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In situ Infrared Spectroscopy of Iridium Oxide

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ABSTRACT

The structural change of an electrochemically grown iridium oxide film upon its electrochromic effect has been investigated in 1N H₂SO₄ and HClO₄, using *in situ* electrochemically modulated infrared spectroscopy (EMIRS). Modulation of the main redox couple operating within the film was found to be associated with the appearance of a O—H stretching band at the bleached state, which is similar to that of pseudoböhmite. Likely oxide species at the bleached and the colored states are considered in view of the reported findings.

The structure of electrochemically formed oxides is of great interest in several fields of electrochemistry: corrosion (Fe), electrocatalysis (RuO₂), batteries (NiO₂), etc. In particular, oxide films which undergo a process of reversible double injection of ions and electrons have been studied extensively during recent years (1-9), mainly in connection with the electrochromic properties of the films, but also because of their high electrocatalytic activities for the oxygen evolution reaction in the case of iridium and ruthenium oxides. *In situ* optical measurements in the visible spectral region have been applied to the study of hydrous oxide films, providing valuable information with regard to film growth, conductivity change with bias potential, and its highly hydrated porous nature (3, 4).

It is well known that the electrochromic effect of iridium oxide is associated with a reversible change of the oxidation state of iridium ions in the oxide film, which involves double injection/ejection of protons and electrons to/from the oxide. However, the structural change of the oxide upon coloring/bleaching has not yet been well understood, because of the lack of a suitable vibrational spectroscopic method, which could probe the system *in situ*.

In view of this situation, infrared spectroscopy utilizing the electrode potential modulation method (EMIRS) (10, 11) is most promising in studying the structural change of the oxide film *in situ* upon modulation of the main redox couple operating in the oxide film. The rapid coloration and bleaching times (≈ 40 ms) observed for electrochromic iridium oxide films in aqueous electrolytes (1, 8) make this system suitable for study by EMIRS, which employs a potential modulation of *ca.* 10 Hz in a thin layer type spectro-electrochemical cell. It is particularly interesting to investigate the change in the spectral region of O—H vibrations upon the modulation of the redox couple, because the double injection of protons and electrons associated with it may give rise to formation of new O—H bonds or to a change in the water structure in the oxide.

The work presented here is the first attempt to apply *in situ* infrared spectroscopy to the investigation of the structural change of iridium oxide upon coloring and bleaching.

Experimental

The principle of the EMIRS (10, 11), the design of the infrared spectrometer, and the thin layer type spectro-electrochemical cell employed in the present study, have been described elsewhere (12). The electrode was an 8 mm diam iridium disk, sealed into Pyrex glass. Solutions were prepared from Merck suprapur sulfuric or perchloric acid, and Millipore water. In some cases, mixtures of H₂O and D₂O (Merck) were used. The optical window, a 2 mm thick silicon disk attached to the cell

with a glass flange at its front end (12) brought the p-polarized incident radiation onto the electrode at an angle of incidence of *ca.* 45°. The electrode was polished to a mirror finish with successively finer grades of alumina down 0.05 micron, then immersed in hot sulfuric acid, and rinsed with Millipore water, before being introduced into the solution. Voltammograms were taken to check on surface cleanliness and on complete removal of the residual oxide films. The iridium oxide film was grown to different thicknesses by means of potential cycling at 100 mV/s between 0.0 and 1.45V(NHE), with the electrode taken away from the window. Electrochromic changes were clearly seen after the film thickness had reached a critical value. Occasionally a method of pulsing at 0.5 Hz (1) was employed for a better efficiency, although it could lead to nonuniform structures. After the pulsing, the electrode potential was cycled between 0 and 1.45V at 100 mV/s, for a while, to make the conditions comparable. Most of the results of the EMIRS measurements were obtained with films of *ca.* 1500Å thick. The thickness was estimated roughly from the main peak current of the redox couple in the oxide observed by cyclic voltammetry, as shown in Fig. 1.

Fig. 1. Cyclic voltammograms taken at 100 mV/s, observed at the increasing times, showing the gradual growth of the iridium oxide on the Ir electrode in 0.5M H₂SO₄. The approximate numbers of cycles for the voltammograms are 236, 300, 374, 440, and 480, respectively.

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Fig. 2. EMIRS spectrum of the iridium oxide electrode modulated between 0.07 and 0.67V (RHE) in 0.5M H_2SO_4 .

For the EMIRS measurements, the redox couple in the iridium oxide was modulated with respect to the electrode potential between 0.45V(RHE) and 1.30V(RHE) at 11 Hz. No further film growth of the iridium oxide occurred during the EMIRS measurements for this potential modulation with the cathodic limit higher than 0.25V(RHE) in agreement with the results reported by Gottesfeld and McIntyre (1). The modulation frequency, 11 Hz, is low enough to define the colored and bleached states of the iridium oxide, thanks to the fast coloration and bleaching times [~ 40 ms in 0.5M H_2SO_4 (1)].

The change in electrode reflectivity, ΔR , in response to the potential modulation was observed as a function of wavelength by using a synchrotrack lock-in amplifier, NF LI-575. The detector employed was an InSb cooled at liquid nitrogen temperature. Signal averaging, typically 4 scans, was conducted to improve the signal/noise ratio, taking ca. 1h per spectrum. A slit width of 3 mm was employed throughout the present study.

Measurements were conducted at room temperature and all the potentials are referred to the RHE scale.

Results

Figure 1 shows cyclic voltammograms taken at the increasing times after starting the potential cycling. The voltammograms demonstrate that the iridium oxide grows gradually with time as potential is cycled.

A flat featureless EMIRS spectrum was obtained, as shown in Fig. 2, when the potential modulation range was restricted to the lower potentials, between 0.07 and 0.67V, where the main redox couple in the oxide is not modulated. The redox couple was then modulated by square wave pulses between 0.45 and 1.3V. A typical current-time response for the modulation is shown in Fig. 3. A typical value for the modulated charge was ca. $1200 \mu\text{C}/\text{geo} \cdot \text{cm}^2$.

Figure 4a shows the electrode reflectivity change in the O—H stretching region, measured in a vectorial mode, $|\Delta R|$, in response to the potential modulation. The corre-

Fig. 3. Current-time transients for the potential modulation between 0.45 and 1.30V (RHE) on the iridium oxide electrode in 0.5M H_2SO_4 .

Fig. 4. (a) Absolute value of the reflectivity change, $|\Delta R|$, for the potential modulation between 0.45 and 1.30V (RHE) in 0.5M $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ and (b) background energy, R , observed in terms of the detector output.

sponding background energy curve, R , is shown by curve b in Fig. 4. Figure 5 shows the EMIRS spectrum obtained by calculating $|\Delta R|/R$. The data presented in Fig. 4 and 5 demonstrate that the electrode reflectivity change upon the coloration/bleaching is extremely small, ca. 0.1%, in the infrared spectral region, compared to a reflectivity change of as much as ca. 70% observed in the visible spectral region at 546 nm (1). We can see a broad, but clear, O—H stretching band upon the coloration/bleaching in Fig. 5. Contrary to an increased light absorption at the colored state in the visible spectral region, the data in Fig. 5 show an increased infrared absorption in the O—H stretching region at the bleached state. This point will be described in more detail later. The band has a maximum around 3450 cm^{-1} and a shoul-

Ir/0.5M H_2SO_4

Modulated : 0.45 to 1.30 V(RHE),

Fig. 5. EMIRS spectrum, $|\Delta R/R|$, modulated between 0.45 and 1.30V (RHE) in 0.5M H_2SO_4 .

Fig. 6. EMIRS spectrum, observed in-phase to the potential modulation between 0.45 and 1.30V (RHE), in 0.5M H_2SO_4 . ΔR is defined by $R(1.3\text{V}) - R(0.45\text{V})$.

der around 3250 cm^{-1} . Figure 6 shows an EMIRS spectrum observed by the same electrode potential modulation for a wider spectral region, down to 2100 cm^{-1} . The electrode reflectivity change was observed in-phase to the potential modulation in this case. Agreement between the vectorial and the in-phase measurements, as shown in Fig. 5 and 6, indicates that the reflectivity change is almost in-phase to the potential modulation. The spectra shown hereafter were observed in-phase unless stated otherwise.

As demonstrated in Fig. 5 and 6, the EMIRS spectrum for the potential modulation, including the redox couple in the oxide, has a rather flat background component, as well as an absorption band in the O—H stretching region around 3450 cm^{-1} with a shoulder around 3250 cm^{-1} .

Similar bands were observed in 1M HClO_4 , Fig. 7, and in the isotopic mixture of 7% H_2O in D_2O , as shown in Fig. 8. In all the solutions studied, the O—H or O—D stretching bands have a shoulder at the lower wave number side. After deconvolution, the band in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ is shown to have two components, the main one, at 3434 cm^{-1} , with a line width of ca. 320 cm^{-1} and a shoulder at 3280 cm^{-1} , as shown in Fig. 9.

An EMIRS spectrum being the spectral difference between the modulation limits, it is important to know the band sign, i.e., whether these bands represent an increased infrared absorption of the O—H or O—D stretching vibrations at either side of the potential modulation. The band sign was determined by observing the optical transients at 3438 cm^{-1} and 2728 cm^{-1} , Fig. 10 (i.e., the change in electrode reflectivity in response to the potential modulation at fixed wavenumbers near the band maximum of the O—H stretching band, and away from the band, respectively).

The optical transient at 3438 cm^{-1} is almost a square wave with a rapid initial decrease of electrode reflectivity upon the potential step from 1.3 to 0.45V. The rapid decrease of the reflectivity is followed by a small slow reflectivity increase, with further duration of time. The transient at 2728 cm^{-1} , i.e., away from the O—H stretching band, also shows a rapid initial reflectivity de-

Fig. 7. EMIRS spectrum, modulated between 0.45 and 1.35V (RHE), in 1M HClO_4 .

Fig. 8. EMIRS spectrum, modulated between 0.45 and 1.35V, in 0.5M H_2SO_4 (7% H_2O in D_2O).

crease, but is followed by a large slow reflectivity increase, which almost compensates for the initial decrease.

The optical transient at 3438 cm^{-1} confirms that the sign of the O—H stretching band, in Fig. 5 and 6, corresponds to an increased infrared absorption in this spectral region, as the potential is stepped from 1.3 to 0.45V. The background component in Fig. 5 and 6, which is almost flat and featureless between 2100 and 4500 cm^{-1} , has the same sign as the O—H stretching band; there is an electrode reflectivity decrease, even away from the water band, when the potential is stepped from 1.3 to 0.45V. The origin of the background reflectivity decrease cannot be well understood, referring to only these data. The origin of the large reflectivity increase, following the fast initial decrease of reflectivity at 2728 cm^{-1} could be related to a slow process, such as diffusion in the oxide, as will be discussed later.

The band intensity, as measured from the area under the peak, increased with the film thickness, although it was unclear whether the relationship was a linear one, as the intensity underwent some changes from one set of measurements to another. The band maxima intensities ranged from 6×10^{-4} to 6×10^{-3} units of $\Delta R/R$, when the peak current of the redox couple varied between 6 and 8 mA per unit of geometric area.

The O—H bending region was explored in a number of experiments looking for a band, or lack of one, which might have helped us assign the O—H stretching bands. However, the measurements were not successful, due to the low sensitivity of the HgCdTe detector.

Discussion

Iridium oxide films are supposed to be highly hydrated, poorly crystalline, and open-structured. Thus, the

Fig. 9. Deconvolution of the in-phase EMIRS spectrum, modulated between 0.45 and 1.35V (RHE), in 0.5M H_2SO_4 .

Fig. 10. Optical transients observed at 3438 and 2728 cm^{-1} in response to the potential modulation between 0.45 and 1.3V in 0.5M H_2SO_4 .

film refractive index is only slightly larger than that of water (3) and its density was found to be ca. 2.0 g/cm^3 , a value much lower than that for bulk IrO_2 [11.7 g/cm^3 (2, 4)]. Furthermore, the underpotential deposition of hydrogen at the underlying bare metal can still be observed in the presence of thick oxide layers on the electrode surface (6), which is also indicative of the heavily hydrated open structure of the oxide. Therefore, the structure of the water/hydroxyl ions in the film should play an important role in determining the EMIRS spectra in the O—H stretching region.

As described in the preceding section, the O—H stretching bands observed for the potential modulation between 0.45 and 1.3V correspond to an increased infrared absorption of the O—H stretching vibrations at the bleached state of the iridium oxide. The rapid initial decrease of the electrode reflectivity in response to the potential modulation, followed by a much slower reflectivity increase, was clearly seen in the optical transients in Fig. 10. Comparing the current-time transient in Fig. 3 with these optical transients, we can see that the initial sharp part of the current-time transient corresponds quite well to the fast change in the electrode reflectivity.

As demonstrated in Fig. 5 through 8, the O—H stretching band observed upon coloring/bleaching is comparatively sharper than the O—H stretching band of liquid water. The band can be deconvoluted into two dominant bands located at (averages over several experiments) 3440 cm^{-1} with a half-width of ca. 320 cm^{-1} and at 3280 cm^{-1} , respectively, while liquid water (13) has a broad band maximum at 3420 cm^{-1} with a line width of ca. 450 cm^{-1} . The spectral feature of the O—H stretching band of the iridium oxide looks very similar to that of the pseudoböhmite (14).

Fig. 11. Proposed structure of the iridium oxide at the bleached and colored states.

According to these results, and in the light of previous findings, we may speculate on the structure of the oxide. The colored form could be formulated as $\text{IrO}_2 \cdot x\text{H}_2\text{O}$, as no hydroxyl species have been detected, either in the present work, or in other reports (8). The bleached state is likely to be $\text{IrOOH} \cdot y\text{H}_2\text{O}$. The existence of cross-linking chains in the structure of iridium oxide have been proposed, based on the configuration of polynuclear iridium complexes with the metal ion placed at the center of edge sharing octahedra (9). Hence, tentative structures for the states comprising the electrochromic system could be represented as shown in Fig. 11.

The exact number of water molecules coordinated to the central metal ion is uncertain as they form more extended nets. The water molecules are likely to undergo reorientation as the charge on the metal is altered and, concomitantly, protons are injected into, or released from, the oxide. Observation of the O—H stretching bands, similar to the pseudoböhmite, with higher absorption intensity at the bleached state is, most likely, due to the O—H groups produced by the proton injection, as is schematically described above. Observation of the band, on the other hand, supports the proton injection scheme, which is usually assumed for the electrochromic effect of iridium oxide.

It may be worth noting that the appearance of the O—H stretching bands upon proton injection is similar to the case of the formation of a complex between weakly bound hydrogen and water on Pt (15) and Rh (16).

The origin of the background reflectivity decrease at the bleached state, as shown in Fig. 5-8, is uncertain at the moment, but a similar background reflectivity change was observed for WO_3 (17) in the infrared spectral region. The reflectivity decrease is characteristic of the potential modulation including the main redox couple in the oxide, because no such reflectivity change was detected for the potential modulation between 0.07 and 0.67V, as demonstrated in Fig. 2. The optical transient observed at 2728 cm^{-1} for the potential modulation between 0.45 and 1.3V shows that the background reflectivity decrease takes place almost in-phase to the potential step. This implies that the proton injection is responsible for the increased infrared absorption of the O—H stretching vibration, as well as for the change in the refractive index of the oxide, although the mechanism of the refractive index change is not clear.

What happens upon the proton injection could be the liberation of the water molecules which had existed as H_3O^+ , assuming the source of the protons is H_3O^+ in 0.5M H_2SO_4 . This should be followed by the diffusion of H_3O^+ into the oxide from the bulk of the solution, and of counter anions, such as HSO_4^- and SO_4^{2-} , into the solution out of the oxide to keep the electrical neutrality. The diffusion process, which would be slow in the oxide, is likely to be responsible for the slow reflectivity increase following the fast initial reflectivity decrease observed in the optical transients, most significantly at 2728 cm^{-1} .

Conclusion

An *in situ* EMIRS study of the structural change of an electrochemically grown iridium oxide upon coloring/bleaching has shown the following: (i) An O—H stretching band is observed with a peak intensity of ca. 0.1% upon bleaching of the oxide, and this is probably due to IrOOH type species produced upon double injec-

tion of protons and electrons to the oxide. (ii) The fast coloring/bleaching process is associated with a background reflectivity increase/decrease contrary to the behavior in the visible spectral region, and is followed by a slow process, which gives rise to a reflectivity change opposite in sign to the fast initial change of reflectivity. Diffusion of ions in the oxide to keep the electrical neutrality, is probably responsible for the slow process.

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Piezoelectric Response to Surface Stress Change of Gold Electrode in Sulfate Aqueous Solutions

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ABSTRACT

The interfacial properties of gold electrode in sulfate solutions of different pH values have been investigated from the piezoelectric response of surface stress change induced by a potential modulation. The potential of electrocapillary maximum, E_{max} , obtained from the piezoelectric signals is independent of pH in acidic and neutral range but shifts to the less noble direction at pH higher than 8. The piezoelectric signals could sensitively respond to the structural changes of electric double layer which are ascribed to the reorientation of water dipoles in acidic solution and the charge transfer of electro-sorbed OH^- ions in alkaline solution. It is expected that the sign of surface charge of gold electrode in alkaline solution changes gradually from plus to minus at the high anodic potential of oxide formation. It seems that the sign reversal of surface charge is associated with the aging process of hydrous oxide, $\text{Au}(\text{OH})_3$, initially formed on gold.

The properties and structures of electric double layer of noble metal electrodes in different electrolyte solutions have been mainly investigated from the capacity measurement. The potential of zero charge (pzc) is conventionally evaluated from a minimum in the differential capacity-potential curve. Besides the capacity measurement, the measurement of surface stress of gold electrode, if possible, would provide not only supplemental information on the electric double layer but also new information on the electrode surface subjected to faradaic current flow.

The technique for surface stress measurement of solid electrode, however, encounters difficulties compared with that for liquid metal electrodes. Gokhshtein (1-3) first developed a piezoelectric technique which is capable of detecting sensitively a small change in surface stress of solid electrode. Afterwards, Malpas *et al.* (4) employed a simplified electrode for piezoelectric detection. This technique was successfully applied to several studies (5-8) on the solid electrode/solution interfaces. In our previous study (8), the application of this technique to platinum electrode has brought forth the information on the pH dependence of pzc and phase change of oxygenated surface layer. In comparison with platinum, gold

has a wide potential region of electric double layer and a different reactivity with electrolyte solution.

In this study, the piezoelectric detection of surface stress change of gold electrode has been conducted to reveal the interfacial characteristics different from that of platinum electrode.

Experimental

The electrode design and the technique used for piezoelectric detection of surface stress change are the same as those previously reported (8). The working electrode was constructed by attaching a polycrystalline gold foil ($20 \mu\text{m} \times 5\text{mm} \times 20\text{mm}$) via a thin polyimide film ($7.5 \mu\text{m}$) for electrical isolation to a piezoelectric ceramic element ($1 \times 5 \times 20\text{mm}$) with strain gauge cement and by doubly coating with epoxy cement and silicon sealant. A handmade potentiostat connected with a function generator was used to supply a linear potential sweep ($20 \sim 100 \text{ mV s}^{-1}$) to the electrode. A sinusoidal signal of 5 mV at 200 Hz was superimposed on the linear potential sweep. This small superimposed alternative signal, dE , to the electrode induces an alternating change in surface stress, $d\gamma$, of the electrode producing a corresponding response from the piezoelectric element mechanically attached to the electrode. The signal from the piezoelectric element was synchronously detected at the same fre-

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