

# Hydrous Ir oxide films: the mechanism of the anodic prepeak reaction

V.I. Birss, C. Bock, and H. Elzanowska

**Abstract:** The origin and significance of the anodic prepeak (peak  $A_0$ ), seen in cyclic voltammetric studies of hydrous Ir oxide films in acidic solution just prior to the large Ir(III)/(IV) redox peaks ( $A_1/C_1$ ), has been examined in this work. By also studying only very thin films, a corresponding cathodic feature (peak  $C_0$ ) has also been identified. The pH dependence of the  $A_0/C_0$  peaks, assumed to also depict the Ir(III)/(IV) process, has been examined in sulfuric acid solutions, indicating that a ca.  $-80$  mV shift per pH unit applies to this reaction. By also taking into consideration the measured in situ mass changes as the potential is scanned through the  $A_0/C_0$  peaks, it is shown that these peaks are associated with a greater involvement of anions and more extensive water exchange than is the reaction in the main  $A_1/C_1$  peaks. Other results also indicate that the film sites that react in the  $A_0/C_0$  peaks are located deep within the oxide film, likely near the Ir – oxide film interface.

**Key words:** Ir oxide, hydrous oxide films, cyclic voltammetry, quartz crystal microbalance (QCMB), prepeak, pH dependence, electrochemistry.

**Résumé :** On a examiné l'origine et la signification du prépic anodique (pic  $A_0$ ) observé dans les études de voltampérométrie cyclique de fils d'oxyde d'Ir hydreux, en solution acide, juste avant les importants pics redox Ir(III)/(IV) ( $A_1/C_1$ ). En n'étudiant que des films extrêmement minces, on a pu identifier aussi une caractéristique cathodique correspondante (pic  $C_0$ ). La dépendance des pics  $A_0/C_0$  sur le pH, qui décrirait aussi le processus Ir(III)/(IV), a fait l'objet d'un examen en solutions d'acide sulfurique; ces études suggèrent que, pour cette réaction, il faut appliquer un déplacement d'environ  $-80$  mV par unité de pH. Si l'on tient aussi compte des changements de masse in situ mesurés lors du balayage du potentiel à travers les pics  $A_0/C_0$ , il est démontré que ces pics sont associés à une implication plus importante des anions et à un échange d'eau plus important que dans la réaction dans les pics  $A_1/C_1$  principaux. D'autres résultats indiquent aussi que les sites de film qui réagissent dans les pics  $A_0/C_0$  sont situés en profondeur de l'oxyde de film, probablement près de l'interface Ir – film d'oxyde.

**Mots clés :** oxyde d'Ir, films d'oxyde hydreux, voltampérométrie cyclique, microbalance à cristal de quartz (MBCQ), prépic, dépendance sur le pH, électrochimie.

[Traduit par la rédaction]

## Introduction

There is a significant amount of interest in the electrochemical properties of hydrous Ir oxide films, primarily due to their very promising and wide-ranging applications as electrochromic materials, in supercapacitive devices, as battery electrodes, as interneural stimulating electrodes, etc. The particular advantage of Ir oxide films is their very rapid (reversible) redox kinetics, even when very thick films of this material are being used, as well as their long-term stability.

In some of our previous work (1–4) with electrochemically

formed, hydrous Ir oxide films, carried out in a range of aqueous solutions, one of the points of focus has been the problems associated with the aging/unaging of the electrochemical response of the oxide film, as seen most readily in cyclic voltammetry (CV) experiments. Reversible aging is characterized by a notable positive shift of the main anodic peak (peak  $A_1$ , representing the oxidation of Ir(III) to Ir(IV) within the oxide film) and is also associated with a diminishment in the kinetics of this reaction. In our prior work (1, 2), it was suggested that reversible aging, which is induced primarily by time spent at sufficiently negative potentials, may be connected with the reaction that occurs in the prepeak,  $A_0$ , seen in most solutions at the foot of the principal  $A_1$  peak in CV experiments. This was partly justified on the basis of the observation that time spent at negative potentials also has a marked effect on the  $A_0$  peak by shifting it positively so that it merges together with peak  $A_1$ , especially for relatively thick films. Also, Mozota and Conway (5, 6) have shown that the kinetics of the  $A_0$  process are very slow and have suggested that the reaction involves a slow rearrangement of atoms. Therefore, it is reasonable to expect that the kinetically slow  $A_0$  reaction, which is the first step in the conversion of the film from its Ir(III) to Ir(IV) state, may have a significant impact on the overall Ir oxide redox kinetics.

There is little agreement in the literature concerning the

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nature of the process occurring in peak  $A_0$ . It has been suggested by some that it reflects the oxidation of Ir sites in a particular region of the film, likely to be near the metal-oxide interface, or at Ir sites that are partially complexed to solution anions (5–8). Peak  $A_0$  is readily seen for films formed in sulfuric acid solutions, but its presence and characteristics depend strongly on the oxide growth conditions employed in solutions such as phosphoric acid (3) and the peak has sometimes been reported to be absent altogether in this solution (5–9). Therefore, it is feasible that peak  $A_0$  reflects the oxidation of a region of the film having a different microstructure, degree of hydration, etc., or possibly that it represents a reaction of different stoichiometry from that in the principal redox peaks,  $A_1/C_1$ . Another interpretation of prepeaks of this kind is that they are artifactual, in that they arise as the consequence of the large change in conductivity of these films as they are oxidized (10). However, it has subsequently been pointed out (1, 2) that this explanation for the Ir oxide prepeak would be inconsistent with its absence during the oxidation of Ir oxide in alkaline solutions, where the transition from nonconducting Ir(III) to conducting Ir(IV) oxide also takes place.

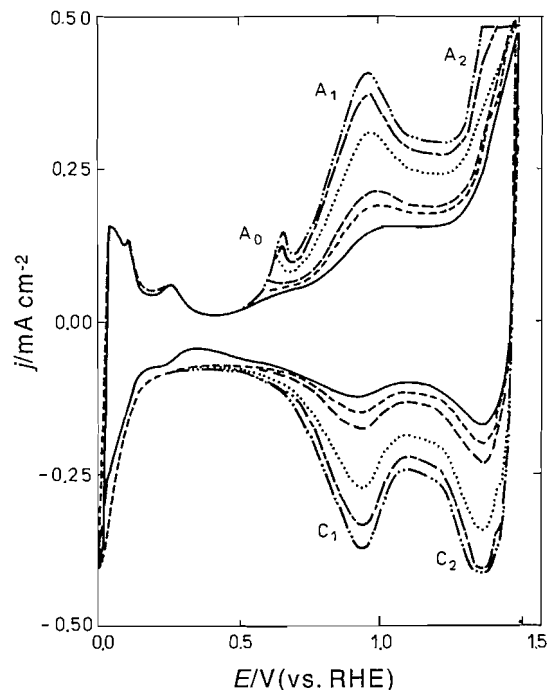
In the present work, the electrochemical properties of the process occurring in peak  $A_0$  have been examined more closely, with the goal being to better understand the origin and significance of the peak. As part of this, the pH dependence of the  $A_0$  peak, as well as the mass changes associated with it, as determined using the in situ quartz crystal microbalance (QCMB) technique, have been examined in sulfuric acid solutions. Based on these results, a mechanism for the reaction in the  $A_0/C_0$  peaks is suggested.

## Experimental

The experimental details concerning the growth of Ir oxide films (carried out by cycling at either 0.1 or 1 V/s, or by using 1 s pulses, usually between a lower potential limit,  $E_-$ , of  $-0.05$  or  $0.0$  V vs. RHE and an upper potential limit,  $E_+$ , of  $1.55$  V vs. RHE) in the appropriate solution and the transfer of the electrode between various solutions have been described previously (1–4, 11). Briefly, the working electrode (WE) in the electrochemical experiments consisted of an Ir wire (99.9% purity, 0.5 mm diam., ca.  $0.1$  cm<sup>2</sup> geometric area) embedded in soft glass tubing. For the WE used in the mass measurements, standard 5 MHz AT-cut quartz crystals (2.5 cm diam.) were obtained from Valpey-Fisher and were sputter-coated in the usual keyhole pattern, first with 25–35 nm of Ti and then with 100–150 nm of Ir. Electrical contact was made on each side of the crystal to Pt wires using conducting epoxy. Frequency (mass) data were collected using a Philips (model 6654C) frequency counter, connected to a standard oscillator (12). Ir wire electrodes were cleaned by heating in a fuel-rich flame, while Ir-coated quartz crystals were used as sputtered. A Pt gauze counter electrode, and either the reversible hydrogen (RHE) or a saturated calomel (SCE) electrode, were employed as the reference electrodes. All potentials are given versus the RHE in this paper.

All experiments were carried out at room temperature, with oxygen removal from solution achieved by vigorous bubbling with argon or nitrogen gas. All reagents were Fisher Certified or ACS grade and were used as received.

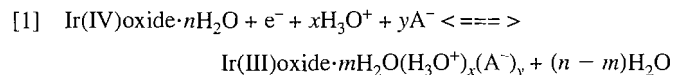
**Fig. 1.** CV response during Ir oxide growth at 100 mV/s with continuous cycling between 0 and 1.5 V in 0.5 M H<sub>2</sub>SO<sub>4</sub> (maximum CEF = 12). The response is shown for cycle number 1, 4, 7, 15, 21, and 24.



## Results and discussion

### (a) General cyclic voltammetric behavior

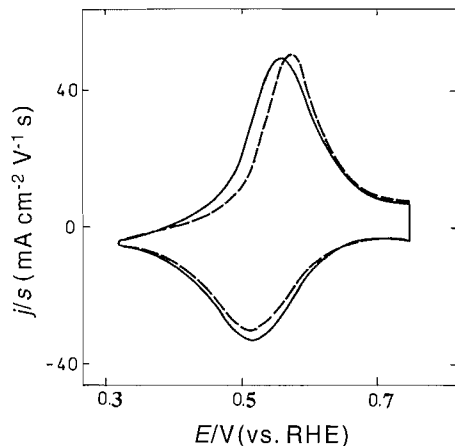
Figure 1 shows a typical set of CVs, obtained in 0.5 M sulfuric acid at 100 mV/s, as a series of Ir oxide films of increasing thickness were formed via the continuous potential cycling method. It is notable that the principal redox peaks,  $A_1/C_1$ , remain reversible and centered at a constant potential as the film thickens. For these relatively thin films, the potentials of peaks  $A_1$  and  $C_1$  are independent of the normally achievable sweep rates, and the peak currents are linearly proportional to sweep rate, up to ca. 1 V/s. Thicker films become diffusion controlled, even at sweep rates lower than 0.1 V/s. A general form of the reaction, which can be suggested to represent the  $A_1/C_1$  process in acidic solutions and is consistent with the  $>60$  mV/pH dependence of the  $A_1/C_1$  peaks (7, 8, 11–13), is as follows,



where  $\text{A}^-$  represents the electrolyte anion and the  $x$ ,  $y$ ,  $m$ , and  $n$  coefficients depend on the particular experimental conditions employed. Peaks  $A_2/C_2$  in Fig. 1 reflect the Ir(IV)/Ir(V or VI) redox process.

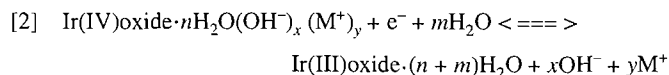
In contrast, peak  $A_0$ , which also increases in magnitude as the film thickens, is seen in Fig. 1 to move positively as more Ir oxide film is formed. Also, unlike the  $A_1/C_1$  reaction, a complementary cathodic peak to  $A_0$  is not seen when the high  $E_+$  value of Fig. 1 is employed. The oxide film in the last cycle shown in Fig. 1 has a charge enhancement factor (CEF) of ca. 12, where the CEF is considered to be an estimate of the

**Fig. 2.** Normalized CV response ( $j/s$ ) of Ir oxide film (CEF = 35, grown in 0.5 M  $\text{H}_2\text{SO}_4$ ) in 1.0 M NaOH at  $s = 2$  (—) and 100 (---) mV/s.



number of monolayers of hydrous film present (5, 6, 14, 15). CEFs of up to 500 or more can be readily achieved with Ir oxide films. Therefore, the film formed in Fig. 1 is still very thin and should not be susceptible to film aging effects, which would be seen, in part, by the merging together of the  $A_0$  and  $A_1$  peaks (1, 2).

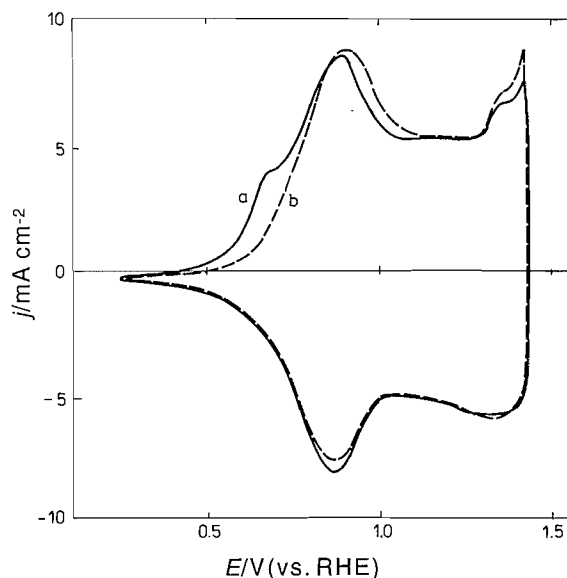
A positive shift of the  $A_0$  peak with increasing film thickness, similar to that shown in Fig. 1, has also been reported for oxides grown in 1 M perchloric acid (5, 6, 13, 16), 1 M nitric acid (1–4), and in 0.5 M  $\text{Na}_2\text{CO}_3$  (5, 6) solutions. The  $A_0$  peak is seen only if particular growth conditions (pulsing times) are employed in phosphoric acid solutions (1, 3), and other previously published work has suggested that the peak is absent entirely in this growth medium (5, 6, 9, 16). Based on the proposed involvement of solution anions in reaction [1], peak  $A_0$  has sometimes been linked to the presence of anions in the oxide film, particularly as the  $A_0$  peak represents the first step in film oxidation (5, 6). It is interesting to note that when Ir oxide films, grown in 0.5 M  $\text{H}_2\text{SO}_4$ , are transferred to a highly alkaline solution, e.g., 1 M NaOH (Fig. 2), the CV shows no evidence of the  $A_0$  peak, even when thin films and very slow sweep rates are employed. Reaction [2] shows that, in base, hydroxide ions and solution cations are involved in the reaction (no anions are available other than  $\text{OH}^-$ ) and that, in the reduced state, the film has a negligible ion content, compared to the oxidized form of the film (11, 12).



It is expected that when Ir oxide films are transferred from typical growth media such as sulfuric or nitric acid solutions into alkaline solutions, protons and anions incorporated in the film would be replaced by hydroxide and alkali metal ions in the first few cycles of potential cycles. Indeed, it is possible to see a trace of the  $A_0$  peak in the first one or two cycles in base, especially in 0.1 M KOH solutions (11, 12), but the peak then disappears with longer cycling times.

The results shown above lend support to the notion that the presence of anions in the oxide film, particularly in the reduced state, may be related to the appearance of the  $A_0$  peak.

**Fig. 3.** CV response of Ir oxide electrode (CEF = 200) at 100 mV/s in 0.5 M  $\text{H}_2\text{SO}_4$  before (curve a) and after (curve b) potential holding at  $E_- = 0.20$  V for 75 min.



It should also be noted that reactions [1] and [2] show that water may be expelled during Ir oxide reduction in acidic solutions, but injected in alkaline media, and hence these differences in the water content of the reduced form of the film may also be significant in terms of whether or not the  $A_0$  peak appears.

The existence of a prepeak prior to the main oxidation peak has been reported for some polymer films (10) for which, like Ir oxide, the conductivity is very much lowered as the film becomes fully reduced. It has been suggested that film oxidation is initially delayed until a small fraction of the film has been oxidized. The sudden increase in film conductivity then results in a prepeak in a CV experiment. According to this model, the prepeak would not be related to the oxidation of any specific region or component of the film. When modelled mathematically, it is seen (10) that a positive shift and an increase of the prepeak with increasing sweep rate is predicted, but that the prepeak must be crossed before the reaction in the main peak can commence. That is, the film conductivity must be substantially increased before the bulk of the film can react, and the merging together of the prepeak and the main peak would not be predicted by this model. In the case of Ir oxide films, experiments carried out at somewhat higher sweep rates result in the merging together of the  $A_0$  and  $A_1$  peaks (1–3). Figure 3 shows an example of this, where the potential has been first continuously cycled (curve a), revealing peak  $A_0$  as distinct from peak  $A_1$ , whereas complete film reduction by maintaining the potential at 0.2 V for a period of time results in the (reversible) merging together of peaks  $A_0$  and  $A_1$  in the next set of potential cycles. This is not consistent with the explanation given (10) for the prepeak. Also, this model does not predict that the prepeak would be present in one solution (acidic) and would disappear in another (basic) when the identical film is transferred back and forth between the solutions and the same conductivity changes occur. Rather, this strongly suggests that the  $A_0/C_0$  peaks are associ-

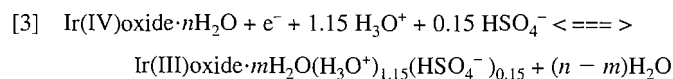
**Table 1.** Dependence of potentials (vs. RHE) of peaks  $A_0$  and  $A_1$  on sweep rate and on sulfuric acid concentration.

Sweep rate (mV/s)	0.5 M H <sub>2</sub> SO <sub>4</sub>		0.1 M H <sub>2</sub> SO <sub>4</sub>		0.5 M vs. 0.1 M	
	$A_0$ (mV)	$A_1$ (mV)	$A_0$ (mV)	$A_1$ (mV)	$A_0$ (mV)	$A_1$ (mV)
20	645	970	625	960	20	10
50	680	970	660	965	20	5
100	705	975	690	965	15	10
200	735	975	715	960	20	15

ated with the particular nature of the involvement of ions and (or) solvent in this reaction in acidic solutions.

### (b) pH dependence of the $A_0/C_0$ reaction

It has previously been reported that the principal Ir(III)/(IV) redox process, which occurs in peaks  $A_1/C_1$ , exhibits a super-Nernstian pH response over the bulk of the pH range (7, 8, 11–13). An example of this can be seen by comparing Figs. 1 and 2, where the potential of the main peaks, which is independent of the sweep rate in both solutions under these conditions, is >300 mV more negative (vs. RHE) in the 1 M NaOH solution than in the 0.5 M sulfuric acid medium, leading to an overall pH dependence of ca. –80 mV/pH unit. This is similar to what has previously been reported, when many different pH's were examined (11, 12). It is also consistent with the formulation of reactions [1] and [2], in which the ratio of the pH-determining ion to the number of electrons passed is greater than 1, in both acidic and alkaline conditions, such that the pH dependence must be greater than –59 mV. A recent more careful study (3) of the pH dependence of the hydrous Ir oxide redox potential over a narrow range of acidic pH's in various acidic solutions has shown values between ca. –65 and –70 mV/pH unit. The value in sulfuric acid, in particular, is –68 mV/pH unit, which is consistent with the following reaction stoichiometry for the  $A_1/C_1$  peaks in solutions between 0.1 to 0.75 M sulfuric acid:

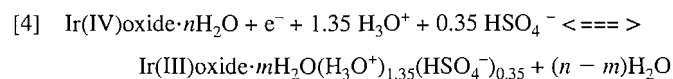


In the present work, the pH dependence of the peak  $A_0$  potential was compared in two solutions, 0.5 and 0.1 M sulfuric acid, in order to determine whether the stoichiometry of reaction [3] also applies to the reaction in peak  $A_0$ . The Ir oxide films in this study were formed in the 0.5 M acid solution by cycling at 200 mV/s between 0 and 1.5 V vs. RHE. Only very thin oxide films were formed (CEF ca. 14) in order to ensure that peaks  $A_0$  and  $A_1$  would remain separated, even at higher sweep-rates. The sweep-rate dependence of peak  $A_0$  was then established in the growth solution, after which the film was transferred to a 5× diluted acid solution in which the  $A_0$  peak was examined once again for the sweep-rate dependence of its potential. It is notable that the shape and width of peak  $A_0$  was the same in these two solutions.

As the pH of these two acidic solutions is not known with

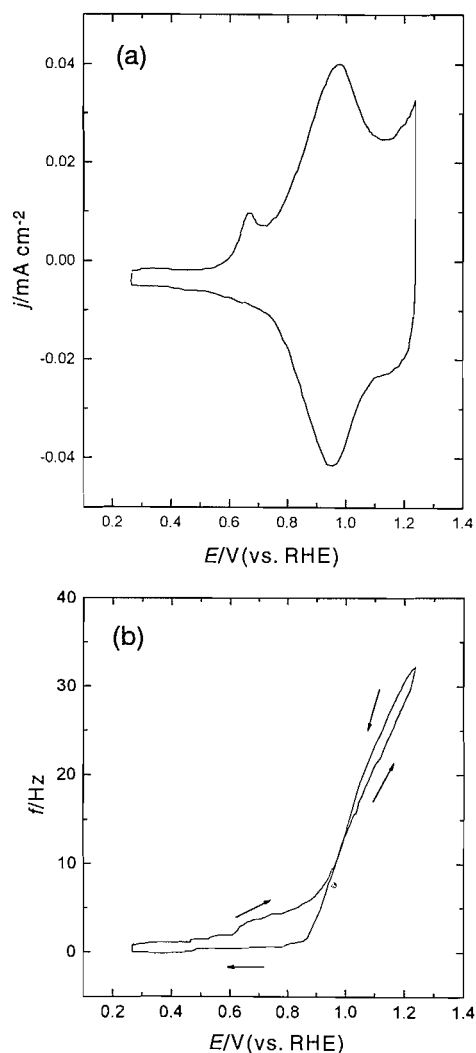
certainty, the pH dependence of peak  $A_0$  was established by tracking its potential relative to the  $A_1/C_1$  peak potentials in the two solutions. As stated earlier, the pH dependence of the  $A_1/C_1$  process is now known to be –68 mV/pH unit in sulfuric acid solutions, based on careful measurements of the variation in the peak potential with solution pH and corroborated by the determination of the  $\text{HSO}_4^-$  content of the oxidized vs. reduced form of the film by ion chromatographic methods (3).

Table 1 lists the potentials of the  $A_0$  and  $A_1$  peaks, at four different sweep-rates, in the two sulfuric acid solutions after equilibration of the films by multicycling between 0.05 and 1.4 V for a period of time. It can be seen that the  $A_1$  peak potential is independent of sweep-rate in each solution, and there is a small negative shift by 5–15 mV (this range depicts the error in identifying peak potentials from the CVs recorded on an X/Y recorder) in the 0.1 vs. 0.5 M sulfuric acid solution, consistent with that reported previously (3). It is also seen from the data in Table 1 that the  $A_0$  peak potential is shifted more negatively in the 0.1 M solution vs. than in the 0.5 M sulfuric acid solution, than is peak  $A_1$ , by an average of ca. 20 mV, i.e., by 5–15 mV more than the shift of the  $A_1/C_1$  peaks. Based on the –68 mV pH dependence of the main redox peaks, this translates to a ca. –73 to –83 mV pH dependence for the  $A_0/C_0$  process, which in turn indicates a greater anionic involvement in the reaction in peak  $A_0$  than in peak  $A_1$  (compare reaction [4] with reaction [3]). The following stoichiometry is suggested for the prepeak reaction, assuming a –80 mV per pH dependence.



It is also notable (although not shown in Table 1) that when the oxide film was transferred between solutions, the initial potential scans were carried out only over the range of the  $A_0/C_0$  peaks, i.e., between 0.05 and 0.7 or 0.8 V. Under these conditions, the  $A_0/C_0$  peak potentials were more similar to those of the prior test solution than indicated in Table 1, and it was only after the completion of several full potential cycles, up to 1.4 V or more, that the steady-state potentials of Table 1 were obtained. This was not the case for the potential of the  $A_1/C_1$  peaks, which immediately reflected the new solution conditions and did not change further with time, potential limits, or sweep rate. These results suggest that, unless the ionic

**Fig. 4.** CV at 10 mV/s (a) and associated frequency response (b) of Ir oxide film (CEF = 10) on Ir sputter-coated quartz crystal in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



content from the prior solution is fully expelled from the oxide film by scanning to sufficiently positive potentials, the local conditions of the Ir oxide sites that react in the  $A_0/C_0$  peaks remain similar to those of the prior test solution. This, in turn, suggests that the  $A_0/C_0$  sites are located deep within the film, probably in the region of the metal-oxide interface.

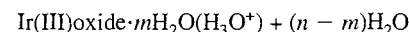
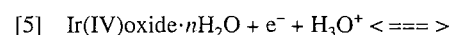
#### (c) Mass change associated with the $A_0/C_0$ reaction

To attempt to corroborate the pH dependence data for the  $A_0$  peak (reaction [4]) and to complete the reaction stoichiometry, the film mass change was measured as the potential was scanned very slowly through the potential range of peak  $A_0$ . Figure 4 shows a typical CV and the corresponding frequency change in a full cycle of potential for a very thin Ir oxide film (CEF = 10), conditions under which the  $A_0$  and  $A_1$  peaks are again well separated. A mass loss during film oxidation, and corresponding mass gain during reduction, is seen to be consistent with the predictions of reactions [1], [3], and [4] in acidic solutions. It is notable that the mass gain observed dur-

ing Ir oxide reduction is essentially complete at potentials just negative of peak  $C_1$ ; neither peak  $C_0$  nor any additional mass gain associated with this process are seen. This suggests that the  $A_0$  sites reduce in peak  $C_1$  under the conditions of this experiment. When the frequency change over peak  $A_0$  is converted to a mass change, using a crystal constant of  $-57 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^2$  from the Sauerbrey equation (17), and the charge density in peak  $A_0$  is also taken into consideration, a mass change of ca. 11 grams per mole of electrons passed is obtained in this particular case. Several other experiments have shown that this ratio varied between 10 and 12, considering both experimental error and the fact that slightly thicker films result in some shift of the  $A_0$  charge into the foot of the  $A_1$  peak, making charge measurement more difficult.

Considering the stoichiometry of reaction [4], this overall net mass change would predict that  $n - m$  is 2.7, i.e., that 2.7 moles of water are gained by the film per mole of electrons passed (i.e., per mole of Ir sites reacted) during the  $A_0$  reaction, and vice versa, during its reduction. In comparison, the mass-to-charge ratio for the  $A_1/C_1$  reaction is ca. 6–7 grams per mole of electrons, which suggests that only ca. 1.5 moles of water are injected into the oxide per mole of Ir sites reacted, based on the stoichiometry of reaction [3]. This interpretation of the data would indicate that the  $A_0/C_0$  sites are characterized by a proportionally greater water exchange per mole of Ir sites reacted, as well as a higher anionic to protonic ratio, as compared to the case in the main  $A_1/C_1$  peaks (cf. reactions [3] and [4]).

It should be pointed out that the mass-to-charge ratio of 10–12 grams per mole of electrons observed experimentally for the  $A_0$  process could also be explained on the basis of only protonic and water exchange. Based on reaction [5], ( $n - m$ ) would then be much smaller, ca. 0.4, such that 0.4 moles of water would be injected into the film for each mole of electrons and hydronium ions expelled during film oxidation in peak  $A_0$ , and vice versa, during film reduction.



However, a pH dependence of ca.  $-59 \text{ mV}$  would then be observed, which is not the case here; therefore, reaction [5] can be ruled out.

A final possibility is that the greater negative shift of the  $A_0$  peak vs. the  $A_1$  peak with increasing pH (Table 1) originates, not from a higher ratio of anionic to protonic charge compensation than in the main  $A_1/C_1$  peaks, but rather from the large changes in water content and hence complex activity changes deep within the Ir oxide film. In this case, if the stoichiometry of the principal redox peaks (reaction [3]) is also assumed to hold for the  $A_0/C_0$  reaction, then the mass-to-charge ratio of ca. 10–12 would yield an  $n - m$  value of 1.3, whereas for the  $A_1/C_1$  process,  $n - m$  would remain equal to 1.5. This would suggest that more water exchange is occurring in the main redox peaks vs. in the  $A_0/C_0$  peaks and that large changes in water content in the  $A_0/C_0$  reaction are not responsible for anomalous activity effects, which would then be expected to be more predominant in the  $A_1/C_1$  redox reaction.

Overall, it is clear that the mass-to-charge ratio obtained for the  $A_0$  peak as compared to that in the main  $A_1/C_1$  redox peaks is significantly larger, 10–12 vs. 6–7 grams per mole of elec-

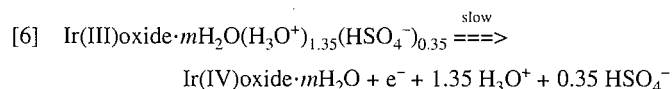
trons. This most likely represents both a greater involvement of anions in the  $A_0$  reaction and a greater degree of water exchange during this process.

#### (d) Suggested mechanism of the $A_0/C_0$ reaction

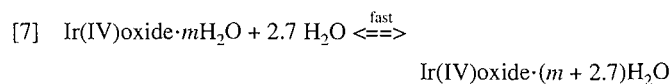
In their examination of the kinetics of the  $A_0$  process, Mozota and Conway (5, 6) showed that at slow sweep-rates the  $A_0$  peak current depends linearly on sweep-rate, while the peak potential depends on the log of sweep-rate. They suggested that the  $A_0$  reaction involves a slow surface adsorption process, limited by the slow rearrangement of sites. However, even at the slowest sweep-rates employed, the  $A_0$  peak potential continued to move negatively, and hence the reaction rate constant could not be determined using sweep methods. Films of reasonable thickness were examined in their work and, under these conditions, a complementary cathodic process,  $C_0$ , could not be distinguished. It was assumed, therefore, that the  $C_0$  peak was located negative of the potential for the hydrogen evolution reaction. Taking into account the pronounced positive shift of the  $A_0$  peak potential with sweep-rate and the presumed very negative shift of  $C_0$ , substantial kinetic limitations of the  $A_0/C_0$  process were suggested (5, 6).

In the present paper, the CV behavior of the  $A_0/C_0$  process was examined more closely using very thin Ir oxide films. The CVs presented in Fig. 5a show that a cathodic counterpart,  $C_0$ , of the  $A_0$  peak can be seen for this very thin film (CEF = 12), as long as the upper potential limit is restricted to the range of the  $A_0$  peak. After first examining the anodic peak, it is seen that the peak current is linearly dependent on the sweep-rate, as reported by Mozota and Conway (5, 6), and that the peak potential shifts anodically with increasing sweep-rate, both characteristics of a kinetically irreversible surface reaction. However, as long as the same  $E_+$  value is used (Fig. 5b), the  $C_0$  peak potential remains constant with increasing sweep-rate, instead of the more typical opposing shifts of the potential of the anodic and cathodic peaks expected for a slow surface process. The apparent positive shift of peak  $C_0$  with increasing sweep-rate in Fig. 5a arises from the need to increase  $E_+$ , hence including some of peak  $A_1$  in the scan, in order to cross peak  $A_0$ .

Based on the QCMB and pH dependence results described in sections (b) and (c) above, the following mechanism could apply to the  $A_0/C_0$  reaction. It is assumed that the reduced film sites that react in the prepeak are more hydrated and contain more solution anions as charge-compensating species than do the oxidized form. After examining the oxidation reaction, the first step is expected to be a slow electron transfer reaction, as suggested earlier (5, 6), consistent with the notable anodic shift of the  $A_0$  peak with increasing sweep-rate.

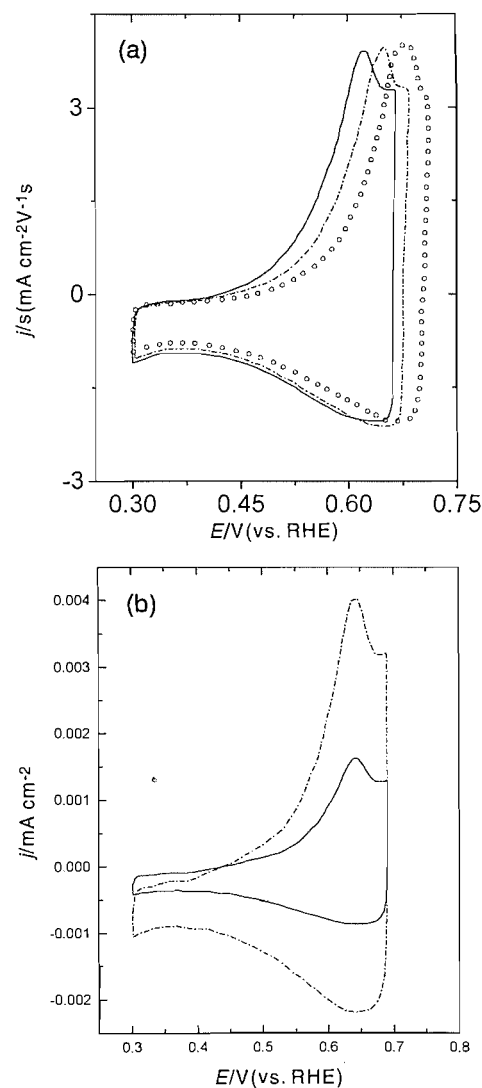


This is then followed by a rapid film hydration process:

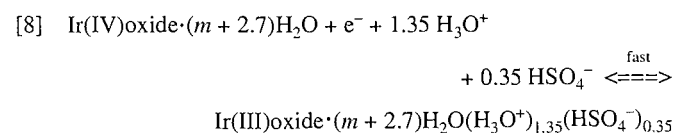


It can be argued that this hydration process changes the formal

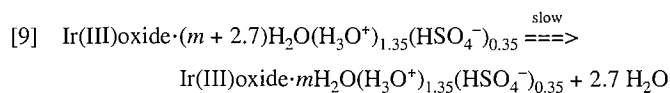
**Fig. 5.** (a) Normalized CV responses ( $j/s$ ) over restricted potential range of peaks  $A_0/C_0$  at 5 (—), 20 (---) and 50 (○○○) mV/s in 0.5 M  $\text{H}_2\text{SO}_4$  (CEF = 12). Note that  $E_+$  was increased with increasing sweep-rate in order to cross the  $A_0$  peak. (b) CV at 10 (—) and 20 (---) mV/s of peaks  $A_0/C_0$  using constant  $E_+$  and  $E_-$  values.



potential of these sites, such that the cathodic reaction can occur at more positive potentials (Fig. 5). Reactions [8] and [9] are suggested for the  $C_0$  process, based also on the electrochemical results. Reaction [8] is a rapid electron-transfer reaction, consistent with the independence of its peak potential on sweep-rate at constant  $E_+$  (Fig. 5b). The slow dehydration process (reaction [9]) is consistent with the fact that holding the potential negative of the  $A_0/C_0$  peaks constant for a long period of time causes a minor increase and a small positive shift of the  $A_0$  peak (although not affecting its kinetics).



This is followed by a relatively slow dehydration process:



The different shapes of the  $A_0$  and  $C_0$  peaks, seen in Fig. 5, can perhaps therefore be explained by the fact that the state of hydration of the reacting sites is different in the two forms, introducing different lateral interactions between redox sites in the two cases (18). Alternatively, it has previously been shown (13) that the Ir oxide  $A_1/C_1$  peaks are broader in solutions of lower ionic strength. Therefore, it is possible that the narrower  $A_0$  peak reflects the higher ionic and lower water content of the reduced state, versus the broader cathodic  $C_0$  peak, reflecting reduction of sites from which ions have been lost and a significant amount of water has been gained.

A final issue to address is the possible reason for the development of energetically different sites in these electrochemically grown Ir oxide films, i.e., those that react in peaks  $A_0/C_0$  and those that oxidize and reduce in the principle redox peaks  $A_1/C_1$ . It is possible that this relates back to the fact that, in order to form these films, the lower potential limit in each growth cycle is usually made more negative than 0 V, at which point hydrogen evolution commences. This reaction, which involves the consumption of water as well as the generation of locally alkaline conditions, occurs at the film-metal interface, as the oxide film is in its reduced, nonconductive state at these potentials. This may lead to the partial dehydration, as well as other possible structural-compositional alterations, of the oxide film in the region of this interface. Consistent with this, it has been found (3) that the potential of peak  $A_0$  depends somewhat on the length of time spent at the negative potential limit in each cycle during the growth of Ir oxide films using potential pulsing techniques.

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