density (▲) at –1.25 V and (b) the net charge of the stabilized cyclic voltammogram (△), in Figure 2, with cathodization time at –1.25 V (same conditions as in Figure 2).

hydrogen gas evolution region, the lowest oxide reduction potential for ruthenium being



Pourbaix's value is based on the assumption that the oxide and the metal are involved only as equilibrium bulk state species which, in the case of the metal, means that the chemical potential,  $\mu^0(\text{Ru})$ , has a value of zero. However, at the oxide/solution interface the hydroxylated Ru (III) cations are immobilized in a surface layer where they are surrounded by oxyligands. Evidently they cannot undergo direct reduction to the stable bulk metal as the first step in this reaction is the formation of virtually isolated Ru atoms. The chemical potential for the latter,  $\mu^0(\text{Ru}_{\text{g}})$ , is 595.80 kJ mol<sup>-1</sup> [38]; hence for the reaction in acid solution (pH = 0)



$$\mu^0/\text{kJ mol}^{-1} \quad -284.22 \quad 0 \quad 2(595.80) \quad 3(-237.2)$$

$$E^0 = -\frac{\Delta\mu^0}{nF} = -\frac{(764.52)}{6(96.487)} = -1.32 \text{ V} \quad (\text{SHE or RHE})$$

The latter value for acid corresponds to -1.56 V (SCE); for base (pH = 14) the corresponding value is also ca. -1.32 V (RHE) (the reversible potential of a conventional metal/metal oxide transition, measured in terms of the RHE scale, does not alter with pH); this value for base corresponds to ca. -1.32 -14 (0.06) = -2.16 V (SHE) or -2.40 V (SCE).

These estimates are merely illustrative as the nature and free energy value of the primary reduction product is unknown. However, this approach clearly indicates a possible source of inhibition in the oxide reduction in the case of RuO<sub>2</sub> cathodes in aqueous media. It is assumed that the bulk of the RuO<sub>2</sub> film is protected by a thin outer layer of hydroxylated Ru<sub>2</sub>O<sub>3</sub> whose reduction at low potential is inhibited due to the involvement of a high energy intermediate state of the metal; however, this hydroxylated layer functions as the electrocatalyst for the hydrogen gas evolution reaction.

### 3.2. The electrocatalytic behaviour of RuO<sub>2</sub> for hydrogen gas evolution

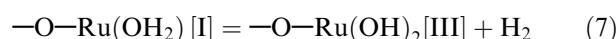
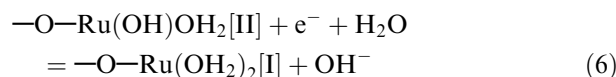
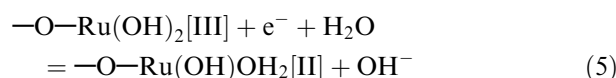
The origin of the electrocatalytic properties of RuO<sub>2</sub>-coated surfaces with regard to hydrogen gas evolution seems to be quite different to that of platinum and related metals. A platinum hydrogen electrode in base, Pt/H<sub>2</sub>(gas), H<sub>2</sub>O(l), usually exhibits a fixed potential determined by the equilibrium



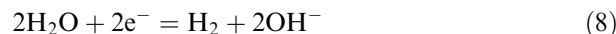
When the platinum was replaced by an RuO<sub>2</sub>/Ti electrode the observed potential (in H<sub>2</sub> stirred 1.0 mol dm<sup>-3</sup> NaOH at 298 K) attained a rest value of

ca. 0.804 V (RHE). The latter is assumed to be an oxide rest potential, i.e. the RuO<sub>2</sub> surface (unlike Pt) does not allow hydrogen gas to equilibrate in accordance with Equation (4). Furthermore, while RuO<sub>2</sub> is an excellent catalyst for H<sub>2</sub> gas evolution, the forward reaction in Equation (4), it exhibited very little activity with respect to the reverse process, hydrogen gas oxidation. Basically, hydrogen gas is inactive at RuO<sub>2</sub> electrode surfaces; catalysis of the hydrogen evolution reaction is evidently due to the interaction of H<sub>3</sub>O<sup>+</sup> or H<sub>2</sub>O (in acid or base, respectively) with the reduced form of an Ru-based interfacial couple as discussed below; the oxidized form of the couple is incapable of oxidizing H<sub>2</sub> gas, hence the lack of H<sub>2</sub> equilibration at RuO<sub>2</sub> electrode surfaces.

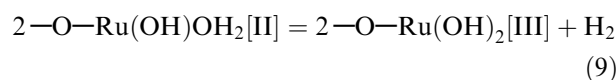
The precise nature of the catalytic mediator system is uncertain but it is assumed to involve low valence, surface bonded, ruthenium hydroxy species. The rapid rate of gas evolution may be due largely to proton switching phenomena between coordinated hydroxy ligands and nearby water molecules; note that in the reaction scheme outlined below there is no rupture of Ru-OH bonds and the central ruthenium ion remains permanently oxygen-bridged to the cathode surface. It is assumed that the active groups at the RuO<sub>2</sub> surface at low potentials are Ru(III) oxyspecies which undergo reduction, yielding labile states which decompose with loss of hydrogen gas, e.g.



The oxidation state of the central metal ion is shown here in the square brackets. In the final step here the mediator is returned to its initial state so that at constant potential the redox cycle, and hence hydrogen gas evolution continues indefinitely, the net reaction being



The generation of the Ru(I) state, Equation 6, is not essential. If two Ru(II) complexes are generated, according to Equation 5, in close proximity, they may interact as follows, viz.

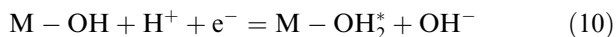


The mediators (or intermediates) involved are assumed to be part of an extended hydroxylated oxide network covering the outer layer of the underlying RuO<sub>2</sub> lattice. All forms of the mediator system are thermodynamically unstable under hydrogen gas evolution conditions but the system behaves in a

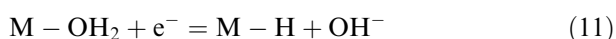
quasi-reversible manner, the redox cycle involved being quite rapid.

Tafel plots, involving  $iR$ -corrected potential values, for hydrogen evolution at  $\text{RuO}_2$  cathodes in base were reported earlier by Cornell and Simonsson [18]. Their curves were non-linear; the slope value rose from ca. 40 to 50  $\text{mV decade}^{-1}$  at low current densities to 230–240  $\text{mV decade}^{-1}$  at high current densities. Also, the slope value at low current densities rose slightly (from ca. 43–46  $\text{mV decade}^{-1}$ ) with increasing cathodic pre-treatment (or outer layer activation) of the  $\text{RuO}_2$  surface. With commercial DSA electrodes in base [18] non-linear Tafel plots were also observed, the slope increasing from 80 to 210  $\text{mV decade}^{-1}$  with increasing current density. The change in slope on increasing the current density was attributed to two possible causes: (i) a bend towards a limiting current density at high overpotentials, or (ii) a change in reaction mechanism. Rather similar Tafel plot behaviour was observed, Figure 4, in the present case. A low Tafel slope, ca. 60  $\text{mV decade}^{-1}$ , was observed at low current densities followed by a switch towards a limiting current density at high values of the latter (the data in Figure 4 are essentially a negative sweep; no ohmic drop corrections was applied). A Tafel slope of 60  $\text{mV decade}^{-1}$  was also reported by Kodintsev and Trasatti [19] for hydrogen gas evolution on pure  $\text{RuO}_2$  in acid solution (in this case also the current density seemed to approach a limiting value at high overpotentials, see Figure 4 in [19]).

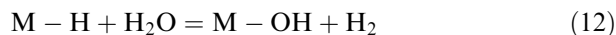
One of the most frequently quoted earlier schemes to explain hydrogen gas evolution at active oxide cathodes [18, 19, 32] assumes that the primary discharge step is



This is assumed to be followed by formation of a metal/hydrogen bond



and, finally, release of hydrogen gas



No direct indication is given that it is the cation in the surface oxycomplex (rather than ligand) which is the main redox active component at the interface. Aside from this, there is a considerable similarity between this scheme proposed by Trasatti [19], Equations (10)–(12), and that suggested here, Equations (5)–(9). A Tafel slope of 60  $\text{mV decade}^{-1}$  for this reaction may be rationalized [19, 32] by assuming that the rate limiting step is a slow chemical process which occurs after the primary discharge reaction.

An interesting feature of the electrocatalytic activity of  $\text{RuO}_2$  deposits is the influence of surface area, which may be altered by varying, for instance, the oxide loading or the annealing temperature. Chlorine gas behaves in a reversible manner at  $\text{RuO}_2$  electrodes in chloride ion solutions [39]; however, the rate of chlorine gas evolution at constant potential is independent of the oxide surface area [39], the reaction being confined largely to the exterior surface of the deposit, i.e. the surface within pores in the oxide are inactive with respect to  $\text{Cl}_2$  gas evolution. The opposite behaviour is observed with oxygen and hydrogen. These do not behave in a reversible manner at  $\text{RuO}_2$  electrodes but the rate of  $\text{O}_2$  [34] and  $\text{H}_2$  [18] gas evolution tends to be proportional to the real surface area of the oxide film (the voltammetric charge for an  $\text{RuO}_2$  surface is proportional to the surface area of the deposit [34]), i.e. virtually all the surface is involved in  $\text{O}_2$  or  $\text{H}_2$  gas evolution. Expulsion of electrolyte by  $\text{H}_2$  gas within small pores, which is equivalent to a decrease in real surface area, with increasing cathodic potential, may well contribute to the non-linear Tafel behaviour, Figure 4. The fact that the electrode rotation rate has no effect on the polarization curve for hydrogen evolution at  $\text{RuO}_2$  cathodes [18] is a further indication that hydrogen behaves in an irreversible manner at  $\text{RuO}_2$ .

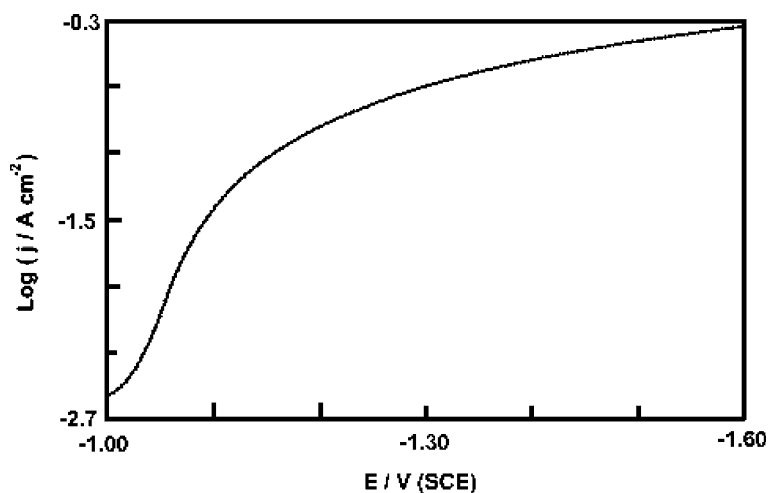


Fig. 4. Tafel plot for hydrogen gas evolution at a  $\text{RuO}_2$ -coated Ti electrode (annealed at 550 °C) in 1.0  $\text{mol dm}^{-3}$  NaOH at 25 °C (same conditions as in Figure 2). This electrode was preactivated by a short period of potential cycling and the Tafel slope at ca. -1.05 V was ca. 60  $\text{mV decade}^{-1}$ .

### 3.3. Comparison with the work of other authors

The reluctance of RuO<sub>2</sub> films to undergo reduction to the metal under hydrogen gas evolution conditions is obviously of crucial importance but this feature has received little attention. Some authors [16, 23] have attributed the effect to the high electronic conductivity of RuO<sub>2</sub>, the inability of hydrogen to penetrate the oxide lattice and the absence of an internal electric field in the oxide to assist the reduction of the latter. However, oxide reduction is expected to commence at the RuO<sub>2</sub>/solution interface and continue until the entire film is reduced.

It seems, as pointed out here earlier, to be a general feature of noble metal electrochemistry that compact ( $\alpha$ ) oxide films are more readily reduced to the metal than their dispersed ( $\beta$ ) equivalents. These  $\beta$  oxides are often highly redox active with respect to intermediate oxide/oxide transitions (this is the basis of the electrochromic behaviour observed with some of these systems [9]) and it is only the final, oxide to metal, step that is severely inhibited, due to the intervention of a high energy state of the metal as the primary reduction product, Equation (3). Usually a  $\beta$  oxide film on a metal surface is porous or non-protective; for instance the presence of a multilayer  $\beta$  oxide film on iridium does not inhibit adsorption/desorption of hydrogen on the metal surface under cyclic voltammetric conditions [9]. In the case of RuO<sub>2</sub> cathodes it is assumed that the surface consists of linked RuO<sub>6</sub> octahedra, some of the ligands involved being OH and OH<sub>2</sub> species. Partial reduction of this outer layer to Ru(III) species may occur, which is assumed to increase both the degree of hydration, and, consequently the barrier to reduction of the oxide to the metal at the electrode surface. Surface hydroxylation plays a vital role in the operation of metastable oxide cathodes as (i) it creates the barrier to the oxide/metal reduction reaction and (ii) it is the basis of the redox transitions which are assumed to be the origin of both the charge storage capacity and the electrocatalytic properties with regard to hydrogen evolution of the oxide surface.

Many authors have reported that the voltammetric charge of RuO<sub>2</sub> cathodes increases, as in Figure 1, under prolonged cathodic polarization conditions. Trasatti and coworkers [16] have suggested a number of explanations: (i) surface erosion (this was considered unlikely); (ii) under cathodic conditions oxide reduction results in the formation of a redox active hydrous oxide film; (iii) hydrogen evolution promotes wetting of hydrophobic sites on the oxide surface as a consequence of surface hydroxylation. The latter interpretation was deemed most valid, although the distinction between (ii) and (iii) is unclear. An interesting point is that the degree of hydroxylation, or cathodically induced activation, is limited; it is confined to the outer layers of the RuO<sub>2</sub> lattice, possibly to those regions where the oxide structure is most defective and the degree of cross-linking of RuO<sub>6</sub> octahedra is low. A number of authors

have claimed, on the basis of ESCA [40, 41] and XPS [24] data, that surface reduction of RuO<sub>2</sub> to Ru does not occur under cathodic conditions.

One of the most characteristic features of RuO<sub>2</sub> (and IrO<sub>2</sub>) electrode surfaces in aqueous media (apart from their reluctance to undergo reduction) is their ability to undergo surface redox, or pseudocapacitive, transitions; this behaviour, which has been discussed in earlier publications from this laboratory [34, 36, 42], has been surveyed by Conway (see chapter 11 in [27]). The electrocatalytic properties of RuO<sub>2</sub> electrodes, both for hydrogen evolution and for the oxidation of organics at more positive potentials [36], is assumed to depend on the variation in oxidation states, and high reactivity, of the cations in hydroxylated Ru(OH)<sub>x</sub> surface species.

The use of Tafel slopes as mechanistic indicators for hydrogen evolution on RuO<sub>2</sub> needs to be viewed with caution. The thermally prepared oxide deposits are porous, rather high surface area, materials [34] so that gas entrapment may hinder reaction in small pores. Also, as pointed out recently by Blouin and Guay [21], there may be a time factor involved, especially in the first few experiments, due to the fact that the oxide surface gradually undergoes spontaneous hydration or activation under cathodic conditions. These authors stated that with oxide cathodes it is difficult to get reliable values for the Tafel slope; their Tafel plots (like those of other authors which were discussed here earlier) are clearly non-linear but were in the region of 40–60 mV decade<sup>-1</sup> before activation and close to 40 mV decade<sup>-1</sup> after activation. These values (taken from data obtained without iR compensation) relate to low current densities.

## 4. Conclusions

- (i) The use of RuO<sub>2</sub>-coated titanium electrodes as cathodes for sustained hydrogen gas evolution in aqueous media is an interesting illustration of an MMOE system. The retention of the thermodynamically unstable film is attributed to the hydroxylation of the surface oxyruthenium groups, plus the barrier to reduction of the latter due to the intervention, as a primary reduction product, of a high energy (metastable) form of the metal.
- (ii) It is well established that RuO<sub>2</sub> surfaces (or Ru(OH)<sub>x</sub> surface groups) are redox active and it is postulated that a reduced, metastable, surface oxide species acts as a mediator in the hydrogen evolution reaction (the involvement of adsorbed hydrogen at a hydroxylated RuO<sub>2</sub> surface is regarded as improbable).
- (iii) The notion of metastable, redox active, surface states was postulated recently [1] to account for the unusual catalytic and electrocatalytic properties of gold. In both cases, RuO<sub>2</sub> and Au, the pre-

cise identity of the low coverage, metastable, transient state may be difficult to ascertain.

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