Hydrous Ir Oxide Film Properties at Sol-Gel Derived Ir Nanoparticles

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Ir oxide (IrOx) films, formed on Au substrates using the sol-gel (SG) technique, have been characterized electrochemically in sulfuric acid solution. The highest film charge densities can be reached by using higher withdrawal rates of the substrate electrode from the Ir-containing sol solution, as well as by applying multiple successive coats. Allowing films to dry at *ca.* 100°C also yields higher charge densities. The kinetics of the Ir(III)/(IV) redox process are excellent, significantly higher, on a mole or mass IrOx basis, than for IrOx films formed by potential cycling/pulsing of standard bulk Ir electrodes in acidic solutions. The SG-derived films are electrochromic, highly capacitive, appear to be particularly catalytic toward the oxygen evolution reaction, and have excellent adhesive properties at Au. It appears that small area planar substrates are preferred over curved (*e.g.*, wire) electrodes in terms of SG-formed IrOx film uniformity and the maximum achievable charge density. The measurement of the mass of fresh SG-formed Ir films and the maximum IrOx charge density which can be obtained indicates that one out of every 2 to 3 Ir atoms are used in IrOx formation.

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There has been much interest in the practical applications of Ir oxide films in supercapacitive,[1-3] electrochromic,[4-6] and energy storage devices,[6] as interneural stimulating electrodes,[7,8] electrocatalysts,[9-13] and pH electrodes.[14-16] In many cases, Ir oxide films have been formed electrochemically, *i.e.*, by cycling or pulsing the potential of an Ir metal electrode between critical limits in various aqueous solutions.[4-6,17-27] This can result in the formation of relatively thick films (up to several micrometers in thickness), which are hydrous in nature (coded as activated iridium oxide films (AIROFs) in the prior literature[2,15,28-30]) and exhibit very rapid oxidation/reduction kinetics when the films are switched between their conducting Ir(IV) and insulating Ir(III) states. However, this method of film growth is both time and energy intensive, requires a metallic Ir substrate (often not fully reacted), and also usually involves some simultaneous loss, through dissolution, of the Ir metal substrate.

Other methods[2,15,28,29] which have been used to form Ir oxide films have involved the thermal oxidation of iridium salts, or the sputtering of Ir onto a conductive substrate in an oxidizing plasma environment. Sputtered iridium oxide films (SIROFs) are known to be less hydrous in nature, have a more featureless cyclic voltammetric (CV) response, and yield lower maximum charge densities than do AIROFs.[2,15,28,29] Ir oxide films have also been formed by induction heating[31] and by electrodeposition at constant anodic potentials from alkaline Ir-containing solutions,[32] although insufficient data are available for the properties of these films to be assessed relative to AIROFs and SIROFs.

The present paper is a continuation of our previous work,[33] involving the use of the sol-gel (SG) technique for the preparation of Ir oxide films. The SG method has been employed before to prepare IrO_2[34] and mixed oxides such as IrO_2-Ta_2O_5,[34] $IrO2$-SnO_2,[35] and RuO_2-IrO_2,[36] in powdered form. IrO_2 coatings were also obtained by painting[37,38] and dip-coating[38] techniques, using substrates such as amorphous silica microbeds[37] and glass,[38] followed by drying at temperatures between 350 and 600°C. However, only compositional/structural studies of these materials were performed,[34-38] and no prior electrochemical characterization has been reported.

In our previous paper,[33] it was shown that the Ir-containing films formed by the SG method actually consist of Ir metal nanoparticles. These can be transformed easily into the oxide by potential cycling within the limits normally used for the electrochemical growth of IrOx films at bulk Ir electrodes. The resulting films, which were not

studied in detail previously by us,[33] were shown to exhibit the general properties of AIROFs. In the present work, SG-formed Ir oxide films are demonstrated to be electrochromic, to yield high charge densities, as well as to exhibit excellent (Ir(III)/(IV)) oxidation/reduction kinetics. A range of experimental conditions, *e.g.*, the mode of drying of the SG film, the size and shape of the substrate and the use of multiple coatings, have been investigated here in order to maximize the charge density of the SG formed Ir oxide films, while retaining their excellent kinetic properties. Also, the total amount of Ir initially in the SG-formed metallic film was determined in order to establish the efficiency of use of the metal in forming the IrOx films. The simplicity of the SG methodology, combined with the adherent, high surface area materials which result, makes this a highly promising approach for the synthesis of Ir oxide films for future applications.

Experimental

Sol-gel method employed for film deposition.—The SG solution was prepared as described elsewhere,[33,39] using a molar ratio of $IrCl_3$ (or $IrCl_3 \cdot 3H_2O$) to Na ethoxide of 3:1, both dissolved in ethanol. The solution was typically refluxed under Ar for *ca.* 2 h, then stirred under Ar for *ca.* 20 h, and filtered. Au foils and wires (Aldrich, 5N purity, 0.5 mm diam wire of 1 cm length, or 0.5 × 0.5 cm foil) were sealed in soft glass tubing or were held in a Teflon holder. They were then coated by withdrawal from the SG solution at a constant rate ranging between 6 and 240 cm/min. The coated electrodes were then heated in air at temperatures ranging from 100 to 650°C for times varying from 15 min to 1 h, or were dried in air and at room temperature for 25-150 h. For the preparation of multiple coatings, the dip-coating and drying procedures were repeated successively.

Electrochemical characterization of SG-formed films.—All electrochemical experiments were carried out in a two-compartment electrochemical cell. The reversible hydrogen electrode (RHE) served as the reference electrode and was placed in one compartment. The SG-coated Au or Pt electrode served as the working electrode (WE) and was placed in the second compartment, which also contained the high surface area Pt gauze counter electrode. In other experiments, an Ir wire WE (Johnson Matthey, 99.9%, 0.5 mm diam), embedded in soft glass tubing, was oxidized electrochemically (referred to as IrOx formation on "bulk Ir" in this paper). The IrOx films were removed from the surface of the WEs at the completion of the experiment by heating in a fuel-rich flame, or by cycling between −0.05 and 1.8 V *vs.* RHE in 0.5 M H_2SO_4 or 2 M HCl solutions. All charge and current densities are given *vs.* the apparent surface area of the WE.

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The equipment used for CV experiments consisted of a PARC EG&G 173 potentiostat and 175 programmer, with the electrochemical data recorded either on a Goerz Instruments X/Y Servogar 790 recorder, a HP 7045B X/Y recorder, or a HP 7090A plotter. All electrochemical measurements were conducted in 0.5 M H_2SO_4, which was deaerated by the continuous passage of nitrogen either through or above the solution in the WE compartment of the cell. All experiments were conducted at room temperature, 22 ± 2°C.

Coating mass determination.—For the measurement of the mass of the SG-derived coatings, AT-cut 5 MHz quartz crystals (2.5 cm diam, Valpey-Fisher) were first sputter coated on both sides in the standard keyhole pattern with Ti to a thickness of *ca.* 10 nm and then with a thicker (*ca.* 120 nm) layer of Au. To make electrical contact, Cu wires were attached to each side of the crystal using silver epoxy. The quartz crystal was then sandwiched horizontally between two rubber O-rings at the base of the main compartment of a two-compartment glass cell. The mass active area of the crystal was 0.31 cm^2, while the electrochemistry took place on an area of *ca.* 0.5 cm^2.

Surface characterization techniques employed.—For the transmission electron microscopy (TEM) analyses, the SG films were coated on plain copper or on carbon supported copper grids (J. B. EM Services Inc.), and were then fired at temperatures ranging from 200 to 300°C for 15 min, or were air-dried for 50 h. The analyses were performed using a Hitachi H7000 TEM (Health Sciences Center, University of Calgary).

Results and Discussion

General comparison of IrOx films formed via SG route vs. at bulk Ir.—It was shown in our prior work[33] that the sol-gel (SG) method can be employed to generate nanoparticulate Ir thin films. Figure 1 shows a TEM image of a SG-formed coating, deposited on a carbon support Cu grid using a withdrawal rate of 24 cm/min, and dried at room temperature for *ca.* 24 h. The deposit is shown to consist of approximately spherical particles, *ca.* 2 nm in average diam. The electron diffraction data confirmed that these particles are metallic Ir. This was shown to be true, as long as the SG-formed coatings are dried at temperatures below *ca.* 600°C.[33]

Figure 2 shows the CV response, in 0.5 M sulfuric acid, for one of these freshly formed SG-derived Ir films, deposited on a Au plate electrode at a 36 cm/min withdrawal rate and then dried at 190°C for 15 min. When the potential is initially cycled between 0.05 and 0.45 V (Fig. 2, solid line 1), the hydrogen underpotential deposited (upd) peaks, typical of what is seen at bulk Ir metal, are observed.[2,15,28-30] With time of cycling over this narrow range of potential, only a small decrease in the H upd peak charge is seen (Fig. 1, solid line 2), perhaps indicative of the loss of some of the Ir nanoparticles from the Au substrate. As the potential is extended positively to 1.5 V, the CV response gradually changes (dashed curves in Fig. 2). In the first few cycles, the CV normally seen for compact Ir oxide
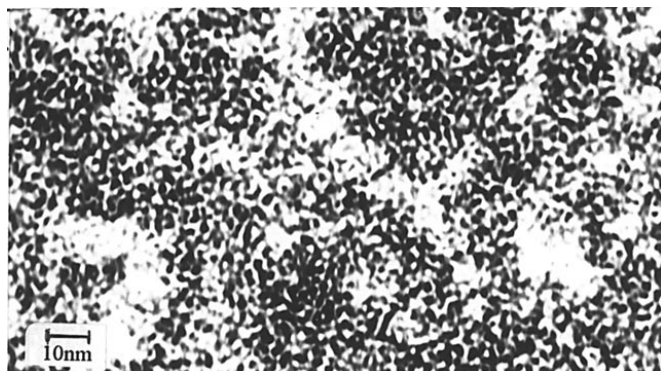
Figure 2. CV response (20 mV/s) in 0.5 M sulfuric acid of SG-formed Ir oxide with continuous potential cycling. Only 1st and 2nd cycle to 0.45 V (solid line), and 1st, 2nd, and 10th cycle to 1.45 V (dashed line) are shown. Film formed on Au foil (0.6 cm^2) using a withdrawal rate of 36 cm/min, and then dried for 15 min at 190°C.

formation and removal on Ir (anodic and cathodic features at *ca.* 1.2 and 0.3 V, respectively) is obtained. However, with longer cycling times (10-25 cycles, depending on the coating), the CV response changes to that for hydrous Ir oxide [redox peaks centered at *ca.* 1.0 V, due to the Ir(III)/(IV) redox process].[3-6,17-27,33] Note that, as the hydrous IrOx film forms, the H upd peaks essentially disappear, as is shown in Fig. 2. The implications of this observation are discussed in greater detail below. It is interesting that the conversion to hydrous IrOx appears to be quite rapid at the SG-formed surface. An upper limit of 1.3 V is sufficient[33] to achieve this conversion, while on bulk Ir, 1.55 V is normally employed to achieve the full conversion in a similar time frame.

Figure 3a (solid line) shows the CV response, in 0.5 M sulfuric acid, of an equilibrated (10 full cycles of potential) comparatively low charge density (6.7 mC/cm^2) SG-derived IrOx film. This is compared (Fig. 3a, dashed line) with the response of a bulk Ir wire electrode, immediately after the compact film has been converted to an IrOx film in *ca.* 5-10 full cycles of potential. In fact, to achieve charge densities similar to those seen for the SG films, the potential of a bulk Ir substrate must be cycled or pulsed between critical upper and lower potential limits for relatively long times, typically for 15-45 min, depending on the desired final charge. As was shown previously for IrOx films formed at bulk Ir, a charge density of 0.11 mC/cm^2 (integrated up to 1.3 V, the potential at which a charge density equivalent to the conversion of all of the Ir(III) sites to Ir(IV)[18,23]) is equivalent to one monolayer of IrOx.

Figure 3b shows that the CV currents (and hence, charges) can indeed be increased significantly at an Ir wire substrate, thereby forming a thicker IrOx film, by, in this case, cycling the potential at 100 mV/s between 0.00 and 1.45 V for times from 2 to 60 min. However, this is a time and energy consuming process, compared to the

Figure 1. TEM view (900,000 times magnification, 100 kV accelerating voltage) of Ir nanoparticulate film, formed on carbon cupported Cu grid by the SG technique using a withdrawal rate of 24 cm/min and drying in air for 24 h.
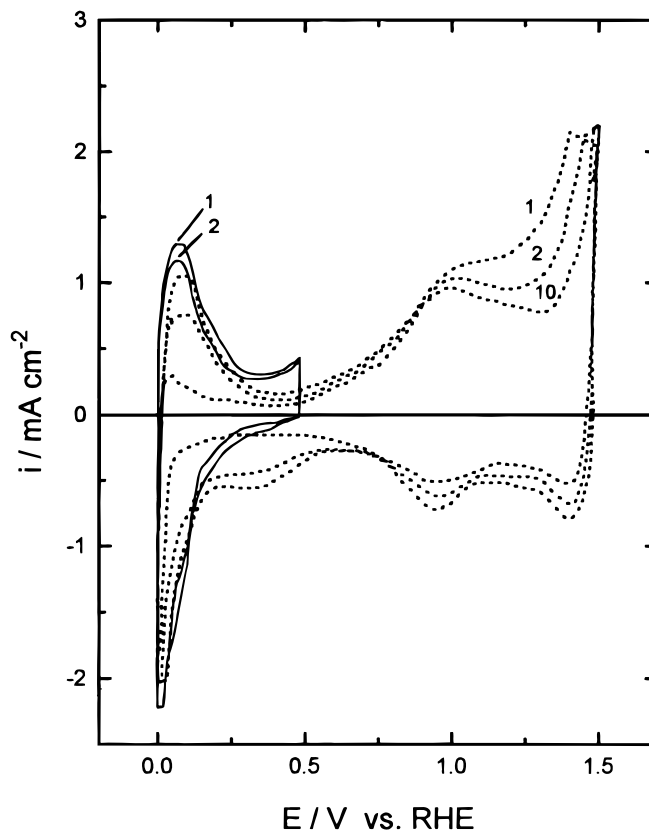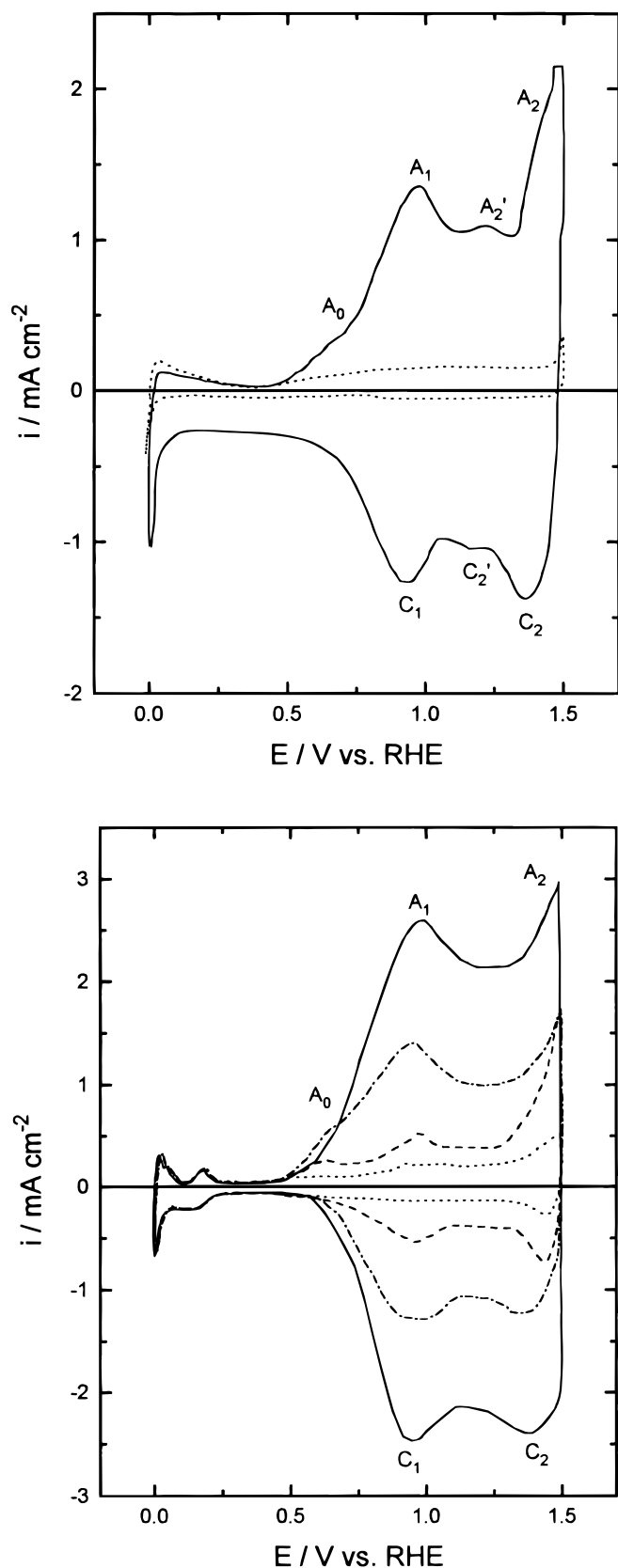
Figure 3. CV response (100 mV/s) in 0.5 M sulfuric acid of: (a, top) (—) SG-formed Ir oxide deposited on Au foil (0.5 cm^2) at withdrawal rate of 24 cm/min and then dried in air for 24 h, and (- - -) Ir oxide film formed on bare Ir wire (*ca.* 0.3 cm^2) after 2 min of cycling between 0 and 1.5 V. (b, bottom) Oxide films formed electrochemically on Ir wire electrode by potential cycling between 0 and 1.5 V for 2, 15, 30, and 60 min (CVs increase in size with cycling time).

large charge densities which can be achieved without long cycling times using the SG technique.

Not unexpectedly, considering that both of the IrOx films examined in Fig. 3 (at the SG-derived nanoparticulate Ir film and at bulk Ir) have been formed by potential cycling methods, many similarities exist between the two film materials. This is seen by their very similar CVs and especially by the fact that both films show kinetically reversible behavior. The A_1/C_1 peak potentials and widths are almost identical, suggesting that the nanostructure and composition of the films are very similar. Both IrOx films exhibit an anodic pre-peak, A_0, previously related to the presence of anions in the film[4,5] and/or reflecting the oxidation of film sites located deep within the oxide film, likely near the metal-oxide interface.[17] Also, both of these IrOx films are electrochromic, and are dark blue at positive potentials and transparent in the reduced state.

It is notable that the SG formed IrOx films often display another set of redox peaks (labeled as A_2'/C_2' in Fig. 3a), centered at *ca.* 1.1 V, which are not normally seen to the same extent in the case of IrOx films formed at bulk Ir electrodes. These peaks likely reflect the Ir(IV)/(V) redox process,[4-6] which may occur more readily in the SG-derived films. This observation may be related to the fact that the oxygen evolution reaction (OER), considered to be mediated by higher oxidation states of Ir in IrOx films,[12,13] is more highly catalyzed at the SG-derived IrOx films, *vs.* at IrOx films formed at bulk Ir electrodes.

A more obvious difference in the CVs of the two IrOx films is the appearance of the hydrogen adsorption/desorption (H upd) peaks for IrOx formed at bulk Ir (Fig. 3b), but not in the case of the SG-derived IrOx film (Fig. 3a). Figure 2 shows that, after deposition of the SG mixture on Au and drying of the film, the hydrogen peaks greatly diminish in size with time of potential cycling, as the CV of metallic Ir is converted to that of IrOx. At bulk Ir, it has been proposed[3,4] that the H upd peaks, which are characteristic of the exposure of metallic Ir sites to solution, are a reflection of the continued full access of solution to the Ir substrate, even in the presence of a thick, overlying IrOx film. This is a strong indication of the high degree of porosity of these films. The fact that the H upd peaks disappear as the nanoparticulate SG-formed Ir deposit is converted to IrOx likely indicates that all of the Ir is converted to IrOx.

The magnitude of the H upd charge can be used to determine the real area of Ir electrodes, using the published value of 0.21 mC/cm^2 for the deposition of 0.65 of a full monolayer of H atoms on Ir.[40] The SG-formed Ir deposit examined in Fig. 2 therefore has a real surface area of 20 cm^2 (on a 0.64 cm^2 Au substrate), yielding a roughness factor for this film of 31. In other experiments, roughness factors as high as *ca.* 100 have been obtained for some SG-derived Ir coatings. These high surface areas are consistent with the nanoparticulate nature of the deposit,[33] typical of SG formed materials. This is in agreement with the Brunauer-Emmett-Teller (BET) determined surface area[41] of nanocrystalline films of TiO$_2$, ZnO, and ZrO$_2$, formed by the SG method, showing that the true, internal surface area of these oxides is more than 100 times their geometric areas. In other recently published work,[13] a commercially obtained electrode material consisting of Ir nanoparticles deposited on high surface area carbon has been studied. High IrOx charge densities, indicative of a high surface area, were also observed, although the contribution of the Ir *vs.* C area to the observed charges was difficult to separate. The real charge density of the SG-derived IrOx film in Fig. 2 is, therefore, *ca.* 0.3 mC/cm^2, based on the true area of Ir of 20 cm^2. This demonstrates that only very thin IrOx films are actually formed on the high surface area SG-formed Ir deposits, equivalent to *ca.* 2-3 monolayers.

As indicated above, the amount of IrOx film formed on a bulk Ir substrate can be increased by large factors by using very long cycling/pulsing times and by optimizing the potential limits during film growth.[4-6,17,18,20-22,44] However, films of 30 mC/cm^2 charge density or more formed at bulk Ir are prone to transport limitations and kinetic aging effects.[18,44] In fact, the charge density passed in the CV of the SG-derived IrOx films (Fig. 3a) can be increased further by only

ca. 10-15% by the use of long cycling times and upper potentials of *ca.* 1.55 V. However, it is shown below that the charge densities of SG-derived IrOx films can be increased substantially by altering the variables used in the film preparation steps. To date, charge densities as high as 70 mC/cm^2, theoretically equivalent to *ca.* 650 monolayers of film,[18,23] have been achieved using the SG method for IrOx film formation.

Effect of preparation conditions on oxide characteristics.—One of the main advantages of the SG formation of films is the ability to control and vary the film thickness,[33,42-43] assumed here to be proportional to the equilibrium CV charge densities. In this work, variable film thicknesses have been achieved by changing the withdrawal rate (WR) of the electrode from the SG solution, by controlling the drying time and temperature, and also by applying multiple coatings on the same substrate.

Effect of substrate withdrawal rate from SG medium.—It has been reported that, the more rapid the substrate WR from a SG solution, the thicker the resulting film.[33,42-43] The thickness of the deposited film is governed by competition between several forces in the film deposition process, *i.e.*, a viscous drag upward on the liquid by the moving substrate, the downward force of gravity, the surface tension of the concave sol meniscus, etc. The lower the WR, the thinner the film should be. Figure 4 shows a set of data for SG-derived IrOx films, formed identically except for their variable WRs, ranging from 24 to 60 cm/min. As predicted,[42,43] the CV peak current (charge) densities increase linearly with the WR, suggesting that the WR is linearly related to film thickness under these conditions. Above this and up to *ca.* 250 cm/min, the IrOx charge density does not increase further. It is not clear if no further film is being deposited at these high WRs, or if additional film is deposited, but much of it is electrochemically inaccessible, and therefore, inactive.
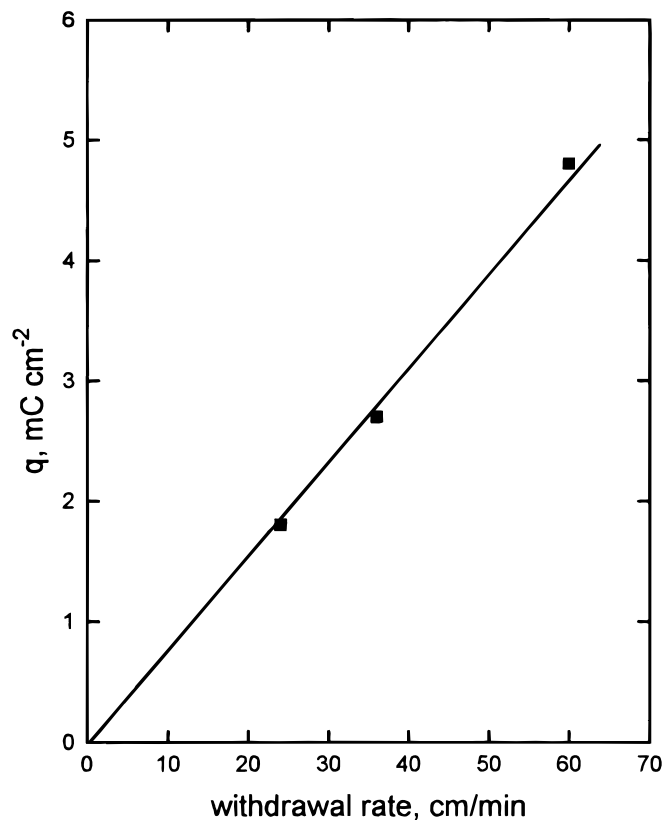
Multiple coatings.—The SG film thickness and, thus, the IrOx charge density, can also be varied by the application of multiple coatings, formed in successive coating/drying steps. For example, the IrOx film charge density has been found to increase by a factor of *ca.* 7 when eight successive coatings are deposited (Fig. 5). The CVs continue to show the same general characteristics, similar to Fig. 2 and 3, even though, as each new coating is applied, the inner layers are experiencing increasingly long heating times. However, the higher the number of coatings applied, the slower the redox kinetics become, consistent with our previously reported effects of film thickness on IrOx redox kinetics.[18,44]

Mode of drying of SG-derived films.—In a series of experiments involving the use of the same substrate (Au foil of *ca.* 0.4 cm^2 area) and withdrawal rate (24 cm/min), the SG-derived IrOx coatings were dried in air at room temperature, or at temperatures ranging between 100 and 650°C. Similar to our findings with SG-formed Ni-Co oxide films,[43] a maximum in the film charge density is seen with drying temperature, in this case at *ca.* 100°C (Fig. 6). The lower charges for room temperature dried films may be due to the blocking effect of adsorbed organic species or chloride ion, not fully removed from the coating under these conditions. The observed decrease in the electrochemical activity at drying temperatures above 100°C probably results from the growth of the Ir nanoparticles,[42] through sintering, and hence, a diminishment in the real surface area. It is also possible that drying at higher temperatures results in a decrease in the interparticle distance (*i.e.*, film shrinkage effects[42]), so that complete solution access to all parts of the film can no longer occur.

Water content of SG synthesis medium.—Since the water content of electrochemically formed IrOx films, normally considered as hydrous materials, is quite crucial in terms of their electrochemical properties,[4-6,17-27] the effect of water in the SG synthesis procedure was tested by making the sol up using both anhydrous and hydrous Ir chloride. The other experimental conditions were rigorously kept
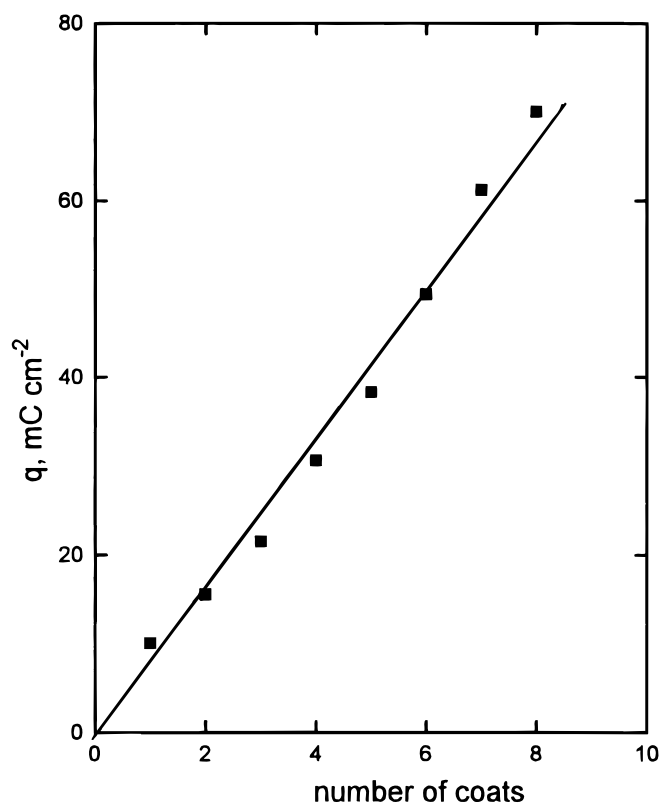
Figure 4. Effect of the withdrawal rate of Pt foil substrate (0.6 cm^2) on the charge density of SG-formed Ir oxide films, in 0.5 M sulfuric acid, after drying for 15 min at 190°C.

Figure 5. Effect of multiple coats on the charge density of SG-formed Ir oxide films, in 0.5 M sulfuric acid, formed on Au substrate (0.5 cm^2) using 240 cm/min withdrawal rate and drying for 15 min at 100°C.

constant (WR = 24 cm/min, dried at 190°C for 15 min). These experiments were repeated several times, showing that the Ir oxide charge density was usually higher (*ca.* 10-12 mC/cm^2 *vs.* 5-7 mC/cm^2), when the synthesis medium was prepared using the anhydrous salt, thus lowering the water content of the SG solution.

The impact of the amount of water present during SG synthesis on the IrOx properties is not yet fully understood. It is possible that water in the synthesis medium may affect the mechanism of metallic Ir formation, yielding larger particles, and resulting in lower real surface areas. Water may also be a problem in terms of lowering the ethoxide concentration, or in complexing Ir^{3+}, thus reducing the effective concentration of Ir^{3+} available for reaction with ethoxide.

Effect of substrate identity, shape, and size.—The charge densities of the SG-formed Ir oxide film deposited on Au and Pt foil electrodes are generally much higher, sometimes up to five times higher than those obtained on wire electrodes, similar to what was seen in the case of SG-formed Ni/Co oxide films.[43] This could reflect the effect of the nature of the metallic substrate on the nucleation of the Ir nanoparticles (and hence, their size and surface area), or on the extent and quality of the electrical contact between the substrate and the Ir deposit. Au substrates were found to yield higher IrOx charge densities than did Pt. Au is not likely to be oxide-coated, which may be preferred for metallic Ir deposition.

The reproducibility of the results for the wire electrodes was found to be poor, so that the dependence of the charge density on the withdrawal rate and on the number of coatings could not be easily obtained. For the foil electrodes, when the same substrate was used in different experiments, the reproducibility of the measurements was much improved. Table I shows that, under these conditions, higher charge densities are obtained using smaller area foil substrates. This may reflect the tendency for the SG solution to spread to the edges of larger substrates, so that the resulting film is very thin in the central regions, and thicker on the edges. It is possible that not
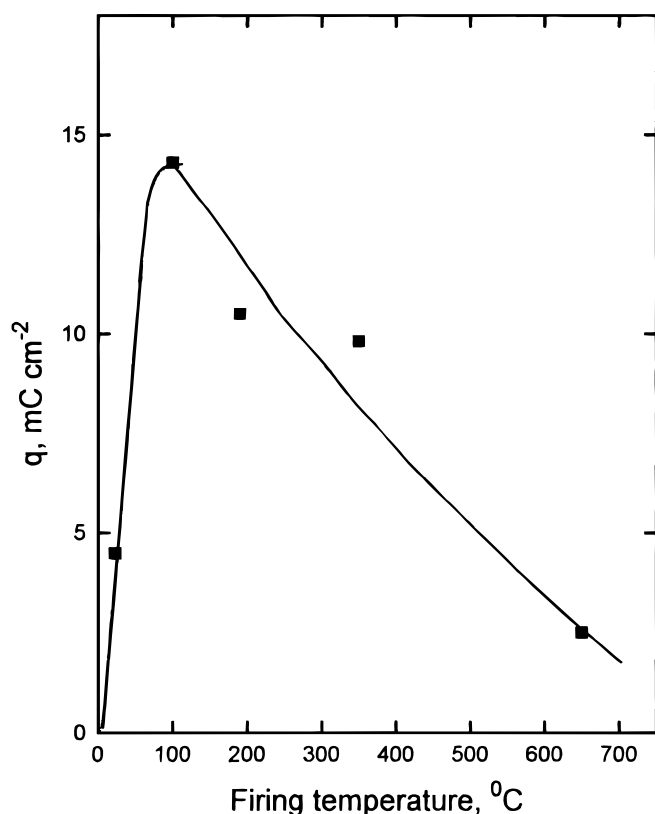
Table I. Charge density *vs*. electrode area for SG-formed Ir oxide films.[a]

Area (cm^{-2})	Charge density[b] (mC cm^{-2})
0.25	4.7
0.40	5.0
0.54	7.3
4.65	1.2
5.65	1.5

[a] Ir oxide films deposited on Au foil substrates of a range of apparent areas using a withdrawal rate of 24 cm/min and drying at room temperature.
[b] Charge density per geometric area, determined by integration of CV, collected in 0.5 M sulfuric acid at 100 mV/s, up to 1.3 V *vs*. RHE.

all of the Ir sites at the edges are stable and electrochemically active. Overall, it was determined in this work that the best reproducibility and the highest charge densities are obtained when relatively small area (0.2-0.5 cm^2) Au foil electrodes are employed as the substrate in the SG formation of IrOx films.

Redox kinetics of SG-formed IrOx.—For most of the practical applications of IrOx films, *e.g.*, as electrochromic or supercapacitive materials, rapid oxidation/reduction kinetics are essential. IrOx films, formed by potential cycling methods on bulk Ir, have been shown to exhibit reversible behavior at low rates of perturbation, becoming diffusion controlled at higher sweep rates or frequencies.[18,21-27,44,45] The onset of diffusional limitations has been demonstrated to depend on the film charge density, known to be proportional to film thickness at bulk Ir substrates (75 mC cm^{-2} per μm of IrOx [27]). Therefore, one of the goals of the present investigation was to establish the redox kinetics of IrOx films formed at the SG-derived Ir nanoparticles, relative to those formed at bulk Ir electrodes.

In these experiments, CV was used as the principal technique to assess the film kinetics, using IrOx films of the same charge densities, but formed electrochemically at an Ir wire, *vs*. at the SG-derived nanoparticulate Ir. Figure 7 shows the logarithmic dependence of the anodic peak current densities *vs*. sweep rate for these two types of oxides, but for films having almost identical equilibrium charge densities, as determined from the slow sweep rate CVs. At slow sweep rates, the peak current densities for both films are seen to be linearly proportional to *v* (slope of unity in Fig. 7), exhibiting equilibrium adsorption-like behavior[6,18,21-27]

$$i_p = 1.12 \times 10^6 n^2 dCv \qquad [1]$$

where *n* is the number of electrons involved in the reaction (= 1), *C* is the concentration of redox sites in the film, *d* is the film thickness, and *v* is the sweep rate. At high sweep rates, diffusional limitations are seen (slope in Fig. 7 is 0.5) and the currents become proportional to $v^{1/2}$, where *F* is the Faraday constant and *D* is the diffusion coefficient of the transport limiting species[6,18,21-27]

$$i_p = 2.7 \times 10^{-5} n^{2/3} FD^{1/2} Cv^{1/2} \qquad [2]$$

Importantly, the sweep rate, v', at which diffusion limitations commence, *i.e.*, at which the deviation from a slope of 1 to 0.5 occurs, can be used as a measure of the kinetics of the redox process in the film.[3,4,18,21-27,44,45] This can be easily understood in that a kinetically superior system will behave reversibly (*i* proportional to *v*) up to the highest possible rate of perturbation (large v' values), and vice versa. As discussed above, the thicker the film, the lower the v' value is expected to be, as transport within the film will increasingly dominate the kinetics under these conditions. It can be seen from Fig. 7 that v' is *ca.* 0.01 V/s for IrOx at bulk Ir and *ca.* 0.100 V/s for IrOx formed at the Ir nanoparticles. This shows that there is a real kinetic advantage, on an Ir content basis, of *ca.* 10 when employing the SG-derived IrOx film.
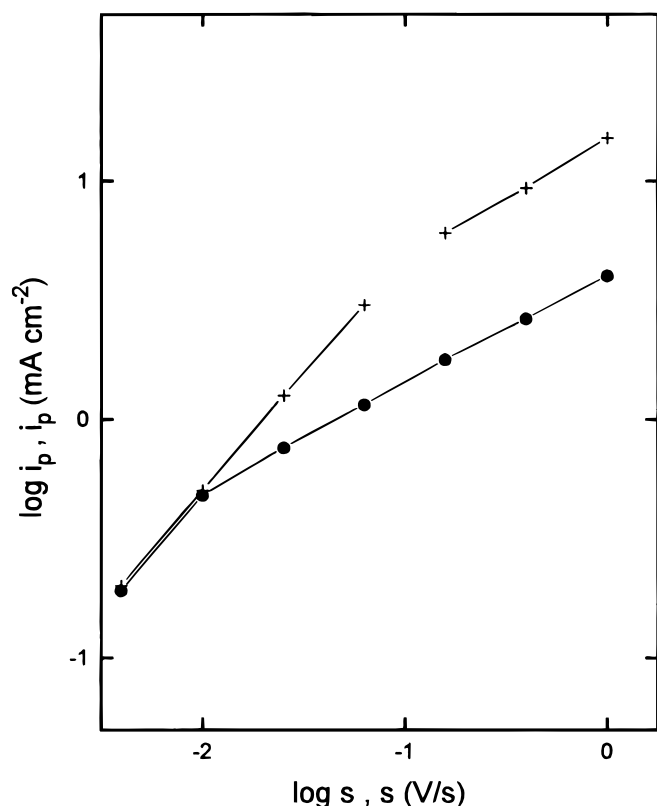

Figure 6. Effect of the drying temperature on the charge density of SG-formed Ir oxide films, deposited on Au substrate (0.4 cm^2) using 24 cm/min withdrawal rate and drying for 15 min.

Figure 7. Dependence of current density of peak A_1 on sweep rate, in 0.5 M sulfuric acid, for (+) SG-formed Ir oxide film (on 0.6 cm² Au, 120 cm/min, 15 min drying at room temperature) and (●) electrochemically formed Ir oxide film on bulk Ir (0.1 cm²) of the same charge density per geometric area.

One obvious interpretation of the excellent kinetics in the case of the SG-derived film is that the oxide is substantially thinner than at the Ir wire. Indeed, it was shown above that, when the true surface area of the Ir nanoparticles is determined from the H upd peaks, the charge densities are relatively low, suggesting that only a few monolayers of IrOx can be formed at the Ir nanoparticles.

In Fig. 7, the current densities were calculated based on the geometric area of the electrodes. If the current densities are recalculated, based on the true Ir areas obtained from the H upd charge (*ca.* 10 times larger for SG formed Ir than for the Ir wire electrode), the data for the SG-formed film will drop by one logarithmic unit in Fig. 7. The SG-formed IrOx film is therefore likely *ca.* 10 times thinner than the film formed at the Ir wire. On a film thickness basis, the kinetics of these two films are therefore similar, suggesting that the IrOx films formed at the two different Ir substrates also have very comparable structural/compositional characteristics, so that the C and D

terms in Eq. 2 are close. However, on a charge density or mass basis, a very significant kinetic advantage is demonstrated for IrOx films formed at Ir nanoparticles *vs.* films formed at bulk Ir substrates.

Efficiency of use of SG-formed Ir deposit.—Another goal of this work was to establish whether all of the SG-derived nanoparticulate Ir substrate is consumed in IrOx formation, as could be inferred from the disappearance of the H upd peaks after conversion of the compact oxide to hydrous IrOx (Fig. 2 and 3). In these experiments, the Ir-containing SG solution was deposited onto Au, which had been sputtered onto quartz crystals, followed by long times of drying at room temperature or at 190°. The mass of the dry Ir deposit was determined, in air, from the Saurbrey equation, using the crystal constant of −56.6 Hz/μg cm⁻². [45] While these films are expected to have a nanoparticulate structure, they are metallic and have been dried for lengthy periods of time, and therefore the mass measurements should be reliable. Table II shows that the dry mass of three freshly SG-formed metallic Ir coatings was between 15 and 35 μg, which was then converted to the number of moles of Ir.

CVs were then collected for these films, in order to first establish the fraction of the total Ir deposit which is accessible as a surface site, based on the charge passed in the H upd peaks in the first few cycles of potential when the film is still in the metallic state. The charge in the H upd peaks gives the total number of surface Ir atoms (subsequently converted to moles of Ir), assuming that the ratio of adsorbed H to surface Ir atoms is 0.65.[40] Table II shows that the ratio of the total, to the surface Ir atoms, is between 2 and 3, for the three films under study. Assuming a spherical geometry and a crystalline Ir structure having the density of bulk Ir, a volume to surface ratio of 2.5 is predicted for spheres that are *ca.* 2 nm in diam. This is in excellent agreement with our TEM observations (Fig. 1).

Subsequently, the maximum IrOx charge (Table II) was obtained by integration of the slow sweep rate CVs up to 1.3 V, [23-27] after forming hydrous IrOx films by multiple cycling between 0 and 1.3 V. The IrOx charge yields the total amount of Ir in the film, as IrOx films are known to have completed a one electron redox process [Ir(III) to Ir(IV)] in an anodic scan to 1.3 V. Table II shows that only approximately 1/2 to 1/3 of the total Ir is involved in the IrOx redox chemistry, a similar fraction as was found to be at the surface of the nanoparticles, *vs.* the total amount of Ir present.

In our earlier discussion of Fig. 2 and 3, it was shown that potential cycling up to 1.3 V causes the Ir CV to convert to that for hydrous IrOx, with the novel feature (*vs.* the case at bulk Ir substrates) being that the H upd peaks disappear completely. The present results could suggest that 1/2 to 2/3 of the total Ir originally present dissolves during IrOx formation. It is known that some Ir dissolution occurs during IrOx growth at bulk Ir electrodes.[3,4,23-27] Therefore, the final SG-formed film would contain no unused metallic Ir. Alternatively, unreacted Ir may still be present, beneath the very thin IrOx film. Its function may be to maintain electrical contact between adjacent Ir nanoparticles and could therefore be inaccessible for the H upd reaction. A third possibility is that 1/2 to 2/3 of the nanoparticles are not in good electrical contact with each other

Table II. Comparison of total and surface moles of Ir nanoparticles.

Total Ir mass (quartz crystal microbalance) (μg)	Total Ir moles (quartz crystal microbalance)[a]	H_{upd} charge[b] (mC)	Moles surface Ir from H_{upd} charge[c]	IrOx charge[d] (mC)	Moles Ir in IrOx	Moles Ir(total) / Moles Ir(surface) (from H_{upd})	Moles Ir(total) / Moles Ir(IrOx)
33.5	1.7×10^{-7}	3.9	6.2×10^{-8}	7.0	7.2×10^{-8}	2.7	2.4
33.7	1.7×10^{-7}	5.1	8.2×10^{-8}	4.4	4.5×10^{-8}	2.1	3.8
16.1	0.7×10^{-7}	2.0	3.2×10^{-8}	3.6	3.7×10^{-8}	1.9	2.2

[a] Ir density = 22.5 g cm⁻³.
[b] From CV charge in 0.5 M H_2SO_4 at 0.02 V s⁻¹.
[c] Assuming 0.65 monolayers of H atoms in H_{upd} peaks.[40]
[d] Integrated CV up to 1.3 V, 0.5 M H_2SO_4, 100 mV s⁻¹.

and are therefore electrochemically inactive. This would again then suggest that all of the Ir at which the H upd process occurred is subsequently fully used in IrOx formation.

Conclusions

The formation and properties of IrOx films, formed at Au and Pt substrates using the SG technique, have been studied in detail in this work. SG-derived films were deposited using a constant withdrawal rate methodology, and were then dried for a range of times at room temperature or at temperatures between 100 and 600°C. As formed, the films consist of metallic Ir nanoparticles, with diam of *ca.* 2 nm, and yielding a similar CV response to that for bulk Ir metal. These high surface area Ir films can be easily converted to hydrous Ir oxide (IrOx), resulting in a CV response very similar to that for IrOx films formed electrochemically on bulk Ir foil or wire substrates. However, the hydrogen adsorption/desorption (H upd) peaks disappear rapidly at the SG-derived films, suggesting the complete usage of the Ir in IrOx formation.

IrOx films formed at the SG-derived nanoparticulate Ir deposit are electrochromic, adhere well to the metallic substrate, and yield charge densities of up to 100 mC/cm^2, depending on the experimental conditions employed. For example, drying the films at 100°C, use of a high withdrawal rate of the substrate from the Ir sol, use of anhydrous Ir salts, and successively applying multiple coatings (at least eight) all yield higher film charge densities. By determining the true Ir surface area from the H upd peaks, it is found that the IrOx films are only a few monolayers thick. Therefore, these beneficial experimental variables appear to be producing high surface area Ir deposits. This is also verified from the excellent redox kinetics observed at SG-formed IrOx films. When comparing films of the same charge density, but formed at SG-derived Ir nanoparticles *vs.* by electrochemical oxidation of bulk Ir wires and plates, the kinetics in the former case are much faster, by a factor close to their relative surface areas. This again demonstrates that the SG-formed films are much thinner, and therefore the reaction does not become diffusion controlled until very high sweep rates are employed.

Mass measurements have revealed that, at freshly formed nanoparticulate Ir films, *ca.* 1/3 to 1/2 of all of the Ir in the film is located on the outer surface, undergoing both the H upd reaction and, subsequently, IrOx film formation. The unused Ir may be located in particles which are not in good electrical contact with the rest of the film, or it may be used for electrical contact between particles. Some Ir may also dissolve during IrOx film formation.

Overall, the SG method for IrOx formation shows many advantages, including the simplicity of the process, the fact that long times of potential cycling are not required, flexibility in terms of choice of substrate, and the presence of many film preparation variables which can be used to controllably alter the IrOx properties. Importantly, in comparison with IrOx films formed at bulk Ir, the redox kinetics are greatly improved, on an Ir mass (or mole) basis.

Acknowledgments

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