**In situ Infrared Spectroscopy of Iridium Oxide**

R. O. Lezna and K. Kunimatsu

Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

T. Ohtsuka and N. Sato*

Electrochemistry Laboratory, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

**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 0.5 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. Electochromic 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. 1500 Å 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.](image-url)
Vol. 134, No. 12

IN SITU INFRARED SPECTROSCOPY

3091

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 H2SO4 (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 μA·cm⁻²·g⁻¹.

Figure 4a shows the electrode reflectivity change in the O–H stretching region, measured in a vectorial mode, ΔR, in response to the potential modulation. The corresponding background energy curve, R, is shown by curve b in Fig. 4. Figure 5 shows the EMIRS spectrum obtained by calculating ΔR/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 shoulder at ca. 3600 cm⁻¹.
The spectra shown hereafter were observed in-phase between the vectorial and the in-phase measurements, as 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 3250 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\(_2\)O in D\(_2\)O, 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 H\(_2\)SO\(_4\)/H\(_2\)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 decrease, 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 \times 10 \(^{-4}\) to 6 \times 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.

**Discussion**

Iridium oxide films are supposed to be highly hydrated, poorly crystalline, and open-structured. Thus, the
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 IrO$_2$·xH$_2$O, as no hydroxil species have been detected, either in the present work, or in other reports (8). The bleached state is likely to be IrOOH·yH$_2$O, to be formed by 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.

To a great number of 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 pseudobohmite, 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, as is schematically described above. Observation of the band, on the other hand, supports the proton injection.

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 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$_2$O, assuming the source of the protons is H$_3$O$^+$ in 0.5M H$_2$SO$_4$. This should be followed by the diffusion of H$_2$O 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.

Acknowledgments
The authors gratefully acknowledge JICA (Japan International Cooperation Agency) for financial support and general organization given to R. O. Lezna from October 1984 to February 1985. R. O. Lezna would like to thank Professor Enyo for supporting his leave of absence taken at the Research Institute for Catalysis in the winter of 1984/1985, and Professor Aramata for providing the iridium electrode.

Manuscript submitted Nov. 18, 1985; revised manuscript received Jan. 27, 1987.

The Research Institute for Catalysis, Hokkaido University, assisted in meeting the publication costs of this article.

REFERENCES
1. S. Gottesfeld and J. D. E. McIntyre, This Journal, 126, 742 (1979).