Quartz crystal microbalance measurements during oxidation/reduction of hydrous Ir oxide electrodes

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Abstract

QCMB data were obtained for Ir oxide films formed by standard potential cycling methods on an Ir sputter-coated quartz crystal. In sulfuric acid solutions, the mass change of the electrode in a single potential sweep was found to vary linearly with the oxide film charge density, obtained under equilibrium conditions, indicating that no artifacts due to a significant degree of flexibility of the surface film were being introduced in this solution. In sulfuric acid solutions, the mass of the oxide film increased/decreased by ca. 6 g per mole of Ir sites being reduced/oxidized. This is consistent with the injection of 1.5 H^+ and 0.25 SO_4^{2-} per electron during reduction, as predicted from the unusual ca. 90 mV pH dependence usually observed, and the concurrent loss of 1 H_2O. In KOH solutions, the mass change is smaller and is in the opposite direction from that in acidic media. The oxide film loses ca. 3–4 g per mole of Ir sites during reduction, which would be consistent with the expulsion of OH^- and a small amount of K^+, together with the gain of one H_2O during the negative step. These QCMB results confirm that hydrous Ir oxide films exhibit many of the characteristics of a number of polymer-modified electrodes, and provide support for the involvement of solvent and the injection/expulsion of counter ions in addition to H^+/OH^- during the oxidation/reduction of Ir oxide films.

INTRODUCTION

Hydrous oxide films formed electrochemically at Ir have received a great deal of attention over the years, particularly due to their potential applicability in elec-

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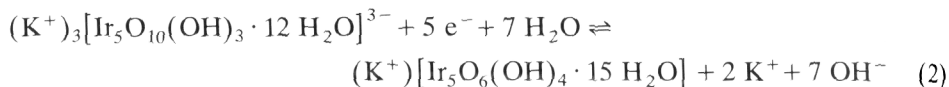[*] To whom correspondence should be addressed.
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trochromic devices [1,2], as electrocatalysts [3,4], as inter-neural stimulating electrodes [5,6], etc. We have focussed our recent efforts on exploring the mechanism of hydrous Ir oxide film formation and growth [7,8] and the properties of the resulting films in a range of solutions [9,10]. Like Burke et al. [11,12], we have viewed these oxides as highly hydrated in nature, and have contributed [9] to the evidence which shows that the observed greater than 60 mV pH dependence for this oxide is an indication of its different acid/base character in the oxidized vs. reduced states. This would result in the requirement for solution ions other than H^+ (in acidic solutions) to be involved in the oxidation/reduction reaction. We have demonstrated that this is the case by the analysis of the ionic content of the film in both states [9], from which the following reaction was suggested to occur in HF solutions:

$$(IrO_2 \cdot 3\ H_2O)_5 + 5\ e^- + 7\ H^+ + 2\ F^- \rightleftharpoons \left[Ir_5O_3(OH)_7 \cdot 15\ H_2O\right]^{2+}(F^-)_2 \quad (1)$$
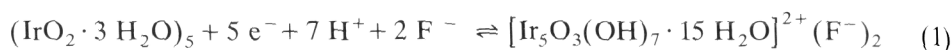
The involvement of ions in addition to H^+ in Ir oxide electrochemistry has also been supported by the XPS detection of sulfate in Ir oxide films, formed in sulfuric acid solutions [13]. In addition, support for the presence of sulfate ions inside the oxide film primarily in the reduced state is currently being obtained [14] by emersing sulfuric acid grown Ir oxide films and transferring them to successive aliquots of other acidic solutions, which are subsequently analyzed by ion chromatography for sulfate as a function of potential and time.

In KOH solutions, the analysis of the content of Ir oxide films [9] in the oxidized vs. reduced states has shown that OH^- as well as K^+ ions are injected during oxidation and expelled during reduction, according to the reaction:

$$(K^+)_3\left[Ir_5O_{10}(OH)_3 \cdot 12\ H_2O\right]^{3-} + 5\ e^- + 7\ H_2O \rightleftharpoons$$
$$(K^+)\left[Ir_5O_6(OH)_4 \cdot 15\ H_2O\right] + 2\ K^+ + 7\ OH^- \quad (2)$$

To verify the occurrence of reactions (1) and (2), it was of interest to examine the in-situ mass changes undergone by an Ir oxide electrode during oxidation/reduction cycles in acidic and basic solutions, similar to prior investigations [15–19] carried out with various polymer-modified electrodes. In these latter studies, quartz crystal microbalance (QCMB) data have served a valuable role in demonstrating the involvement of both ions and solvent during the electrochemical reactions.

EXPERIMENTAL

Standard 5 MHz AT-cut quartz crystals (2.5 cm dia.) were obtained from Valpey-Fisher and were sputter-coated in the usual keyhole pattern first with 25 to 35 nm of Ti and then 100 to 150 nm of Ir. Electrical contact was made on each side of the crystal to Pt wires using conducting epoxy. The crystal was mounted into the side of a Teflon cell and pressed between O-rings to avoid solution leakage to the back of the crystal. A high area Pt gauze counter and a saturated $Hg/HgSO_4$ ($E = 0.40$ V vs. SCE) reference electrode were used in this work. All potentials are

given vs. the SCE in this paper. The solutions used were 0.2 M sulfuric acid and 0.2 M KOH and were deoxygenated with nitrogen. All experiments were carried out at room temperature.

Ir oxide films were grown in sulfuric acid solutions using standard potential cycling procedures [7–10] in the range of ca. -0.25 to 1.30 V at sweep rates, v, between 0.1 and 1 V/s. Oxide films having charge densities ranging from 1 to 35 mC/cm^2 were studied, as determined by measuring the charge passed to 1.0 V vs. SCE in acidic solutions, established in our previous work [8] to be the potential at which one electron has passed per Ir site within these oxide films. Oxide films examined in basic solutions were grown in sulfuric acid solutions and were then transferred to base, as it is not possible to form the film directly in alkaline media. Frequency (mass) data were generally collected at sweep rates of 10 mV/s or lower.

The data from the frequency counter (Philips, Model 6654C), the EG&G 175 function generator and a home-built potentiostat were collected and plotted via an HP computer. The frequency to mass conversion factor was 60 Hz per 1 μ/cm^2.

RESULTS AND DISCUSSION

General electrochemistry and QCMB results in sulfuric acid solutions

Figure 1a shows a typical CV obtained at the Ir sputter-coated quartz crystal in 0.2 M sulfuric acid after numerous oxide growth cycles ($q = 13$ mC/cm^2). The current–potential characteristics are identical to those observed previously with Ir wire electrodes [7–10], indicating that standard Ir oxide films are being formed at these sputtered Ir electrodes. The concurrent mass change over the course of one potential cycle is shown in Fig. 1b, revealing remarkably little hysteresis. Superfi-
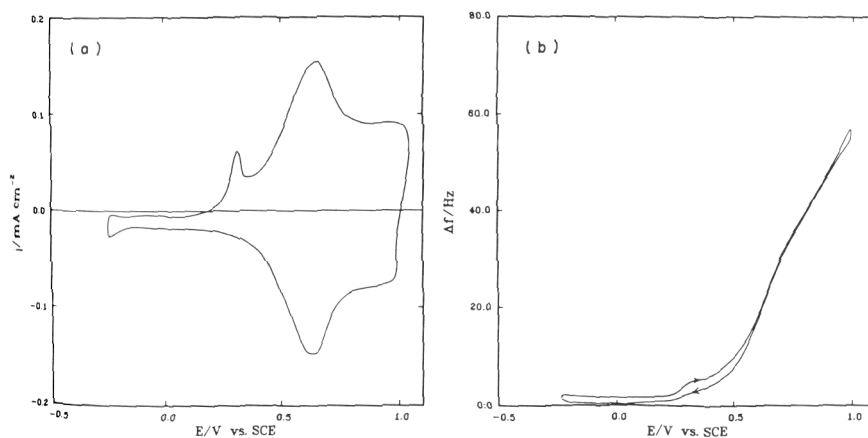

Fig. 1. (a) Cyclic voltammogram of Ir oxide film ($q = 13.2$ mC/cm^2) in 0.3 M H$_2$SO$_4$ obtained at $v = 5$ mV/s. (b) Variation of QCMB frequency with potential during oxidation/reduction of Ir oxide as in (a).
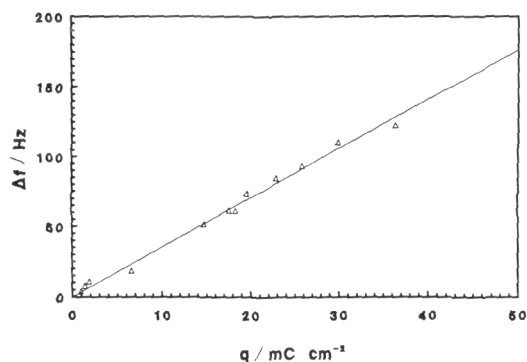
Fig. 2. Dependence of magnitude of QCMB frequency change in one oxidation/reduction cycle on the Ir oxide charge density in 0.3 M H_2SO_4, obtained in slow sweep experiments.

cially, the mass decrease of the electrode during oxidation supports the involvement of protons in the reaction (vs. OH^- ions, as suggested in a previous study [20], in which case, the mass would have increased).

One initial concern with respect to the ability to interpret the QCMB data quantitatively was whether the Ir oxide film has a rigid enough character to avoid any alterations of the visco-elastic properties of the crystal surface, particularly when the oxide film was thick. The lack of artifacts of this kind was confirmed by the observed linear relationship (Fig. 2) between the oxide charge density, obtained at a slow sweep rate to ensure that the reaction is at equilibrium, and the magnitude of the quartz crystal frequency change during one oxidation/reduction cycle, even for the thickest film formed (ca. 36 mC/cm^2, predicted to be ca. 170 nm in thickness [7]).

Absolute QCMB data were also recorded at a potential of ca. 0 V as a function of oxide film thickness. The relationship between the absolute mass change of the crystal and the oxide film charge density, as measured during a slow sweep, was used to calculate the apparent film molar mass, found to be 65 g/mol. As the minimum molar mass of an Ir oxide film is ca. 240 g/mol [8], this result is useful only in supporting earlier reports [4,8] that hydrous oxide growth at Ir involves substantial amounts of Ir dissolution during each sweep to positive potentials. Therefore, the absolute mass change of the electrode with oxide growth yields only the difference between the amount of oxide film formed and the quantity of Ir lost by dissolution during film growth.

Interpretation of mass data in acidic solutions

The QCMB data obtained in this work show that the mass of an Ir oxide film increases by ca. 6 g during the reduction of one mole of Ir sites. Considering first the anticipated result if no unusual pH effects were seen with Ir oxide (i.e. if a 60 mV pH dependence were observed experimentally), then only one H^+ (or H_3O^+) should be injected per Ir site during the negative scan. The corresponding mass

change would then be either 1 (or 19) g per mole of Ir in the film. The observed value, which is highly reproducible, is not close to either of these. One explanation could be that a mixture of sites is present and that ca. 70% of the sites require the injection of H^+, while 30% involve H_3O^+. This is similar to the explanation provided for the observed mass change of ca. 11 g per mole of electrons passed during the oxidation/reduction of thermally formed Ru oxide films in acidic solutions [21].

If a 90 mV pH dependence (close to the experimentally observed value [9]) is now considered, the corresponding mass change for the injection of 1.5 H^+ and 0.25 SO_4^{2-} ions per Ir site during reduction would be ca. 25.5 g, and for 1.5 H_3O^+ and 0.25 SO_4^{2-}, ca. 43 g. As these mass changes are both larger than observed here, it could again be suggested that a mixture of sites involving these ions and other sites requiring only H^+ ions are present.

However, it is more likely that, similar to the case of many polymer-modified electrodes [16,17,19,22–24], water, as well as ions, is involved in the Ir oxide reactions, consistent with the obviously hydrous nature of these films. In a parallel study [14], we have observed significant effects of time spent in the reduced state of the oxide film on the subsequent oxidation step, similar to those reported for numerous polymer-modified electrodes [17,23,24], where film expansion and contraction effects due to changes in ion and solvent content have been invoked. Our electrochemical results with Ir oxide [14] have indicated that, in acidic solutions, water may be expelled from the film during reduction, possibly to make room for the required solution ions, and is re-injected during oxidation. This is also the anticipated effect based on ion (Ir(III) and (IV) sites) hydration arguments.

If the Ir oxide reduction process in these acidic solutions involves the injection of 1.5 H^+ and 0.25 SO_4^{2-} ions (cf. reaction 1) and the concurrent expulsion of one water molecule from the film, the anticipated mass change is 7.5 g per mole of Ir sites, very close to that observed in this work. Such an exchange of ions and solvent, which would be consistent with the anticipated less flexible structure of Ir oxides as compared to most organic polymer films, has also been proposed [16] in the case of nickel ferrocyanide films, for example.

QCMB results in alkaline solutions

Another interesting result of the present study is that the mass changes in alkaline solutions have been found to be in the reverse direction from those seen in acidic solutions, clearly indicating the involvement of OH^- vs. H^+ in this medium (reaction 2). This confirms our previous results [9] in which alkali metal ions were found to be injected during oxidation in basic solutions, implying the participation of OH^- ions in the reaction, as well as those obtained recently by the measurement of the refractive index of the solution near the Ir oxide electrode as a function of potential and solution pH [25].

Figure 3a shows a voltammogram obtained with an Ir oxide film, formed in sulfuric acid solutions, and then transferred, after careful rinsing with the basic solution, to the 0.3 M KOH solution. Figure 3b demonstrates that the mass change
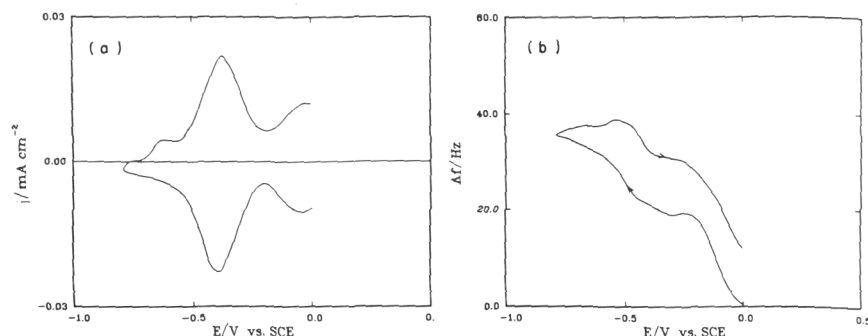
Fig. 3. (a) Cyclic voltammetric response of Ir oxide film ($q = 20$ mC/cm^2), grown in 0.3 M H$_2$SO$_4$, in 0.3 M KOH at 3 mV/s. (b) QCMB response during CV experiment in (a).

in basic solutions is smaller than in acidic media, i.e. ca. 3–4 g per mole of Ir sites. It is also noteworthy, that although all of the results obtained in basic solutions showed a mass increase during oxidation, the results were generally somewhat less reproducible and showed more hysteresis than those in acidic solutions, with the magnitude of the mass change dependent to some extent on the history of the electrode.

If one first considers that 1 mole of OH$^-$ is injected per mole of Ir sites oxidized (60 mV pH dependence), a mass increase of 17 g would have been expected during the oxidation step. If a 90 mV pH dependence is considered, this would be equivalent to the injection of 1.5 OH$^-$ and 0.5 K$^+$ per electron, i.e. a mass increase of ca. 45 g would have been anticipated per mole of Ir sites oxidized. In order to explain the relatively low mass increase observed during oxidation, the involvement of water in the reaction is again indicated. If it is assumed that the injection of one OH$^-$ ion during oxidation is accompanied by the expulsion of one water molecule, then a mass loss of ca. 1 would be expected during oxidation. This is both smaller and in the opposite direction to the observed result (Fig. 3b). When K$^+$ ions are considered to be co-injected and co-expelled with OH$^-$ and water to exchange with these ions, then a number of possibilities could fit the observed data. For example, considering reaction (2) (ca. 80 mV pH dependence), the net insertion of 0.4 K$^+$ and 1.4 OH$^-$ ion per electron during oxidation, and the concurrent loss of 1.4 H$_2$O (as per the stoichiometry shown) would lead to a mass increase of 14 g, while the loss of 2 H$_2$O would result in a mass increase of 5 g during oxidation. If a slightly different pH dependence is considered (e.g. 65–70 mV, 1.1 OH$^-$ + 0.1 K$^+$ per electron) and one water molecule is lost, a mass change of 4.5 g, more like that observed in this work, would be obtained.

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