FUNDAMENTAL ASPECTS OF ELECTROCATALYSIS AT METAL AND METAL OXIDE ELECTRODES

by

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To my family

献给我的家人
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LIST OF SYMBOLS

A - Electrode area
Acq - Acquisition number
E - Potential
\(E^{O_2}_{onset}\) - Onset potential for O₂ reduction
\(E^{HAM}_{onset}\) - Onset potential for hydroxylamine oxidation
i - Current density
I - Current
k - Rate constant
n - Number of electrons
N - Collection efficiency
Q - Integrated charge
\(R_{ref}\) - Reflectance at reference potential
\(R_s\) - Reflectance at sampling potential
R(R)DE - Rotation (ring) disk electrode
SCE - Saturated calomel electrode
\(\lambda\) - Wavelength
\(\Delta \phi_{sol}\) - Potential difference between two positions in solutions
\(\Delta m\) - Distance between two microreference electrodes
\(\Delta M\) - Distance between working electrode and the closer microreference electrode
\(\Delta R/R\) - \((R_{ref} - R_s)/R_{ref}\) – normalized differential reflectance
\(\xi\) - Ratio of the total currents for a Hm|GC and GC rings
\(\nu\) - Scan rate
\(\omega\) - Rotation rate
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Fundamental Aspects of Electrocatalysis at Metal and Metal Oxide Electrodes

Abstract

by

YOUJIANG CHEN

This work explores certain aspects of the behavior of interfacial systems of relevance to areas fundamental and technical interest from a strictly physical electrochemistry viewpoint. Attention was focused on four distinct topics:

i. The dynamics of charge injection into/from iridium oxide (IrO$_x$) films using a combination of simultaneous chronocoulometry and in situ time-resolved normalized reflectance spectroscopy. This tactic enables charge storage contributions derived from capacitive (due to the finite conductivity of the film) and pseudocapacitive processes (due to changes in oxidation state of Ir sites in the film) to be independently determined. The rates of charge-discharge dynamics were found to be faster in alkaline compared to acidic aqueous electrolytes. These films displayed no detectable activity for oxygen reduction in neutral phosphate buffer (pH = 7) over a potential range of about 0.9 V, allowing 90% of the total charge stored in the film to become available for functional neural stimulation without producing harmful oxygen-derived species.

ii. The development and implementation of solution phase ohmic microscopy as a spatially resolved probe of ideal polarizable electrode|electrolyte interfaces
by two microreference electrodes to monitor the potential drop in the solution associated with the passage of current through the interface using.

iii. The rational design and assembly of electrocatalytic interfaces capable of performing sequential transfers of multiple electrons using the reduction of nitrate in a weakly buffered acetate solution as a model system. The specific electrode architecture involved Au nanoparticles supported on a hemin modified glassy carbon surface. Polarization of the electrode in solutions containing a Cd salt at negative potentials promoted reduction of nitrate to nitrite which was then reduced on the Hm modified GC surface to yield further reduced products including hydroxylamine.

iv. Fundamental studies of the oxidation of hydroxylamine on Au surfaces in pH 4 buffered solutions employing rotating disk and ring disk electrodes and normal incidence differential reflectance spectroscopy. The results obtained provided evidence that the oxidation of hydroxylamine proceeds via two sequential steps in the potential range negative to the onset of Au oxide formation to yield first nitrite and then nitrate products.
INTRODUCTION

Metal oxides have been the subject of many recent researches because of their unique and intriguing properties for optical, photochemical, biological and catalytical applications.1-5 Among them, iridium oxides (IrOx) are promising materials for biosensor, supercapacitor and neural stimulation due to their biocompatibility and outstanding electrochemical characteristics which include good stability in many aqueous media, great cyclability, and the ability to accommodate a large amount of charge which can be injected and released reversibly in a very short time.4,6-8 Usually, the charge stored in IrOx has two contributions, capacitive and pseudocucapacitive, the latter involving redox change. The most common oxidation states for IrOx are +3 and +4. During charge injection, the color of the IrOx film changes from transparent to blue-black and the oxidation state of Ir sites increases from +3 to +4, i.e. a phenomenon well known as electrochromism.9

It should be pointed out that the electrochemical and optical properties of IrOx are highly dependent on the methods of preparation and properties of the substrate. The most widely used method to prepare IrOx film is to apply repeated potential cycles or potential pulses between fully reduced and fully oxidized states on an iridium metal surface in aqueous solution.10-12 However, the high electrochemical activity and large capacity of iridium metal may complicate the investigation of capacitive and supercapacitive properties of the IrOx film. This is avoided if the IrOx film is deposited on less active substrates, such as gold, ITO or glassy carbon (GC), which have the much smaller
capacitive current and wider potential window (> 1 V) in the double layer region, which is where the redox reaction of IrO$_x$ take place.

The optical properties and kinetics of surface redox change of electrodeposited IrO$_x$ film can be studied by using in situ time-resolved differential reflectance spectroscopy. Reflectance spectroscopy is very sensitive for studying electrode | electrolyte interface and it has been used for the in situ investigations of surface reactions, thin film formation and electrolytic deposition on metals and semiconductors. The change of reflectance signal is characterized by using normalized reflectivity, $\Delta R/R$,\textsuperscript{13}

$$\Delta R/R = \frac{R(E_s) - R(E_{ref})}{R(E_{ref})}$$

where $R(E_s)$ and $R(E_{ref})$ are reflectance signals for the electrode polarized at a sampling potential, $E_s$, and the reference potential, $E_{ref}$.

It is well-known that current passing through the electrolyte involves electrostatic potential changes within that solution phase. Newman theoretically mapped the potential and current distribution in the electrolyte for a disk electrode embedded in an insulating surface.\textsuperscript{14} The potential drop is much more dramatic between two positions in the neighborhood of the electrode surface compared with that for the two positions far away, which can be monitored experimentally using two microreference electrodes.

Reduction of nitrate and nitrite are widely studied on different substrates, including transition metals and coinage metals, because of their potential impact in
environmental remediation, electrochemical synthesis and sensor technology.\textsuperscript{15} Among all the metals studied, rhodium and platinum are the best electrocatalysts for the reduction of nitrate and nitrite, respectively.\textsuperscript{16} Gold is not a good material for the reduction of nitrate and nitrite; this may be partly due to the hydrogen evolution taking place at the same potential region where the nitrate and nitrite are reduced. However, cadmium underpotential deposited (UPD) on gold inhibits hydrogen evolution, and improves the ability of gold to reduce the two species.\textsuperscript{17,18} Besides the metal substrates, the macrocycles on glassy carbon electrodes are also proved to be good electrocatalysts for only nitrite reduction,\textsuperscript{19} which provides a way to distinguish nitrite from nitrate as the product of oxidation of some nitrogen compounds at lower valence, such as hydroxylamine and nitric oxide.

The oxidation of hydroxylamine (HAM) has been the subject of investigations, mainly on Pt electrodes, in recent years.\textsuperscript{15} It was claimed that HAM could not be reduced on gold electrodes in acidic electrolytes, due to poor adsorption of HAM on the gold surfaces.\textsuperscript{20} However, the oxidation of HAM on Au electrodes was observed recently in our laboratory, for acidic buffered solutions within the double layer region, yielding the voltammetric curves with two consecutive waves.\textsuperscript{19}

This work holds fundamental and technical importance for energy storage and energy conversion, biomedical applications and environmental remediation. It emphasizes four areas of research:

1. Functional neural stimulation.
2. The design of highly active and highly specific multifunctional electrocatalytic surfaces for the sequential transfer on multiple electrons.

3. The development of methods for the real time, spatially resolved mapping of electrostatic solution potentials resulting from the passage of current across electrodes.

4. Electrochemical oxidation on gold surfaces.

REFERENCES


CHAPTER 1: SUPPORTED IRIDIUM OXIDE FILMS IN AQUEOUS ELECTROLYTES: CHARGE INJECTION DYNAMICS AS MONITORED BY TIME RESOLVED DIFFERENTIAL REFLECTANCE SPECTROSCOPY
1.1 ABSTRACT

Dynamic aspects of the electrochemical charge-discharge of hydrated Ir oxide, IrO$_x$, films in aqueous 0.5 M H$_2$SO$_4$ have been investigated by simultaneous chronocoulometry and time-resolved, normal incidence ($\lambda = 633$ nm) differential reflectance spectroscopy, $\Delta R/R$. Experiments were performed by applying potential steps between two judiciously selected values to IrO$_x$ films electrodeposited on smooth Au disk microelectrodes to reduce the overall time constant of the cell. The analysis of the results obtained revealed that the rate at which charge is injected into or released from the films, as determined from the chronocoulometric response, is faster than the rate at which Ir sites in the lattice undergo redox transitions, as monitored by $\Delta R/R$. This behavior appears consistent with the relatively high electronic conductivity of IrO$_x$, which allows charge to be stored on the highly convoluted surface of this structurally disorganized material, i.e. strictly capacitive, a process that occurs in parallel and at much higher rates than changes in the oxidation state of the Ir sites, i.e. pseudocapacitive.
1.2 INTRODUCTION

Electrode materials capable of accepting or releasing large amounts of charge over very short periods of time are finding increased application, not only in energy storage devices, such as electrochemical capacitors,\textsuperscript{1} but also in functional neural stimulation.\textsuperscript{2,3} In particular, hydrated forms of Ru and Ir oxides, to be denoted hereafter as RuO\textsubscript{x} and IrO\textsubscript{x}, respectively, have been shown to display rather extraordinary capacitive properties in aqueous electrolytes and, as such, continue to be the subject of numerous investigations.\textsuperscript{1,4-9} Despite these efforts, detailed aspects of the mechanism of charge storage still remain to be elucidated.

This chapter focuses on dynamic aspects of charge injection into IrO\textsubscript{x} in strongly acidic aqueous media, as monitored simultaneously by chronocoulometric and time-resolved differential reflectance techniques, and represents an extension of the pioneering work of Gottesfeld and McIntyre reported almost three decades ago.\textsuperscript{10,11} As has been amply documented, changes in the oxidation state of Ir sites in the IrO\textsubscript{x} lattice elicit corresponding modifications in the optical properties of the material,\textsuperscript{12} a phenomenon known generically as electrochromism,\textsuperscript{13} which can be conveniently monitored by UV visible spectroscopic techniques. In order to reduce the time constant of the cell, and, thus, gain access to the intrinsic dynamics of the processes involved, IrO\textsubscript{x} films were electrodeposited onto Au microelectrodes using reported methods.\textsuperscript{14} An analysis of both coulometric and transient optical responses recorded simultaneously revealed that both charge injection and release following the application of potential steps, occur over times which are shorter than those required for the Ir sites in the IrO\textsubscript{x} lattice to change the
oxidation state. This behavior has been tentatively ascribed to the rapid injection of charge into the delocalized d-band responsible for the relatively high intrinsic electronic conductivity of certain forms of IrOx, which then dissipates into localized Ir states in the lattice at comparatively much slower rates.

1.3 EXPERIMENTAL

Gold microelectrodes were fabricated by melting a glass micropipette (Clay Adams 10 μL) around a Au wire (25 μm in diameter, Alfa Aesar 99.95 %). The end of the glass-encased wire was then polished mechanically to a mirror finish with fine sandpaper (P2400) to expose an embedded disk, which served as a substrate for the electrodeposition of IrOx films, and as a reflecting surface for the optical measurements (see below). Prior to film deposition, the Au microelectrodes were cleaned by electrochemical cycling (via repetitive linear scans) in neat deaerated (Ar) aqueous 0.5 M H2SO4 (Ultrex ultrapure) within the potential (E) range -0.20 < E < 1.35 V vs a saturated calomel electrode (SCE) at a scan rate, \( \nu = 50 \text{ mV s}^{-1} \), in a conventional three electrode cell, using a carbon rod as a counter and a SCE as a reference electrode.

IrOx films were electrodeposited galvanostatically (35 μA/cm² for deposition times, \( t_{\text{dep}} \), of ca. 8 min) on the Au microelectrode surface from 6 mM IrCl₃ (Pressure Chemical) in 30 mM H₂C₂O₄ (Aldrich)|0.15 M K₂CO₃ (Fisher, certified ACS) aqueous solutions (pH = 10), as described by Petit et al.\(^{14}\). Subsequently, the IrOₓ|Au microelectrodes were rinsed with ultrapure water (Resistance, R = 18 MΩ) and transferred to a quartz cell (1 x 1 x 4.5 cm, Starna Cells) filled with deaerated (Ar) 0.5 M H₂SO₄, where simultaneous voltammetric and in situ normalized \( \Delta R/R \) measurements
were performed. For these experiments, a much larger Au foil (1.5 cm²) was used as a pseudo reference|counter electrode, the potential of which was calibrated against a SCE.

Normalized $\Delta R/R = (R_{\text{ref}} - R_s)/R_{\text{ref}}$, data, where $R_{\text{ref}}$ and $R_s$ represent, respectively, the intensity of light recorded by the detector for the electrode polarized at a reference, $E_{\text{ref}}$, and sampling, $E_s$, potentials, were collected using a focused CW laser beam (HeNe, 633 nm, JDS Uniphase 1144P, 15 mW), impinging at normal incidence onto the surface of the Au microelectrode, as described in detail elsewhere. The applied potential, and both the current, and the reflectance response signal (amplified by a high-speed ThorLabs PDA155, Si detector), were recorded and stored in a 0.5 GHz oscilloscope (Tektronix TDS 744A).

All experiments were carried out at room temperature, ca. 20 °C, using solutions prepared with ultrapure water (Barnstead). The data analysis was carried out using Origin.

1.4 RESULTS AND DISCUSSION

1.4.1 In situ normal incidence normalized differential reflectance of IrO$_x$|Au -
Shown in Fig. 1-1 are averaged cyclic voltammograms ($\nu = 50$ mV/s, number of acquisitions, $\text{Acq} = 11$, black solid circles, left ordinate) and normal incidence $\Delta R/R$ ($\lambda = 633$ nm, $E_{\text{ref}} = 0.20$ V, solid curves, right ordinate) vs $E$ for an IrO$_x$|Au microelectrode ($t_{\text{dep}} = 8$ min) in aqueous 0.5 M H$_2$SO$_4$ acquired simultaneously, prior to the potential step experiments described in the next section. The arrows in the $\Delta R/R$ vs $E$ traces point in the direction of the potential scan. Also displayed in this figure are the small and featureless
current (dotted line, left ordinate) and ΔR/R (solid line, right ordinate) vs E curves obtained for a bare Au microelectrode in the same electrolyte, while scanning the potential linearly toward positive values, under otherwise identical conditions. As indicated, the prominent voltammetric feature centered at ca. 0.67 V brings about very large changes in ΔR/R compared to those observed for bare Au over the same potential range. On this basis, the contributions to both the electrical and optical response due to the underlying substrate may be assumed to be negligible.

Correlations between the optical response and the charge injected into the film, Q, were initially sought by conventional coulometric techniques using a constant current baseline (see the dot-dashed line in Fig. 1-1), yielding a bilinear behavior shown by the solid thick line in Fig. 1-2. In order to avoid possible ambiguities derived from the arbitrary choice of baseline, values of Q were obtained by integrating the transient current response following potential steps both for oxidation (open circles, Fig. 1-2) and reduction (solid circles in the same figure) between a fixed initial, \(E_{\text{ini}} = 0.2\) V, and final potentials, \(E_{\text{fin}}\), in the range 0.47 – 0.8 V vs SCE. A statistical analysis of these data yielded a best-fit straight line (see the solid line) with \(R = 0.9992\), a slope \(S = 0.00885\) nC\(^{-1}\), and a very small intercept \(I = -0.00141\), affording strong evidence that ΔR/R over this specific potential range is indeed proportional to Q, the total charge injected into the film. An upper limit for the number of Ir sites in the IrO\(_x\) film, \(N_{\text{Ir}}\), can be obtained by assuming the voltammetric feature to be symmetric, and for Q to be ascribed entirely to a one-electron redox state change, formally, \(\text{Ir}^{\text{III}}\text{O}_x \leftrightarrow \text{Ir}^{\text{IV}}\text{O}_x\), consistent with in situ X-ray absorption fine structure (XAFS) measurements reported earlier in our laboratory. On this basis, \(N_{\text{Ir}}\) becomes proportional to twice the value of Q obtained following...
application of a potential step between \(E_{\text{ini}} = 0.2\) V (fully reduced film) and \(E_{\text{fin}} = 0.67\), i.e. the potential of the peak maximum (see the data in Fig. 1-3), yielding for this specific film, a value of ca. \(2.1 \times 10^{-13}\) mol.

### 1.4.2 Time-resolved spectroelectrochemical experiments

Preliminary measurements were aimed at determining the time required for the interface to achieve a constant value following a potential step both in the forward (\(E_{\text{ini}} \rightarrow E_{\text{fin}}\)) and reverse (\(E_{\text{fin}} \rightarrow E_{\text{ini}}\)) directions. As evidenced by the results obtained, a time of 2 s was found to be sufficient for the current to drop to average values not exceeding a fraction of a nA, and for the optical signal to reach a constant value, regardless of the direction of the step. The actual potential protocol is shown as an insert in the lower panels in Fig. 1-3, where \(\tau_{\text{ini}}\) and \(\tau_{\text{fin}}\), represent the time elapsed between application of the corresponding step. Due to memory constraints imposed by the digital oscilloscope employed, it was necessary to acquire the electrochemical and optical data separately for a positive step and a negative step over a time window shorter than 2 s (see the grey area in the inserts in the lower panels, Fig. 1-3), while applying continuously the potential protocol for fixed values of \(E_{\text{ini}}\) and \(E_{\text{fin}}\). Using this approach, the time resolution of the current response was significantly increased allowing a full quantitative comparison with the optical results in the short time domain.

Shown in Fig. 1-3 are plots of averaged (Acq 59 for oxidation, left panel; Acq 43 for reduction, right panel) \(\Delta R/R\) vs \(t\) (upper panel), and current vs \(t\) (middle panel), recorded simultaneously in aqueous 0.5 M H\(_2\)SO\(_4\), following application of the potential protocol in the inserts, i.e. \(E_{\text{ini}} = 0.20\) and \(E_{\text{fin}} = 0.67\) V vs SCE, i.e. between the fully
reduced and half-oxidized film, respectively, for $\tau_{\text{ini}} = \tau_{\text{fin}} = 2$ s (see the lower panel). Expansion of the curves in the middle panels of Fig. 1-3 (labeled as $\times 20$ and $\times 40$ and thus corresponding to a common time scale) revealed that, immediately after the step is applied, the absolute value of the current, $|i|$, undergoes an initial rapid increase, reaches a maximum, and then decreases gradually to negligible values regardless of the direction of the step. In fact, the time required for $|i|$ to attain a maximum was very similar for both the forward and backward steps.

Similar $\Delta R/R$ vs $t$ data were collected for a fixed $E_{\text{ini}} = 0.20$ V, and five other values of $E_{\text{fin}}$, specified in Fig. 1-2, i.e. six different amounts of charge $Q$ injected into the film, yielding the same qualitative behavior. The limiting (long time) values of $\Delta R/R$, recorded following each of the steps, shown by the large, solid grey circles in Fig. 1-1, were found to be slightly lower than those recorded during the potential scan measurements (see the corresponding lines in Fig. 1-1). We do not regard these differences as very significant, as independent runs yielded points very close to those of the dynamic measurements. In fact, the cyclic voltammogram and optical measurements collected simultaneously before initiation (see the solid black circles and the black line in Fig. 1-1) and after completion (see the empty circles and the grey line in Fig. 1-1) of the entire series of potential step experiments, were found to be virtually identical, indicating that the films do retain their overall integrity, even after ca. 550 stepwise charge-discharge cycles.

As clearly evidenced from the data shown in Fig. 1-3, (as well as that for other values of $E_{\text{fin}}$ not presented here), the current (center panel) drops to a very small value
before the optical signal (upper panel) reaches steady state, regardless of whether the film undergoes stepwise oxidation or reduction. Further insight into this behavior was obtained by comparing the rate of net electrochemical oxidation and reduction as measured by the current response, and the rate at which the Ir sites in the lattice undergo a change in oxidation state based on the optical signal.

Shown in Fig. 1-4 are plots of normalized $\Delta R/R$ and charge, $Q$, vs time (left ordinate) based on the integration of the current, following potential steps between ($E_{\text{ini}} \rightarrow E_{\text{fin}}$) (upper subpanels) and ($E_{\text{fin}} \rightarrow E_{\text{ini}}$) (lower subpanels) for $E_{\text{ini}} = 0.20 \text{ V}$ and $E_{\text{fin}} = 0.67 \text{ (panel A)}$ and $E_{\text{fin}} = 0.60 \text{ V (panel B)}$. The ordinates in the two curves in each panel were normalized, to match the initial and final values of $\Delta R/R$ and $Q$, yielding for each observable values between 0 and 1. As evidenced from these data, the measured time constants for both the charge and optical measurements are on the order of a few tenths of a second, and thus much longer than the RC time constant determined by optical means for a bare Au microelectrode under otherwise the same conditions, i.e. on the order of a few $\mu$s.

A careful inspection of these curves (as well as those involving all other values of $E_{\text{fin}}$ examined not shown here), revealed two important features:

i. The oxidation process is faster than the subsequent reduction, and, most importantly,

ii. The rate at which total charge injection and release occurs, as judged by the electrochemical data, appears faster than that at which the Ir sites undergo redox transitions, as evidenced from the optical data. This phenomenon
strongly suggests that charge can be stored in the film both in non-redox (capacitive, fast) and redox (pseudocapacitive, slow) sites.

In fact, a measure of the extent of charge injection into the two capacitors can be obtained by dividing the normalized $\Delta R/R$ by the $Q$ transients. The resulting curves shown by the jagged traces in Fig. 1-4 (see the right ordinate) yielded initial values as high as 0.80 increasing steadily thereafter to reach 1.0. This is equivalent to stating that the fraction of charge stored in the pseudocapacitor increases from a lowest value immediately after the step is applied to a limiting value as time elapses.

As has been well documented, IrO$_2$ (and RuO$_2$ as well) displays a relatively high electronic conductivity. In fact, band calculations place the Fermi level within the high density of states, mostly d-character band.$^{14}$ On this basis, the material would be expected to exhibit intrinsic capacitive characteristics not unlike those of a metal, and, as such, the extra charge should be localized on its surface. Furthermore, the rates at which an IrO$_2$ (or RuO$_2$) electrode immersed in an electrolyte would undergo charge or discharge would, in all likelihood, be governed (as in the case of a metal) by the RC constant of the cell (see above). It is thus conceivable that charge stored in the double layer intrinsic to this material could migrate into accessible Ir sites in the lattice, leading to a change in the oxidation state of the metal site, and elicit in turn modifications in the optical properties. This pseudocapacitive process would be accompanied by modifications in the geometric environment surrounding the metal sites, i.e. bond distances and bond angles, as eloquently demonstrated by the in situ XAFS studies,$^{14}$ as well as in the degree of protonation of the oxygen moieties, both of which would occur at a time scale slower
than that associated with the charge and discharge of the intrinsic interfacial double layer capacitor.

Similar experiments in other media should provide much needed insight into the role of protons on the overall dynamics of charge storage in IrO$_x$ films in aqueous electrolytes, the results of which will be shown in next chapter.

REFERENCES


Fig. 1-1. Simultaneous cyclic voltammograms (small scattered symbols, left ordinate) and normal incidence $\Delta R/R$ (solid lines, $E_{\text{ref}} = 0.20$ V, $\lambda = 633$ nm, right ordinate) obtained in neat deaerated 0.5 M H$_2$SO$_4$ at $v = 50$ mV/s for an iridium oxide (IrO$_x$) film electrodeposited on a Au microelectrode (25 μm diameter). The data represent the average of 11 acquisition (Acq) cycles. The electrochemical data in solid black and empty circles, and, correspondingly, the optical data in black and grey lines, were collected before and after the potential step measurements were completed, respectively. The dot-dashed line was used as a baseline for the coulometric analyses. The grey circles are $\Delta R/R$ values obtained following each potential step run. Also shown are the small and featureless current (see dotted line, left ordinate) and $\Delta R/R$ (solid line, right ordinate) vs E recorded simultaneously for a bare Au microelectrode surface in the same electrolyte while scanning the potential in the positive direction under otherwise identical conditions.
Fig. 1-2. Plots of $-\Delta R/R$ vs the integrated (or stored) charge $Q$ obtained from the coulometric analysis of the linear scan in the positive direction shown in solid scattered symbols in Fig. 1-1 in neat deaerated 0.5 M H$_2$SO$_4$ (see thick black solid line) using the dot-dashed line in that figure as a baseline for the integration. The data in open and grey circles in this figure correspond to the optical signal measured from the series of potential steps from $E_{\text{ini}} = 0.2$ vs SCE to $E_{\text{fin}}$ as specified next to each of the points, collected following oxidation and reduction, respectively. The best fit (see thin line), $R = 0.9992$, yielded slope $S$ and intercept $I$ of 0.00885 nC$^{-1}$ and -0.00141, respectively.
Fig. 1-3. Plots $\Delta R/R$ (upper panel) and $I$ (middle panel) vs time recorded simultaneously following a potential step between $E_{\text{ini}} = 0.2$ and $E_{\text{fin}} = 0.67$ V, as specified in the lower panel for an IrO$_x$ film in aqueous 0.5 M H$_2$SO$_4$. (left panel: Acq 59 for oxidation, right panel: Acq 43 for reduction). Also shown in the middle panels is the current response in an expanded and common time scale. The grey box in the insert of the lower panels indicates the time within the full protocol at which the data acquisitions were performed.
Fig. 1-4. Comparison between normalized $\Delta R/R$ vs time (jagged curves, left ordinate) and the integrated charge, $Q$, based on current integration (smooth curves, left ordinate) following potential steps between $E_{ini} = 0.20$ and $E_{fin} = 0.67$ V (panel A) and between $E_{ini} = 0.20$ and $E_{fin} = 0.60$ V (panel B). The upper and lower subpanels in each of these panels correspond to the oxidation and reduction steps, respectively. The ordinates in the two curves in each panel were normalized to match the initial and final values of $\Delta R/R$ and $Q$. The jagged traces (right ordinates) represent the ratio $(\Delta R/R)/Q$ based on the (normalized) data shown in the same subpanel.
CHAPTER 2: ELECTROCHEMICAL AND IN SITU OPTICAL STUDIES OF SUPPORTED IRIDIUM OXIDE FILMS IN AQUEOUS SOLUTIONS
2.1 ABSTRACT

The dynamic behavior of electrochemically deposited hydrous Ir oxide (IrO$_x$) films supported on Au microelectrodes during charge and discharge have been investigated by a combination of chronocoulometry and simultaneous in situ normalized reflectance spectroscopy techniques in aqueous solutions. Correlations between the reflectance spectra and the optical properties of the films in its various states of oxidation were sought from in situ transmission measurements for IrO$_x$ films supported on In-doped tin oxide on glass. The current transient response for IrO$_x$|Au microelectrodes following a potential step, within the voltage region in which the films display pseudocapacitive characteristics, was found to exhibit a well defined peak, as opposed to a monotonic decay reported by other groups. Some features of this behavior can be attributed to changes in the conductivity of the film as a function of its state of charge, as has been proposed for electronically conducting polymers. Also presented in this chapter are data collected over the pH range 0.3 – 13, which confirm the much faster charge-discharge dynamics in basic compared to acidic media. A primitive model based on proton conductivity within the hydrated oxide lattice is presented which accounts grossly for this pH induced effect.
2.2 INTRODUCTION

Electrochemical capacitors are expected to play a key role in meeting some of the challenges associated with energy storage and electrical power management in a variety of technological areas including transportation and microelectronics. Particularly attractive are electrode materials that display high specific capacities and fast rates of charge and discharge, such as the hydrated oxides of Ru and Ir in aqueous electrolytes. However, both of these metals are expensive and Ir is very scarce; hence, it is doubtful they will find wide use in large scale devices. Hydrated Ir oxide, to be denoted hereafter as IrO\texttextsubscript{x}, is currently being studied for functional neural stimulation applications, because of its biocompatibility and outstanding electrochemical characteristics. With some notable exceptions, most of the studies on IrO\texttextsubscript{x} have focused on electrochemical techniques aimed at gaining insight into various aspects associated with the charge and discharge of film-type electrodes in aqueous and, to a lesser extent, non-aqueous electrolytes.

From a general perspective, fundamental studies of fast heterogeneous redox dynamics require careful design of the experimental set up, as the physical size of the electrodes and the electrolyte conductivity largely determine the RC constant of the cell and thus the rate of the processes that can be reliably measured. The tactic herein employed for the in situ study of supported IrO\textsubscript{x} films involves a combination of microelectrodes and normal incidence normalized reflectance spectroscopy \(\Delta R/R = [R(E_s)–R(E_{ref})]/R(E_{ref})\), where \(R(E_s)\) and \(R(E_{ref})\) are proportional to the light collected at the detector for the electrode polarized at a sampling, \(E_s\), and reference \(E_{ref}\) potentials. The coupling of these methodologies is especially advantageous, as it exploits the often
high sensitivity and specificity of $\Delta R/R$ to changes in the redox state of molecular species or metal sites within film, and a reduction in the RC time constant of the cell derived from the small electrode size down to the $\mu$s domain.$^{22}$ Recently, implementation of this strategy in our laboratory made it possible to extract from the analyses of chronocoulometric and $\Delta R/R$ transients recorded simultaneously, dynamic redox (pseudocapacitive) contributions to the total charged stored in thin IrO$_x$ films electrodeposited on Au for potential steps within the region in which the material behaves as a pseudocapacitor.$^{24}$ As is well known, the intrinsic interfacial capacity, $C$, of Au in aqueous electrolytes in the voltage range in which IrO$_x$ exhibits redox activity is on the order of few tens of $\mu$F/cm$^2$ $^{25}$ and, thus, much lower than that of metallic Ir, the most common substrate material for studies of this type, over the same range. Such conditions enable the properties of very thin IrO$_x$ films to be examined without significant interference from the pseudocapacitance of the underlying support.

The primary aim of the present study was to expand our preliminary investigation to examine in more detail dynamic aspects of the electrochemical and simultaneous optical response of films of IrO$_x$ supported on Au microelectrodes as a function of their thickness and the initial and final states of charge. Experiments were performed in aqueous electrolytes over the pH range 0.3 to 13. As will be shown, and regardless of pH, the chronoamperometric curves displayed peak-like characteristics as opposed to a monotonic decay reported elsewhere in the literature.$^{26}$ Certain features of these results are consistent with changes in the film resistance with oxidation state as reported originally by Gottesfeld et al.$^{27}$ and, more recently by Fan et al.$^{28}$, and thus not with simple homogeneous diffusion.$^{26}$
2.3 EXPERIMENTAL

Gold microelectrodes were made by encasing a Au wire (Alfa Aesar 99.95%, 25 μm in diameter) in a glass micropipette (Clay Adams 10 μL) followed by polishing as described in Chapter 1. The IrOₓ films were electrodeposited galvanostatically at 35 μA/cm² for 8 min on the Au microelectrode surface from the aqueous solution containing 6 mM IrCl₃ (Pressure Chemical), 30 mM H₂C₂O₄ (Aldrich) and 0.15 M K₂CO₃ (Fisher, certified ACS) as described by Petit et al.²⁹ The equipment and techniques involved in the acquisition of simultaneous electrochemical, i.e. voltammetry and potential step, and in situ normalized reflectance, ΔR/R, data, have also been provided elsewhere.³⁰ Experiments were performed at room temperature in deaerated aqueous 0.5 M H₂SO₄ and 0.5 M HClO₄ (Ultrex ultrapure, pH ca. 0.3), 0.5 M acetate buffer (made by mixing NaOH and 0.5 M acetic acid, Fisher, pH = 4.0), 0.1 M phosphate buffer (made by mixing NaH₂PO₄ and Na₂HPO₄, Fisher, pH = 7.0), 0.3 M Na₂CO₃ (Fisher, certified ACS, pH = 10.9) and 0.1 M NaOH (Fisher, pH = 13) prepared with ultrapure water (Barnstead). The pH of the buffers was measured with a pH meter (Accumet model 15). A large Au foil (1.5 cm²) was used as a pseudo reference|counter electrode, the potential of which was calibrated against a commercial SCE (Fisher).

The transmission spectra of IrOₓ films in the UV visible range (ca. 400-800 nm) as a function of the applied potential were examined using a Cary 50 Bio UV-visible spectrophotometer. For these experiments, IrOₓ films were electrodeposited under galvanostatic conditions, at a constant current, i_{dep} = 35 μA/cm², for a deposition time, t_{dep} = 8 min, on rectangular sections (0.8 cm × 3 cm) of optically transparent, electronically conducting indium-doped tin oxide (ITO) films supported on glass (Delta
Technologies, 150×150×0.2 mm, sheet resistance $R_s < 10 \ \Omega$, PF-651N-1502). Prior to IrO$_x$ deposition, the bare ITO films were cleaned by ultrasonic agitation in a 1:1 ethanol:ultrapure water mixture. Freshly deposited IrO$_x$|ITO films were rinsed with ultrapure water and transferred to a quartz cuvette partially filled with electrolyte, which served as the electrochemical cell. In situ spectroelectrochemical measurements in the transmission mode were performed using a Au wire counter electrode and a SCE reference electrode placed in a separate compartment connected to the cuvette via a Teflon tubing. As evidenced from the results obtained, the voltammetric response of these films was in excellent agreement with those found for IrO$_x$|Au microelectrodes in the same solutions. All potentials in this work are referred to the SCE. Statistical analyses of the data were performed with Origin.

2.4 RESULTS AND DISCUSSION

Prior to performing in situ reflectance spectroscopy measurements on IrO$_x$ supported on Au, efforts were made to determine the optical properties of films as a function of potential in the transmission mode over a wide spectral region to avoid complications derived from the coupling of the optical constants in the reflectance mode to be addressed later in this section.

2.4.1 In situ UV visible spectroelectrochemical measurements of IrO$_x$|ITO in the transmission mode – Shown in the panels A and C, Fig. 2-1, are cyclic voltammograms for a single IrO$_x$|ITO ($t_{dep} = 8$ min) electrode in 0.5 M H$_2$SO$_4$ (panel A) and also in 0.3 M Na$_2$CO$_3$ (panel C) aqueous solutions recorded at a scan rate $\nu = 5$ mV/s. Since the level of the electrolyte could not be controlled accurately, the currents in the two media cannot
be readily compared. Nevertheless, the highly reversible peaks centered at 0.74 V in 0.5 M H$_2$SO$_4$ and -0.19 V in 0.3 M Na$_2$CO$_3$, attributed to the formal Ir$^{3+}$/Ir$^{4+}$ redox transition, as well as that at 0.13 V in the latter solution, ascribed to Ir$^{4+}$/Ir$^{5+}$ couple, are in excellent agreement with those reported in the literature. It can therefore be surmised, that the redox properties of IrO$_x$ films are not significantly affected by the nature of the underlying support. Strong evidence for these formal redox assignments has been obtained from in situ X-ray absorption fine structure from which the Ir-O distances for the proposed Ir$^{3+}$ and Ir$^{4+}$ sites in the oxide lattice were, within experimental error, identical in the two electrolytes. The wide (non ideal) character of the redox peaks is in all likelihood derived from differences in the activity coefficients for the oxidized and reduced sites. Such arguments were originally invoked by Anson for chemically modified electrodes involving single monolayers of surface confined redox active species. The reasons behind the much wider peak observed in acid compared to alkaline solutions, however, still remain to be elucidated.

Also displayed in this figure (panels B and D) are a series of in situ transmission UV-vis spectra of the same IrO$_x$|ITO recorded at different potentials in the two electrolytes, where the dotted line corresponds to the wavelength ($\lambda = 633$ nm) at which the $\Delta R/R$ experiments for IrO$_x$|Au microelectrodes were carried out. The absorbance in this case was calculated using the spectra of a different bare ITO immersed in the same electrolyte at open circuit as a reference. Two important aspects must be considered when analyzing these data:
i. The absorbance of bare ITO films was found to remain virtually unchanged as a
function of the applied potential over the spectral region specified in Fig. 2-1 and
therefore should not contribute to the potential difference measurements involving
the supported IrOₓ films.

ii. The intensity of the light reflected from the bare ITO may be different than that
from the corresponding IrOₓ|ITO. This second factor, as well as the difficulties in
placing the bare and film covered ITO in precisely the same position, may
introduce errors in the actual absorbance values, and could well account for the
negative values in the calculated absorbance (see, e.g. panel D, Fig. 2-1).

However, since the analysis of the ΔR/R involves data collected at a single
wavelength for a single film at a fixed position, such uncertainties should not
compromise the conclusions based on optical data drawn in this study.

In agreement with observations made much earlier in the literature,¹³, 32-36 IrOₓ
films are strongly electrochromic, becoming transparent when reduced and dark when
oxidized, regardless of the pH of the media. Based on these data, the changes in
absorbance at 633 nm as a function of potential are substantial, affording excellent optical
contrast, as will be discussed below. Somewhat surprisingly, the spectra of these
supported films are qualitatively different than those obtained in transmission for solution
phase IrOₓ hydrosols prepared by γ-radiolysis,³⁷ which displayed a very well defined
band centered at 600 nm in the pH range 3.4 to 11.0 at potentials at which the Ir sites in
the lattice would be in the formal 4+ oxidation state.
2.4.2 In situ normal incidence normalized differential reflectance of IrO₅|Au –

Shown in Fig. 2-2, are averaged cyclic voltammograms (v = 50 mV/s, black solid circles, left ordinates) and normal incidence $\Delta R/R$ ($\lambda = 633$ nm, black lines, right ordinates) vs E acquired simultaneously for an IrO₅(tdep = 8 min)|Au microelectrode (25 µm diameter) in 0.3 M Na₂CO₃ (E_ref = -0.70 V, Acq = 10, where Acq represents the number of averaged replicas of the same experiment), where the arrows point in the direction of the potential scan. As indicated, the voltammetric features associated with the Ir⁢³⁺/Ir⁢⁴⁺ couple elicit changes in $\Delta R/R$ ($\lambda = 633$ nm), which are much larger (about 8 times) than those associated with the Ir⁢⁴⁺/Ir⁢⁵⁺ counterpart. Also displayed in this figure are linear scan voltammograms (toward positive potentials, the dotted line) and $\Delta R/R$ vs E curves (the thick black curve) obtained for bare Au microelectrodes in the same electrolyte under otherwise identical conditions. As evident from the results obtained, the contributions of the intrinsic electroreflectance of Au to the total $\Delta R/R$ in the potential region where the Ir⁢³⁺/Ir⁢⁴⁺ transition occurs are indeed very small. As the potential becomes more positive and the Ir⁢⁴⁺ sites are further oxidized, the changes in $\Delta R/R$ for the bare Au and IrO₅|Au solution interface become of comparable magnitude, a factor that would make the differences in $\Delta R/R$ between the two redox transitions more pronounced. In contrast, the corresponding changes in the optical spectra recorded in the transmission mode at $\lambda = 633$ nm are only three times larger. Similar data collected in 0.5 M H₂SO₄ solutions was reported in Chapter 1 and will not be shown here.

It must be emphasized that the fact that Au at $\lambda = 633$ nm is highly reflective does not mean it can be regarded as a simple mirror. In fact, the classical Fresnel equations for
a three-phase stratified system with plane parallel boundaries “entangle” the optical constants of the three media in a highly non-linear fashion (see below).\textsuperscript{25, 38}

Shown in Fig. 2-3 (see the thick black solid line) is a plot of -$\Delta R/R$ vs the charge $Q$ determined from the coulometric analysis of the linear scan in the positive direction (see solid black circles in Fig. 2-2) in neat deaerated 0.3 M Na$_2$CO$_3$ using the dot-dashed line in Fig. 2-2 as a baseline for the integration. As discussed in Chapter 1, this type of analysis introduces uncertainties derived from the rather arbitrary choice of baseline. Far more accurate are measurements involving integration of the current transients following application of potential steps with a common initial value, $E_{ini}$, set here just negative to the onset of the more negative peak, i.e. $E_{ini} = -0.7$ vs SCE, and a final higher potential, $E_{fin}$, i.e. oxidation. The results of this type of analysis are given by the solid circles in Fig. 2-3, where the values specified refer to $E_{fin}$ and the open circles represent data involving the reverse step, i.e. reduction. The $\Delta R/R$ values determined at each potential are also shown in solid grey circles in Fig. 2-2 to illustrate that the optical measurements yield very similar results whether under steady state or dynamic modes. Since there is no a priori reason to assume that the voltammetric peak for the one electron Ir$^{3+}$|Ir$^{4+}$ couple is not symmetric, the total charge associated with the redox peak $Q_T$ is equal to $2Q_p$, i.e. twice the charge obtained from potential step experiments in which $E_{fin}$ was set at the peak potential of Ir$^{3+}$|Ir$^{4+}$ transition. It is interesting to note that films for which $t_{dep}$ was about the same yielded $Q_p$ values which are about 20-25% larger in acid compared to base. Furthermore, the relative changes in $\Delta R/R$ as a function of $Q$ when comparing common states of charge of the films, were also different in the two media. Specifically,
the change in $\Delta R/R$ for a film containing equal amounts of $\text{Ir}^{3+}$ and $\text{Ir}^{4+}$, i.e. half charged state, is 4% in base and about 9% in acid, and thus much larger than the difference in $Q_p$.

As was noted in Chapter 1, a plot of $-\Delta R/R$ and $Q$ in acid media was found to be highly linear, which is equivalent to state that $\Delta R/R$ is proportional to the number of (absorbing) redox sites within the entire redox peak formally attributed to the $\text{Ir}^{3+}/\text{Ir}^{4+}$ redox couple. Such a correlation has also been found in the analysis of in situ $\Delta R/R$ data involving redox active molecular species adsorbed at monolayer coverage on electrode surfaces.\textsuperscript{39-41} In stark contrast, however, the analysis of data collected in 0.3 M $\text{Na}_2\text{CO}_3$ yielded deviations from a strict linear behavior (see circles in Fig. 2-3), which suggests that the optical response cannot always be expressed as the sum of contributions due to the two redox-related species, in the Lambert-Beer’s sense, i.e. $\Delta R/R = \varepsilon_1 \theta + \varepsilon_2 (1 - \theta)$, where $\varepsilon_1$ and $\varepsilon_2$ are regarded as effective or empirical parameters. Also to be considered and not as yet explained is the fact that the transmission spectra for a half oxidized film is not the same in acid and in base.

2.4.3 Spectroelectrochemical Potential Step Experiments

Shown in Fig. 2-4 are averaged plots of $\Delta R/R$ vs $t$ (upper panel), and chronoamperometric transients (middle panel) recorded simultaneously in 0.3 M $\text{Na}_2\text{CO}_3$ for $E_{ini} = -0.7$ and $E_{fin} = -0.2$ V, i.e. from fully reduced to half oxidized states (see arrow). It must be stressed that the duty cycle in the protocol (see inserts, Fig. 2-4) was carefully adjusted so as to allow $\Delta R/R$ to reach a constant value, and for the current to drop to negligible levels, before application of the subsequent step (see below).
Application of the same potential protocol in the insert Fig. 2-4 to a bare Au-electrolyte interface yielded very fast transients (black lines) compared to the response of the supported film (red lines), as shown in Fig. 2-5 (panels B and D) for both the oxidation (panel B) and reduction (panel D) steps. Also depicted in this figure (panels A and C) are the corresponding data collected in 0.5 M H$_2$SO$_4$ for $E_{\text{ini}} = 0.2$ and $E_{\text{fin}} = 0.67$ V, which correspond to a potential step from fully reduced to half oxidized, i.e. the same states of charge as for the basic media. On this basis, the much slower response in both media can be assumed to be intrinsic to the supported IrO$_x$ films.

As evident from a comparison of the four ΔR/R transients involving the same potential protocol specified above (see Fig. 2-6), the oxidation (the black lines) and subsequent reduction (the red lines) processes are much faster in base (upper curves) compared to acid (lower curves). Note that the time scales for the curves in alkaline solution were multiplied by the factors indicated to emphasize this disparity. Also noteworthy is that fact that the oxidation is faster than the reduction in acid media, whereas precisely the opposite trend is found in base. In particular, the reduction step in the latter media was more than an order of magnitude faster than all other processes shown. The same general observation was made by Elzanowska et al.$^{26}$ for IrO$_x$ films formed on Ir metal although the shapes of the current transients did not exhibit the peak-like feature found in our work (see below).

Correlations between the extent of total charge injected, $Q$, and that attributed solely to the conversion of Ir$^{3+}$ to Ir$^{4+}$ sites, or pseudocapacitive contribution, can, in principle, be obtained by comparing the integral of the current transient with ΔR/R vs t.
This approach was implemented in Chapter 1, from which it was concluded that the capacitive charging in acid media was faster than the rate at which the pseudocapacitive Ir$^{3+}$ to Ir$^{4+}$ site conversion occurs. As depicted in Fig. 2-3, however, $\Delta R/R$ in basic media is not proportional to $Q$; hence, a similar analysis is not as straightforward. In fact, very small differences could be discerned for the transient $Q$ and $\Delta R/R$ data collected in 0.3 M Na$_2$CO$_3$, as shown in Fig. 2-7 for potential steps between $E_{\text{ini}} = -0.70$ V and $E_{\text{fin}} = -0.20$ (panel A), i.e. fully reduced and half oxidized states. Nevertheless, and, as would be expected, the transient $Q$, based on the few points specified in Fig. 2-3, appears slightly larger than the pseudocapacitive $\Delta R/R$-derived curve. The same behavior was found for the results of potential steps between $E_{\text{ini}} = 0.14$ and $E_{\text{fin}} = 0.30$ V which correspond, as shown in the insert, to the second peak, i.e. half-oxidized, and further oxidized film (see panel B, Fig. 2-7, Acq 314).

Shown in Fig. 2-8 are plots of the time required for the charge injected to reach half the total expected based on the applied step potentials, denoted as $t_{Q/2}$, both in acid (Panel A) and in base (Panel B). As indicated in the inserts in this figure, the solid circles correspond to oxidation and the open circles to reduction. In the case of the acid solution $t_{Q/2}$ decreases as $E_{\text{fin}}$, and thus the net charge stored, increases. In fact the same behavior is observed for the reduction, except that the overall rates become somewhat slower than for the oxidation. For the basic media, however, for which both processes occur much faster than in acid, the rates of reduction (see open circles) became rather independent of the state of charge for $E_{\text{fin}} > -0.2$ V. However, a very different behavior was found for the corresponding oxidation for which the rates slowed down with $E_{\text{fin}}$ for $E_{\text{fin}} < -0.2$ V, but
increased rather dramatically in the range $E_{\text{fin}} > -0.2$ V to reach for $E_{\text{fin}} > 0.14$ V ca. 0.5 ms.

Strong indication of the stability of the films was obtained by recording both the voltammetric and optical response immediately after the entire set of measurements was completed in both acid (see Ref. 24) and base (shown by open circles and grey lines in Fig. 2-2, respectively), which yielded virtually identical results as those collected at the beginning of the experiments (solid circles and black lines in Fig. 2-2).

In another series of measurements, correlations were sought between $t_{Q_p/2}$, the time required for the film to reach half $Q_p$, and $Q_t$ (see above), a parameter that provides a measure of the film thickness. As shown in Fig. 2-9, $t_{Q_p/2}$ increases with $Q_t$, except for reduction in the basic media, where the changes were hardly noticeable.

It is important to note that for acid solutions the position of the maximum in the chronoamperometric curves, $t_{i,\text{max}}$, remains virtually unchanged as $E_{\text{fin}}$ is changed both for oxidation (panel A, Fig. 2-10) and reduction (panel C in the same figure), yielding, within experimental error, a value of 1.2 ms. It should be emphasized that this value is about one order of magnitude larger than the time required for the full charging of the bare Au interface under the conditions selected for these experiments (see Fig. 2-5). Similar values of $t_{i,\text{max}}$ were observed for the oxidation in alkaline media for $E_{\text{fin}}$ within the potential range of the Ir$^{3+}$|Ir$^{4+}$ transition; however, for higher potentials, $t_{i,\text{max}}$ dropped to much smaller values, i.e. 0.2 ms. As was the case in acid, $t_{i,\text{max}}$ was found to be
independent of $E_{\text{fin}}$ for the reduction process, although its value, ca. 0.2 ms, was smaller than that measured in that media, ca. 1.2 ms.

In agreement with the reports of Gottesfeld et al.\textsuperscript{19} the shape of the chronoamperometric data observed in this work exhibits a peak like shape, as opposed to the simple decay reported by Birss and her group\textsuperscript{26}. This behavior is consistent with that found for the oxidation of poly(vinylferrocene) (PVF) films by Fan et al.,\textsuperscript{28} who implemented a model proposed earlier by Gottesfeld et al.\textsuperscript{27}, which accounts for changes in the conductivity of the material as a function of its extent of oxidation. As evidenced from their simulations, the chronoamperometric curves obtained following oxidation of the PVF not only showed a peak like behavior, but fairly good agreement with experimental data could be found by adjusting the magnitudes of the parameters involved in the model. It is well known that the conductivity of IrO$_x$ films does change with the extent of oxidation; hence, a mechanism of the type invoked by Gottesfeld and later by Fan et al. could well be responsible for the peak observed in the chronoamperogram during oxidation of our films. However, the fact that the same peak like behavior is also found during reduction with $t_{i,\text{max}}$ values that do not seem to depend on the direction of the step, point to other processes, such as plastic deformations induced by the different lattice constants of the film associated with the various redox states of the lattice sites, as contributing to this unique effect.

Perhaps the most interesting outcome of the present work pertains to the pH dependence of the rates at which films undergo charge injection and release using potential steps between the fully reduced and half charged sites in the lattice. Prior to
these experiments, the potential of the more negative redox peak \( E_{\text{peak}}^{\text{ox}} \) was plotted against pH (see Fig. 2-11) yielding for the slope of the best linear fit (see line in this figure) a value of 77 mV/pH (\( R = 0.995 \)), which is well within the range reported earlier in the literature.\(^{42}\) As depicted in Fig. 2-12, \( t_{0.5/2} \) decreased monotonically with pH for the reduction step (open circles) over the entire pH range examined. No such clear correlation was found for the oxidation step (solid circles), although the values for pH > 4 were definitely smaller than those found at the lowest pH. For pH ca. 0.3, two different electrolytes were examined, i.e. 0.5 M H\(_2\)SO\(_4\) (circles) and 0.5 M HClO\(_4\) (triangles). Although the dynamics were found to be faster in the latter compared to the former solution, the results for both media were slower than those observed at higher pH values.

A simple and indeed appealing model that might explain the slower rates found in the more acidic solutions relies on hopping dynamics arguments as will be discussed in the detail in the section to follow.

2.4.4 Hopping Dynamics

From a general perspective, the dependence of conductivity on concentration is sensitively dependent on the type of system in which the transport occurs. In a semiconductor, for example, in which the current is carried by delocalized electrons, which move in a more or less uniform potential, the conductivity increases monotonically with the concentration of electrons. The electron gas moves as a fluid, rather like water in a pipe. In flowing water there is automatically a space for each water molecule to move into, because all the water molecules are moving at roughly the same speed. In a similar
way, an electron in a semiconductor does not need to wait for another electron to move out of its way. Ions in a solid electrolyte, on the other hand, may tend to reside at discrete lattice sites that can only be singly occupied. In order for such an ion to move, there must be a vacancy into which it can hop. If the concentration of ions is too high, then gridlock sets in, and the current is reduced. One can see the mechanism involved in a simple one-dimensional model in which ions hop along a line under the influence of an applied field.

If the probability that a site $n$ is occupied is $c_n$, then the probability $P_{n,n+1}$ per unit time of a hop from site $n$ to site $n+1$ is proportional to $c_n$. It is, however, also proportional to $1-c_{n+1}$, since site $n+1$ must be empty in order to be able to receive the ion, and so

$$P_{n,n+1} = p_c c_n (1-c_{n+1}).$$

Here $p_+$ is the rate at which transitions would occur from site $n$, when it is known to be occupied, to site $n+1$, known to be empty. The probability of a transition in the reverse direction will be $P_{n+1,n} = p_c c_n (1-c_n)$. If we write $p_+ - p_- = \delta p$ and $c_{n+1} - c_n = \delta c$, the net current from $n$ to $n+1$ becomes $j_{n,n+1} = c_n (1-c_n) \delta p - p_\delta c$ when we neglect quantities of second order of smallness. The second term on the right-hand side is the usual diffusion term that arises from a concentration gradient, but the first term contains the significant information that the current due to the applied field is predicted to decrease with increasing concentration when $c > 1/2$. On this basis, it seems conceivable that at very low pH, the number of protonated sites increases leading to a decrease in the rates of oxidation and reduction. Yet another aspect that seems to support this model relates to the pH dependence of the dynamics of oxidation compared to reduction. As shown in Fig. 12, and discussed above, the rate of oxidation is faster than that for reduction only in solutions of the lowest pH examined, whereas the opposite is
observed for all media for pH > 4. Specifically, once the oxidation process is completed, the pH within the convoluted structure of the film should be lower than the pH of the bulk solution. For very low pH values, these conditions will lead to a further decrease in the proton conductivity within the film and thus in a corresponding drop in the rate of reduction as the experimental data indicates.

2.5 CONCLUSIONS

The most important observation emerging from these studies relates to the dependence of the rates of charge injection and release as a function of the pH of the solution. Specifically, and in agreement with the behavior observed by other workers over a much narrower pH range, the dynamics of charge injection and release are considerably slower in concentrated acidic solutions, i.e. pH ca. 0.3 compared to those observed at higher pH values. This behavior has been explained in terms of a hopping mechanism, where an increase in the charge carrier concentration within the film, in all likelihood (hydrated) protons leads to congestion and thus in lower overall mobilities. Further evidence in support of this proposed mechanism is provided by the fact that the oxidation for the most acidic media is faster than the subsequent reduction, a behavior opposite to that found for solutions of higher pH.

REFERENCES


Fig. 2-1. Cyclic voltammograms ($\nu = 5$ mV/s) of a single IrO$_x$|ITO film ($t_{dep} = 8$ min) in aqueous 0.5 M H$_2$SO$_4$ (panel A) and 0.3 M Na$_2$CO$_3$ (panel C) deaerated solutions and in situ UV-vis spectra (panels B and D) of the same film at different specified potentials recorded in the corresponding electrolytes using the spectra of bare ITO at open circuit in the same media as a reference. The dotted line represents the wavelength at which the reflectance spectroscopy measurements were performed, i.e. 633 nm.
Fig. 2-2. Simultaneous cyclic voltammogram ($\nu = 50$ mV/s, solid black circles, left ordinate) and normal incidence $\Delta R/R$ ($\lambda = 633$ nm, sigmoidal black line, right ordinate) recorded in 0.3 M Na$_2$CO$_3$, ($E_{\text{ref}} = -0.70$ V, Acq = 10), obtained for an IrO$_x$ ($t_{\text{dep}} = 8$ min)Au microelectrode (25 $\mu$m diameter). The dot-dash line was used as a baseline for the coulometric analysis. Also shown in the upper thicker solid curves in this figure is the $\Delta R/R$ vs E curve obtained for a bare Au microelectrode surface in the same electrolyte collected during scans toward positive potentials under otherwise identical conditions (see dotted lines). The open circles in the voltammetric curve and the sigmoidal grey $\Delta R/R$ curve were obtained after all the experiments were completed. The scattered grey circles are the amplitudes of $\Delta R/R$ obtained from the series of potential steps (see text for details).
Fig. 2-3. Plot of $-\Delta R/R$ vs the integrated (or stored) charge $Q$ obtained from the coulometric analysis of the linear scan in the positive direction shown in black solid circles in Fig. 2-2, in neat deaerated 0.3 M Na$_2$CO$_3$ (see thick black solid line) using the dot-dash line in Fig. 2-2 as a baseline for the integration. The data in solid black and open circles in this figure correspond to the optical signal measured from the series of potential steps for $E_{\text{ini}} = -0.7$ vs SCE to $E_{\text{fin}}$ as specified next to each of the points, collected following oxidation and reduction, respectively.
Fig. 2-4. Plots of $\Delta R/R$ (upper panel) and $I$ (middle panel) vs time recorded simultaneously following a potential step between $E_{\text{ini}} = -0.7$ and $E_{\text{fin}} = -0.2$ V for an IrO$_x$ film in 0.3 M Na$_2$CO$_3$. (panel A: Acq 130 for oxidation, panel B: Acq 308 for reduction). Also shown in the middle panels is the current response in an expanded time scale.
Fig. 2-5. Current transients for IrO$_x$|Au films (red lines) following a potential step between fully reduced and half-oxidized states in 0.5 M H$_2$SO$_4$ (panels A and C) and 0.3 M Na$_2$CO$_3$ (panels B and D) for both oxidation (panels A and B) and reduction (panels C and D). The black thin lines were collected following a step between the same precise initial and final potential for bare Au in the same two electrolytes.
Fig. 2-6. Comparison of ΔR/R vs t for potential steps between the fully reduced and half-oxidized films in the forward (black lines) and the backward (red lines) directions in 0.5 M H₂SO₄ (Eᵢᵣᵣ = 0.20 V, Eᵢᵣᵣᵣ = 0.67 V) and 0.3 M Na₂CO₃ (Eᵢᵣᵣᵣᵣ = -0.70 V, Eᵢᵣᵣᵣᵣᵣᵣ = -0.20 V). The sign of ΔR/R for the backward step was reversed to emphasize the differences in the rates of the oxidation and reduction processes.
Fig. 2-7. Plots of integrated charge, Q (see smooth curves, left ordinate), and transient normalized ΔR/R (scattered points, right ordinate), following potential steps between \( E_{\text{ini}} \rightarrow E_{\text{fin}} \) (oxidation, upper panels) and \( E_{\text{fin}} \rightarrow E_{\text{ini}} \) (reduction, lower panels) for \( E_{\text{ini}} = -0.70 \) V and \( E_{\text{fin}} = -0.20 \) (panel A), and \( E_{\text{ini}} = 0.14 \) and \( E_{\text{fin}} = 0.30 \) V (panel B, Acq 314) in 0.3 M \( \text{Na}_2\text{CO}_3 \).
Fig. 2-8. Plots of $t_{Q/2}$ as a function of $E_{\text{fin}}$ for the potential steps in the forward (black circles) and the backward (open circles) directions in 0.5 M H$_2$SO$_4$ (panel A) and 0.3 M Na$_2$CO$_3$ (panel B).
Fig. 2-9. Plots of $t_{Q_p/2}$ as a function of $Q_t$ for the potential steps in the forward (black circles) and the backward (open circles) directions in 0.3 M Na$_2$CO$_3$ (panel A) and 0.5 M H$_2$SO$_4$ (panel B).
Fig. 2-10. Series of chronoamperograms recorded for $E_{\text{ini}} = 0.20 \text{ V}$ for various values of $E_{\text{fin}}$ as shown in Fig. 2-8 in 0.5 M $\text{H}_2\text{SO}_4$ (panel A) and 0.3 M $\text{Na}_2\text{CO}_3$ (panel B). The plots in panels C and D were obtained upon reversing the potential step.
Fig. 2-11. Plot of $E_{\text{peak}}^{ox}$ vs pH (see text).
Fig. 2-12. Plot of $t_{Q_{1/2}}$ vs. pH for potential steps in the forward (black circles), i.e. from the fully reduced to the half oxidized states and backward (open circles) directions. The data in open and solid circles were obtained in 0.5 M H$_2$SO$_4$ and the corresponding triangles in 0.5 M HClO$_4$. 
CHAPTER 3: OXYGEN REDUCTION ON SUPPORTED IRIDIUM OXIDE FILMS IN NEUTRAL PHOSPHATE BUFFER: IMPLICATIONS FOR NEURAL STIMULATION
3.1 ABSTRACT

Certain aspects of oxygen reduction on (hydrous) iridium oxide (IrO_x) films deposited galvanostatically on smooth Au and glassy carbon (GC) electrodes have been examined in aqueous O_2-saturated neutral phosphate buffer (pH = 7) solutions. Regardless of the nature of the substrate, the onset potential for O_2 reduction, \( E_{onset}^{O_2} \), as determined by cyclic voltammetry, was ca. -0.1 V vs SCE, which is very close to the corresponding \( E_{onset}^{O_2} \) found for both bare Au and GC electrodes. On this basis, the potential range in which charge stored in the film is available for functional neural stimulation without generation of potentially harmful oxygen-derived species is on the order of 0.9 V. Studies involving a rotating Pt ring-GC disk revealed that the reduction of dioxygen on IrO_x|GC yields predominantly hydrogen peroxide. Further measurements performed with a rotating GC disk showed that IrO_x|GC can oxidize hydrogen peroxide in the potential region associated with the more positive IrO_x redox peak, a factor that might mitigate, at least in part, problems associated with charge imbalance during bipolar neural stimulation.
3.2 INTRODUCTION

Iridium oxide in its hydrous form (IrO$_x$) has emerged as one of the most promising materials for applications in the area of functional neural stimulation (FNS).$^{1,2}$ In addition to its biocompatibility, IrO$_x$ can reversibly store relatively large amounts of charge, which can be released or injected over very short periods of time. As is well known, FNS involves application of short negative current pulses, which can polarize the stimulating electrode at potentials where faradaic processes could ensue. Of particular concern is the reduction of dioxygen, a reaction that can generate species, such as peroxide and superoxide, which can directly or indirectly attack the neural membrane.$^2$ Although no consensus has yet been reached regarding the extent to which such species contribute to the irreversible degradation of neural tissue, it is important to determine the potential range in which such undesirable redox processes could be avoided and whether methods could be implemented to reduce the concentration of such harmful species. This chapter examines certain aspects of oxygen reduction in aqueous O$_2$-saturated phosphate buffer solutions (pH = 7) on IrO$_x$ films grown electrochemically on a host metal support by galvanostatic techniques, which complements data reported in the literature in aqueous acidic media$^{3-5}$ for the same electrode material. As will be shown, the onset of O$_2$ reduction, $E^{O_2}_{\text{onset}}$, on IrO$_x$ supported on either Au or GC is very negative, i.e. ca. -0.1 V vs SCE, and virtually identical to $E^{O_2}_{\text{onset}}$ found for bare Au and GC electrodes. This behavior is in stark contrast with that observed for electrochemically deposited Ir metal on Au for which $E^{O_2}_{\text{onset}} = +0.2$ V. Furthermore, the voltage range in which IrO$_x$ films exhibit pseudocapacitive characteristics i.e. no faradaic processes, in such O$_2$-saturated solutions,
is about 0.9 V, allowing a very significant fraction of the charge stored upon full oxidation to become available for (negative) charge injection as required for FNS. Additional studies revealed that the main product of dioxygen reduction on IrO$_x$ supported on GC is hydrogen peroxide, a species that can be oxidized on the same film to yield O$_2$ at potentials within the region associated with the more positive IrO$_x$ redox peak.

3.3 EXPERIMENTAL

Au microelectrodes were fabricated by melting a glass micropipette around a Au wire (25 μm in diameter) and then polishing the end to expose an embedded disk surface. Additional studies revealed that the main product of dioxygen reduction on IrO$_x$ supported on GC is hydrogen peroxide, a species that can be oxidized on the same film to yield O$_2$ at potentials within the region associated with the more positive IrO$_x$ redox peak.

3.3 EXPERIMENTAL

Au microelectrodes were fabricated by melting a glass micropipette around a Au wire (25 μm in diameter) and then polishing the end to expose an embedded disk surface. Also specified elsewhere are the methods used for the galvanostatic deposition of IrO$_x$ films, i.e. 35 μA cm$^{-2}$ for 8 min, from 6 mM IrCl$_3$ in 30 mM H$_2$C$_2$O$_4$|0.15 M K$_2$CO$_3$ solutions. Ir metal was electrodeposited onto Au galvanostatically, i.e. 20 mA cm$^{-2}$ for 1 h, from 1 g/L (ca. 2 mM) Na$_2$IrCl$_6$ in 0.1 M HCl. A carbon counter electrode was used in all the experiments to prevent metal contamination of the IrO$_x$ films. Experiments involving glassy carbon (GC) were performed using either a GC rotating disk electrode (RDE, Pine Instruments) with a cross sectional area of 0.164 cm$^2$ or a rotating ring (Pt)-disk (GC) electrode (RDE, Pine Instruments) in 0.1 M phosphate buffer solutions (pH = 7) (Na$_2$HPO$_4$, NaH$_2$PO$_4$, Baker ultrapure).

3.4 RESULTS AND DISCUSSION

Shown in Panel A, Fig. 3-1 are cyclic voltammograms recorded for a Au microelectrode (25 μm in diameter) at a scan rate, v = 50 mV/s, before (black), and after deposition of Ir metal (red), and IrO$_x$ (blue) (see Experimental Section for details) in Ar-
saturated 0.1 M phosphate buffer (pH = 7). These curves are in excellent agreement with those believed to be characteristic of the materials in question. Corresponding data collected for these electrodes in the same, albeit O₂-saturated solutions at v = 5 mV/s, are given in Panel B in this figure. Not surprisingly, the overpotential for O₂ reduction was found to be much smaller for Ir metal on Au than for IrOₓ on Au. In fact, in the latter case, the onset for O₂ reduction, E_{onset}^{O₂}, ca. -0.1 V vs SCE, was very similar to that found on bare Au.

Insight into the possible role of the substrate on the electrochemical properties of the IrOₓ films was obtained by performing experiments using a GC electrode as a support. Shown in Panel A, Fig. 3-2, are cyclic voltammograms (v = 50 mV/s) of a GC RDE in N₂-purged (thin line) and O₂-saturated (thick line) 0.1 M sodium phosphate buffer (pH 7), recorded at a rotation rate ω = 400 rpm. Corresponding data for IrOₓ|GC electrodes under otherwise identical conditions are displayed in Panel B in this figure. No changes in E_{onset}^{O₂} could be observed for both types of surfaces upon increasing ω to 3600 rpm (not shown). It may be surmised from these results that the redox peaks characteristic of IrOₓ (at pH = 7) are not affected by the presence of O₂, nor by the rotation rate down to ca. -0.1 V. Furthermore, E_{onset}^{O₂} for the supported IrOₓ films was very close to that found for bare GC. This behavior is analogous to that found for Au. On this basis, the potential range over which IrOₓ films behave as strict pseudocapacitors (no faradaic reactions) is about -0.9 V, which, serendipitously, corresponds to the same range in which virtually all the reversible charge can be stored in solutions devoid of O₂. This range is in good agreement with that reported recently by Wang et al.² for IrOₓ films.
prepared by reactive sputtering on Ti films supported in turn on polymeric layers in similar electrolytes. However, several aspects of that work merit attention; specifically,

i. The potentials limits are more positive than those found by other workers.

ii. The voltammetric curves revealed peaks associated with the pseudocapacitive behavior of IrO$_x$ not as well defined as those published elsewhere in the literature.

iii. The oxidation and reduction counterparts for each of these peaks were very much displaced with respect to one another, a phenomenon related in all likelihood to IR losses within the film.

iv. A rather large charge was found in the negative potential end as opposed to the drop found in our work and that of many others. This additional pseudocapacity could be related to the formation of Ti oxide during the preparation of the film following extensive cycling, which, as shown by Ravichandran et al.,$^{10}$ shows a very well defined peak precisely in the area negative to the more negative peak of IrO$_x$.

Further support for the inhibitory character of IrO$_x$ toward O$_2$ reduction was obtained from experiments involving Ir metal deposited on a Au microelectrode. Shown in Panel A, Fig. 3-3, are cyclic voltammetry curves recorded in Ar-saturated 0.1 M phosphate buffer (pH = 7) solutions ($\nu = 50$ mV/s), as a function of the potential at which the scan in the positive direction was reversed, $E_+$. As clearly evidenced from these data, an increase in $E_+$ gives rise to an increase in the magnitude and position of a peak found in the subsequent scan in the negative direction (centered at ca. -0.2 V and thus positive
to the hydrogen adsorption/desorption region), attributed to the reduction of the IrO\textsubscript{x} formed at the more positive potentials. Polarization curves recorded at $v = 10$ mV/s in O\textsubscript{2}-saturated 0.1 M phosphate buffer (pH = 7) for Ir surfaces following excursion to the same $E_+$ values as those specified in Panel A, Fig. 3-3, are shown in Panel B in the same figure. As indicated, the more positive $E_+$, and thus the thicker the IrO\textsubscript{x} film produced, the more negative $E_{\text{onset}}^{O_2}$ becomes during the negative scan. However, virtually identical curves as those obtained for nominally oxide free Ir metal surfaces, i.e. common $E_{\text{onset}}^{O_2}$, were found upon reversing the scan at $E = -0.6$ V. This observation is consistent with the reduction of such thin IrO\textsubscript{x} films in the negative potential region. In contrast, thicker IrO\textsubscript{x} films formed on Ir metal by cycling repeatedly up to 0.7 V vs SCE could not be reduced even after polarizing the electrode at -0.6 V for several minutes yielding a voltammetric curve (see scattered data in Fig. 3-4, following 28 scans after 10 min at the specified potential) virtually identical to that recorded just prior to holding the potential at this very negative value (see solid line through the scattered points). No evidence for film reduction was also found for IrO\textsubscript{x} films deposited on Au after holding the potential at -0.6 V for 5 min (not shown here).

Despite the inability of IrO\textsubscript{x} films to reduce O\textsubscript{2} in the electrolyte selected for these studies over a wide voltage range, the reduction of other species appears to proceed with relative ease. This behavior is clearly illustrated by comparing the cyclic voltammograms ($v = 10$ mV/s) obtained with a Au microelectrode before (black) and after deposition of an IrO\textsubscript{x} film (blue) in Ar-saturated 0.1 M phosphate buffer (pH = 7) containing 10 mM K\textsubscript{3}Fe(CN)\textsubscript{6} shown in Fig. 3-5, where the red curve was obtained after subtracting
contributions due to the pseudocapacitance of IrOx shown in the insert in the same figure. Based on accepted values for the diffusion coefficient of $[\text{Fe(CN)}_6]^{3-}$, i.e. $7.2 \times 10^{-6}$ cm$^2$/s,$^{11}$ its bulk concentration and the radius of the microelectrode, the theoretically predicted value for the limiting current, $i_{\text{lim}} = 4nFc_oD_or$, was found to be ca. 35 nA and thus in good agreement with those observed in this work (see Fig. 3-5).

Insight into the mechanism of dioxygen reduction on supported IrOx films was obtained using an IrOx film electrodeposited on the GC disk of a Pt|GC rotating ring disk electrode (RRDE). For these experiments, the Pt ring was polarized at +0.5 V, a potential positive enough for the oxidation of peroxide to proceed under pure diffusion control in this specific electrolyte (not shown here). As shown in Fig. 3-6, $E^{\text{O}_2}_{\text{onset}}$ on the disk (Panel A) was found to be identical to that of the oxidation current at the ring (Panel B) regardless of rotation rate within the range examined. As is well known, the ratio of the (diffusion limited) ring, $i_r$, to disk, $i_d$, currents involving the same number of electrons should be equal to the collection efficiency, $N$, of the RRDE (0.22 for this specific unit). Plots of $i_r/i_d$ based on these data given in Panel C, Fig. 3-6, yielded values somewhat lower than $N$, which decreased as $\omega$ increased. This effect is consistent with deactivation of the Pt ring often attributed to impurities in the electrolyte solution, which are often avoided by briefly polarizing the Pt ring to relatively high potentials. Such an approach, however, leads to Pt dissolution which could later deposit on the disk and thus affecting the response of the (disk) material under study. It may, nevertheless, be concluded based on these results, that the reduction of dioxygen on IrOx at pH = 7 yields significant
amounts of peroxide, a species believed to affect adversely and irreversibly biological tissue.

As mentioned earlier, neural stimulation involves application of a negative current pulse which is often followed by yet another pulse of albeit of opposite polarity. It is then of interest to examine the electrocatalytic activity of IrO$_x$|GC toward hydrogen peroxide oxidation. Shown in Panel A, Fig. 3-7 are cyclic voltammograms ($\nu = 50$ mV/s) of IrO$_x$|GC obtained in quiescent 0.1 M sodium phosphate buffer solution (pH = 7) in the absence (black curve) and in the presence (red curve) of 1 mM H$_2$O$_2$. As clearly evidenced from these data, the increase in the current at ca. 0.35 V (which happens to coincide with the onset of the more positive redox peak) is consistent with the oxidation of peroxide to yield O$_2$, which can be detected electrochemically during the scan in the reversed direction starting at about -0.1 V vs SCE, i.e. precisely the same $E_{\text{onset}}^{\text{O}_2}$ that observed previously in O$_2$-saturated solutions. Also shown in this figure are the results obtained for bare GC, for which the current due to peroxide oxidation was significantly smaller. A better illustration of the ability of IrO$_x$ to oxidize peroxide is provided by the plot shown in Panel B, Fig. 3-7, which displays the current due strictly to the redox process determined upon subtraction of the pseudocapacitive contribution intrinsic to the film. Similar results have been reported by Terashima et al. for IrO$_x$ supported on boron-doped diamond.$^{12}$ Despite its relatively slow kinetics the oxygen/peroxide couple appears responsible for the sensitivity of IrO$_x$ to the presence of dioxygen in solution which makes it suitable as a potentiometric sensor material.$^{13}$
In summary, studies involving IrO$_x$ films deposited galvanostatically on smooth Au and GC in O$_2$-saturated neutral phosphate buffer (pH = 7) aqueous solutions showed that the onset for O$_2$ reduction occurs at ca. -0.1 V vs SCE regardless of the nature of the substrate. On this basis, the potential range in which IrO$_x$ films behave as strict pseudocapacitors in this media is about 0.9 V indicating that ca. 90% of the total charge that can be stored in the film could be utilized for neural stimulation without generation of potentially toxic oxygen-derived radicals or other species.

REFERENCES


Fig. 3-1. Cyclic voltammograms of a Au microelectrode (25 μm in diameter) before (black), and after deposition of Ir metal (red) and Ir oxide (blue), recorded in Ar-saturated (Panel A, scan rate, ν = 50 mV/s) and in O₂-saturated (Panel B, ν = 5 mV/s) 0.1 M phosphate buffer (pH = 7). See Experimental Section for details.
Fig. 3-2. Panel A. Cyclic voltammograms ($\nu = 50 \text{ mV/s}$) of a glassy carbon (GC) rotating disk electrode (cross sectional area: $0.164 \text{ cm}^2$), in N$_2$-purged (thin line) and O$_2$-saturated (thick line) 0.1 M sodium phosphate buffer, pH 7, recorded at a rotation rate $\omega = 400$ rpm. Panel B. Same as Panel A after deposition of an IrO$_x$ film on the GC surface under otherwise identical conditions.
Fig. 3-3. Panel A. Cyclic voltammograms of Ir metal deposited on a Au microelectrode recorded in Ar-saturated 0.1 M phosphate buffer (pH = 7) solutions (v = 50 mV/s) as a function of the potential at which the scan in the positive direction was reversed, E+. Panel B. Cyclic voltammograms of Ir metal deposited on a Au microelectrode in O₂-saturated 0.1 M phosphate buffer (pH = 7) recorded at v = 10 mV/s for the values of E+ specified. Note that regardless of the value of E+, all (subsequent) scans in the positive direction yielded a common curve (see text for details).
Fig. 3-4. Cyclic voltammograms (ν = 50 mV/s) of Ir metal deposited on Au microelectrode in Ar-saturated 0.1 M phosphate buffer (pH = 7) before (black curve) and after applying 18 (red) and 28 (blue) scans in the potential region -0.6 V < E < 1.0 V. The corresponding curve in scattered symbols was collected after polarizing the electrode that yielded the blue curve at a potential E = -0.6 V for 10 min.
Fig. 3-5. Cyclic voltammograms ($\nu = 10$ mV/s) recorded with a Au microelectrode before (black) and after deposition of an IrO$_x$ film (blue) in Ar-saturated 0.1 M phosphate buffer (pH = 7) containing 10 mM K$_3$Fe(CN)$_6$. The red curve was obtained after subtracting current contributions due to the pseudocapacitance of the IrO$_x$ film (see insert).
Fig. 3-6. Panel A. Dynamic polarization curves ($\nu = 10$ mV/s) for a IrO$_x$|GC disk of a RRDE ($N = 0.22$) in O$_2$-saturated 0.1 M sodium phosphate buffer solution (pH=7) at different rotation rates $\omega = 400$ (black), 900 (red), and 1600 (blue) rpm. Panel B. Response of the Pt ring electrode polarized at +0.5 V vs SCE. Panel C. Ring Current/Disk Current ($I_r/I_d$) in the range -0.5 to -0.35 V vs SCE.
Fig. 3-7. Panel A. Cyclic voltammograms ($\nu = 50$ mV/s) of IrO$_x$|GC in the absence (black curve) and in the presence (red curve) of 1 mM H$_2$O$_2$ in 0.1 M sodium phosphate buffer solution (pH = 7). Corresponding data for the bare GC substrate for which the currents are much smaller are shown in black and red lines. Panel B. Current associated with hydrogen peroxide oxidation on bare GC (dotted lines) and IrO$_x$|GC electrodes (solid line)
CHAPTER 4: SPATIALLY-RESOLVED INTERFACIAL ELECTROCHEMISTRY: OHMIC MICROSCOPY
4.1 ABSTRACT

A method is herein described that allows spatially-resolved capacitive currents at electrode|electrolyte interfaces to be recorded in situ by monitoring the ohmic drop in the electrolyte, $\Delta \varphi_{\text{sol}}$, using two microreference electrodes. Measurements were performed in 0.1 M H$_2$SO$_4$ aqueous solutions using Au and Pt either as single, or dual working electrodes, i.e. connected to one another, in an otherwise conventional three electrode electrochemical cell. Plots of $\Delta \varphi_{\text{sol}}$ vs E, the potential of the dual Au|Pt electrode with respect to the main reference electrode, recorded during voltammetric cycles, yielded curves bearing features characteristic of the Au|0.1 M H$_2$SO$_4$ or Pt|0.1 M H$_2$SO$_4$ interface depending on where the microreference electrodes were placed close to the Au or Pt electrode surface, respectively. Extensions of this methodology to measurements in the $\mu$m domain are briefly discussed.
4.2 INTRODUCTION

The passage of current through an electrolyte brings about changes in the electrostatic potential, \( \varphi_{\text{sol}} \), within that phase. As described by Miller and Bellavance\(^1\) in their pioneering studies of current distribution to a rotating disk electrode, and by Burnette et al.\(^2\) for the characterization of transport through skin during iontophoresis, such differences in \( \varphi_{\text{sol}} \), denoted hereafter as \( \Delta \varphi_{\text{sol}} \), can be measured using two microreference electrodes. Advantage has been taken of this tactic to acquire local electrochemical impedance spectroscopy data by Isaacs et al.\(^3,4\) and, more recently, by Orazem, Vivier and Tribollet.\(^5\) Also closely related is the work of Amatore,\(^6-8\) who employed a microreference electrode for monitoring concentration profiles within the diffusion boundary layer induced by faradaic reactions at electrode|electrolyte interfaces.

This chapter describes the use of two identical Ag/AgCl microreference electrodes for monitoring current flow in aqueous 0.1 M H\(_2\)SO\(_4\) associated with capacitive interfacial reactions at Pt and Au electrodes during voltammetric cycles. Experiments were performed in which the two noble metal electrodes were electrically connected to one another, yielding, as expected, a combined voltammetric response containing contributions characteristic of both Au and Pt in this electrolyte. As the microreference electrodes were approached to either one of the two working electrodes, while the potential of the dual working electrode was being scanned, \( \Delta \varphi_{\text{sol}} \) displayed features ascribed to the specific neighboring metal|solution interface.

Additional experiments involving either Au or Pt revealed that the magnitude of \( \Delta \varphi_{\text{sol}} \) decreased as the distance of the microreference electrodes from the surface of the
working electrode increased. This behavior is consistent with that expected based on an instantaneous primary current distribution and thus in harmony with interfacial processes for which the rates are infinitely fast compared to the time scale of the voltammetric cycles.

4.3 EXPERIMENTAL

All measurements were carried out in 0.1 M H₂SO₄ (Ultrex) aqueous solutions prepared from ultrapure water (Barnstead) purged with Ar (Praxair) in a glass cell equipped with two side arms separated from the main compartment by glass frits. The potential of the working electrode(s) was controlled by a conventional potentiostat (RDE3 Pine Instruments) coupled to an external waveform generator (EG&G Parc Model 175 Universal Programmer).

Two types of working electrodes were used for these experiments: a set of two individual commercial disks encased in a polymeric resin (Au and Pt, Bioanalytical System, 2 mm in diameter) (see Fig. 4-1), and a composite Au and Pt electrode, made by mechanically contacting two foils (see below). A carbon rod was used as a counter electrode and a commercial Ag/AgCl was used a reference electrode for acquiring conventional cyclic voltammetry.

Microreference Ag/AgCl electrodes were prepared by inserting a 5 cm long polished Ag wire (200 μm diameter, Alfa Aesar 99.95 %), which had been placed in contact with a saturated KCl solution for ca. 2 h, into a pulled (Sutter P2000 micropipette puller) commercial quartz capillary (O.D. 1mm I.D. 0.5mm, Sutter). The settings of the
puller were adjusted to give a taper length of ca. 5 cm and an opening size in the range of 30 to 200 nm. For the series of experiments described in this work, the tip of the microcapillaries was cut to give an opening size of ca. 100 μm. After pulling, the pipettes were allowed to cool off and then placed in saturated solution of KCl overnight in a special filler storage unit (Sutter), to maximize capillary filling action and eliminate bubble formation. Once assembled, the Ag/AgCl microreference electrodes were stored in a KCl(sat) solution and their stability tested against a commercial Ag/AgCl electrode.

The two microreference electrodes (M1 and M2, see Fig. 4-1) were always placed parallel and at a distance Δm from each other along a plane normal to the electrode surface, forming a shallow angle with the respect to the working electrode surface. As indicated in Fig. 4-1, the microreference electrode closer to and further away from the working electrode surface are labeled as M1 and M2, respectively. Efforts were made to shift this dual array with the tips along the axis normal to the electrode surface labeled as z in the figure. For clarity, the distance between the wall of M1 and the electrode surface will be defined as ΔM, i.e. ΔM = 0 corresponds to the position at which the wall of M1 touches the working electrode. Both Δm and ΔM were adjusted using a set of micromanipulators (NRC Fountain Valley). Potential differences between M1 and M2, i.e. Δφ_{sol}, were recorded using a Keithley digital multimeter (Model 2100), while scanning the potential of the working electrode(s).

4.4 RESULTS AND DISCUSSION

Shown in Fig. 4-2 is the cyclic voltammogram of a Pt disk electrode (2 mm in diameter) in 0.1 M H₂SO₄ at a scan rate ν = 1 V/s (left ordinate, thick grey curve),
obtained by conventional means, displaying features characteristic of this interface. Also displayed in thin lines in this figure are $\Delta \phi_{\text{sol}}$ (see right ordinate) vs E data collected simultaneously for $\Delta m$ ca. 1 mm during a single voltammetric cycle, i.e. no averaging, for various values of $\Delta M$ as specified therein. Various aspects of these data are particularly noteworthy:

i. The $\Delta \phi_{\text{sol}}$ vs E curves, within the range $0 \leq \Delta M < 2$ mm, yielded readily resolvable features virtually identical to those of the conventional voltammogram with values of $\Delta \phi_{\text{sol}}$ of a few tens of $\mu V$.

ii. As $\Delta M$ increased within the specified range, the magnitude of $\Delta \phi_{\text{sol}}$ decreased, while the overall shape of the $\Delta \phi_{\text{sol}}$ vs E curves remained virtually invariant. For $\Delta M > 2$ mm, however, $\Delta \phi_{\text{sol}}$ decreased below the level of detection with our current instrumentation.

It becomes evident from a comparison between data collected for $\Delta M = 0$ and all other $\Delta M$ values, that physical contact of one of the tips with the Pt surface does not affect the essential features of the results obtained.

Clear evidence of the local character of the currents being probed was provided by the results of an experiment in which two different disk electrodes of the same diameter (2 mm), Au and Pt, were immersed in the same solution and connected together to the potentiostat.

Shown in Fig. 4-3 (see Panel A) is a cyclic voltammogram recorded by conventional means for the combined Au and Pt working disk electrode arrangement,
yielding, as expected, features characteristic of both the Au|0.1 M H₂SO₄ and Pt|0.1 M H₂SO₄ interfaces. As the microreference electrodes (Δm = 1 mm) approached one of the two working electrodes, the Δφₕₐₗ vs E curves recorded simultaneously during the scan acquired characteristics typical of the corresponding neighboring metal|electrolyte interface. This is clearly illustrated by the results in Panel B and D recorded for ΔM = 0 with respect to either the Pt or the Au disk electrode, respectively. It can therefore be surmised, that Δφₕₐₗ affords a measure of the local current flowing through the solution neighboring the interface and thereby underscore the spatial resolution of the technique. In analogy with the results found for the single working electrode above, Δφₕₐₗ decreased as the microreference electrode array was displaced away from the surface. In fact, Δφₕₐₗ disappeared when the tip of M1 was placed directly on the plane of, and in between the two working electrodes (see Panel C, Fig. 4-3). However, clearly resolved signals did emerge upon displacing M2 along the surface normal away from the electrodes to yield at Δm ca. 5 cm the thin curve in Panel C, Fig. 4-3 which contained contributions from both the Au and Pt electrodes. M1 was then displaced along the surface and placed directly in the middle of the Pt disk in one case and the Au disk in the other (see thin lines Panels B and D, respectively). Not only the signals obtained were found to be characteristic of the individual electrodes, but their magnitude was larger than that found for Δm = 1 mm under these condition, i.e. ΔM = 0.

Evidence that Δφₕₐₗ increases monotonically with the current flowing through the working electrode(s) was obtained from results collected under identical conditions for two different scan rates, i.e. 1 V/s (thick lines) and 0.5 V/s (thin lines) (see Fig. 4-4) for
\( \Delta M = 0 \) and \( \Delta m \) ca. 1 mm, where M1 was placed next to the Pt (middle panel) and Au disks (upper panel).

Efforts were made to examine issues relating to spatial resolution using a segmented Au and Pt electrode (see Fig. 4-5) of dimensions much larger than those of the electrodes used for the experiments so far presented.

Shown in Panel A, Fig. 4-5, is the cyclic voltammogram for the Pt/Au electrode recorded in 0.1 M H\(_2\)SO\(_4\) at a scan rate of \( \nu = 1 \) V/s. The thick lines in the panels in this figure represent \( \Delta \phi_{\text{sol}} \) measured simultaneously for \( \Delta M = 0 \), and \( \Delta m \) ca. 1 mm at different positions on the electrode surface as shown in the central diagram. As indicated in Panel F, the \( \Delta \phi_{\text{sol}} \) vs E curve at the junction (see thick line) contains contributions due to both Pt and Au and the trace is very similar to the conventional cyclic voltammogram. As the tip is moved farther away from the junction along the surface, the \( \Delta \phi_{\text{sol}} \) vs E traces gradually acquire characteristics of each individual metal, either Pt or Au, at the expense of the other metal. At the very extreme position, i.e. 3 mm (thick lines in Panels B1 and B2), the curves are virtually identical to those of the metal in closest proximity to M1.

A semiquantitative assessment of the resolution of this ohmic microscopy technique can be gleaned by comparing the relative contributions of the two metal surfaces to the potential difference detected by the two microreference probes in solution. As shown in panel A, Fig. 4-3, the peak potentials for the reduction of the Au and Pt oxides are separated by as much as 0.4 V; hence, \( \Delta \phi_{\text{sol}} \) measured at the two reduction peaks, to be denoted, respectively, as \( \Delta \phi_{\text{Au}} \) and \( \Delta \phi_{\text{Pt}} \), affords a simple measure of the resolving power of the method under the specific conditions selected for these
experiments (see below). Shown in Fig. 4-6 are plots of $\Delta \varphi_{\text{Pt}}/\Delta \varphi_{\text{Au}}$ (left ordinate, open circles) and $\Delta \varphi_{\text{Au}}/\Delta \varphi_{\text{Pt}}$ (right ordinate, solid circles) as a function of the position of the dual probes along the surface of the bimetallic strip, where the contribution to $\Delta \varphi_{\text{sol}}$ to the values of $\Delta \varphi_{\text{Pt}}$ and $\Delta \varphi_{\text{Au}}$ obtained far away from the junction have been subtracted.

In a different series of experiments (see thin lines), M2 was placed far away ($\Delta m$ ca. 3 cm) while M1 was displaced along the surface. As before, $\Delta \varphi_{\text{sol}}$ vs E recorded for M1 at the junction was very similar to the conventional voltammogram, except that the magnitude of the signal was very much enhanced compared to the corresponding trace in the same panels. In other words, placing M2 farther away from the surface leads to an overall increase in sensitivity; however, this tactic also elicits a decrease in resolution as evidenced by a comparison between the relative contributions of the two metals to the signal observed for M1 at a specified position. The resolving power of the method under this specific set of conditions is shown in grey solid and open circles in Fig. 4-6.

The results obtained in this work can be interpreted in terms of the ohmic drop generated in the electrolyte solution induced by the passage of pseudocapacitive current through the electrode. In particular, Newman, in his seminal work, predicted that for a disk electrode embedded in an insulating surface, the changes in the electrostatic potential in the electrolyte become more pronounced as the surface of the electrode is approached. In fact, extensive use of his theoretical framework has been used in the analysis of localized impedance spectroscopy in which the modulating character of the electrical excitation leads to gains in sensitivity. As shown by the data presented in our work, the sensitivity achieved with our current set up enables ohmic drops in the solution.
to be measured with relative ease without the need of modulation or averaging. Efforts are now under way in our laboratories to decrease the overall size of the microreference electrodes on one hand, coupled to theoretical simulations of the current distribution on the other, to find conditions that will optimize both sensitivity and spatial resolution. It might be expected, however, that capillaries, on the order of a fraction of a μm in diameter, will lead to a decrease in sensitivity due to higher resistance. Two tactics may be envisioned to overcome this problem, to use an amplifier and/or to increase the scan rate to MV/s. It is interesting to note, because of its practical implications, that long, narrow, thin wall glass capillaries have been found bend under pressure allowing for the tip to touch the surface without breaking.

It should be emphasized at the outset that much of this effort was prompted by the possibility of complementing localized optical monitoring of quasi perfect single crystal facets produced by the controlled cooling of a molten sphere formed by heating the end of a wire of relatively small diameter, by spatially resolved measurements of the local current flowing toward the facet. As described in our earlier publication,¹⁰ this tactic enables for a light beam to be focused and reflected from a single facet, while the entire sphere is immersed in the electrolyte. Under such conditions, the electrochemical response is dominated by contributions of areas other than the facet of interest making it impossible to correlate the optical and electrochemical measurements. In fact, if the potential distribution could be mapped with sufficient resolution, it might be possible in principle to deduce from the data the most likely arrangement of surface currents responsible for the observed electrostatic response. Since most often facets of the same
metal or facets of different metals display different pseudocapacitive currents, this type of analysis may be expected to yield spatially-resolved images of multifacett ed surfaces.

REFERENCES


Fig. 4-1. Schematic diagram of the experimental setup for the acquisition of potential difference between two microelectrodes, $\Delta \phi_{\text{sol}}$, M1 and M2, placed in the solution phase, while applying continuously linear potential scans between two prescribed limits to the working electrodes (see text for details) vs a Ag/AgCl reference electrode (RE) using a conventional potentiostat/signal generator and a carbon rod as a counter electrode (CE).
Fig. 4-2. Cyclic voltammogram (left ordinate) of a Pt disk electrode (2 mm in diameter) recorded in 0.1 M H₂SO₄ at a scan rate of $\nu = 1$ V/s (thick grey line). The thin lines represent values of $\Delta \phi_{\text{sol}}$ measured simultaneously (right ordinate) for $\Delta m$ ca. 1 mm and different $\Delta M$, as labeled.
Fig. 4-3. Cyclic voltammogram (panel A) of a Au (2 mm in diameter) and a Pt (2 mm in diameter) connected together recorded in 0.1 M H₂SO₄ at ν = 1 V/s and Δφₜₕₜ measured simultaneously for M1 next to the Pt (Panel B) and Au electrode (Panel D), for Δm ca. 1 mm and ΔM = 0 (thick curves). The featureless thick curve in panel C was recorded for M1 placed over the surface in between the two electrodes. The thin curves were recorded under the same conditions as the thick curves in each panel, except that Δm ca. 5 cm.
Fig. 4-4. Cyclic voltammograms (lower panel) of a Au (2 mm in diameter) and a Pt (2 mm in diameter) connected together recorded in 0.1 M H₂SO₄ and Δφₜₚₒₜ measured simultaneously for M₁ next to the Au (upper panel) and Pt electrode (middle panel), for Δm ca. 1 mm, and ΔM = 0 at two different scan rates, 0.5 (thin curves) and 1.0 V/s (thick curves).
Fig. 4-5. Cyclic voltammograms (Panel A) for a segmented Pt/Au electrode (see central diagram) recorded in 0.1 M H₂SO₄ at a scan rate of ν = 1 V/s. The thick lines in the other panels represent values of Δφₚₒₑₒ (multiplied by 5) measured simultaneously for ΔM = 0, and Δm ca. 1 mm at different positions on the electrode surface as shown in the central diagram. The thin lines represent data collected in the same fashion except that M2 was placed far away from the electrode surface.
Fig. 4-6. Plots of $\Delta \phi_{Pt}/\Delta \phi_{Au}$ (left ordinate, open black circles) and $\Delta \phi_{Au}/\Delta \phi_{Pt}$ (right ordinate, solid black circles) as a function of the position of the dual probes along the surface of the bimetallic strip for $\Delta M = 0$, and $\Delta m = 1$ mm. $\Delta \phi_{Au}$ and $\Delta \phi_{Pt}$ represent the magnitudes of the potential differences at the potential at which the peak for the reduction of the corresponding oxide reaches a maximum, using the potential difference far away from the junction, where the response of the other metal is not detectable, as a reference. Data obtained from a similar analysis for $\Delta M = 0$, and $\Delta m = 3$ cm are shown in open and solid grey circles, respectively.
CHAPTER 5: RATIONAL DESIGN OF ELECTROCATALYTIC INTERFACES:
THE MULTIELECTRON REDUCTION OF NITRATE IN AQUEOUS
ELECTROLYTES
5.1 ABSTRACT

An electrode incorporating two distinct heterogeneous electrocatalysts acting in series was specifically designed to promote the reduction of nitrate beyond the nitrite stage in weakly buffered aqueous solutions (pH = 3) containing Cd\(^{2+}\). This novel interface consists of Au nanoparticles, Au(np), on which underpotentially deposited Cd reduces nitrate predominantly to nitrite, dispersed on a hemin-modified glassy carbon (GC) surface, Hm|GC, where nitrite is further reduced to yield hydroxylamine as the only product detected using a rotating Au ring-Hm|Au(np)|GC disk electrode. Additional evidence in support of this series mechanism was obtained from numerical simulations in which the bifunctional electrode was regarded as a hexagonal, closed-packed array of coplanar concentric Cd|Au(np) disks and Hm|GC rings (with no insulating gap), using rate constants determined independently from rotating Au and Hm|GC disk electrodes in solutions containing either nitrate or nitrite, respectively.
5.2 INTRODUCTION

Redox processes involving the transfer of multiple electrons are of rather common occurrence in a variety of areas of fundamental and technological relevance. Among the most widely studied reactions of this type is the four-electron reduction of dioxygen (4e^- ORR) to yield hydroxyl ion and/or water, which is central to respiration in biological systems and also to the operation of air cathodes in energy conversion and energy storage devices.\(^1\) It has been well established, for example, that Pt electrodes polarized over a rather wide range of potentials, can carry out the 4e^-ORR in aqueous electrolytes in a highly selective fashion without generating solution phase intermediates, such as superoxide and peroxide.\(^1\) A net four-electron transfer can also be achieved by mixing a two-electron catalyst to yield peroxide (2e^-ORR) with a peroxide disproportionation catalyst, a heterogeneous electrochemical-chemical (EC) type mechanism successfully implemented in Zn-air batteries.\(^2\) Yet another means of effectively accomplishing the same goal is by using two electrocatalysts acting in series, as described by Anson and coworkers over two decades ago.\(^3\) Interest in our laboratories has focused on the electrochemical properties of neutral and ionic forms of nitrogen and sulfur oxides in aqueous electrolytes\(^4\) because of their importance in such diverse fields as environmental remediation and nuclear waste management.\(^5\) This contribution describes a novel electrocatalytic interface involving gold nanoparticles, Au(np), dispersed on the surface of a hemin (Hm) modified glassy carbon (GC) electrode, Hm|GC (see Experimental Section), which is capable of reducing nitrate beyond the nitrite step in weakly buffered aqueous solutions (pH = 3) containing Cd\(^{2+}\). As will be shown, this bifunctional electrode promotes reduction of \(\text{NO}_3^-\) on underpotential deposited Cd on Au(np) via a
two-electron step to yield solution phase $\text{NO}_2^-$, which then undergoes subsequent reduction on $\text{Hm|GC}$ generating hydroxylamine as a product.

5.3 EXPERIMENTAL

Electrochemical measurements were performed using either a Au or a glassy carbon (GC) rotating disk electrode (RDE) (area, $A = 0.164 \text{ cm}^2$, Pine Instruments) in 0.1 M acetate buffer ($\text{pH} = 3$) solution prepared from glacial acetic acid (Fisher) and sodium acetate (Fisher) and ultrapure water (Barnstead) containing 0.1 M NaClO$_4$ (Fluka), to be denoted hereafter as the base electrolyte. It should be stressed that the buffer capacity of this solution, although not negligible, is rather small; however, it offers an advantage over more common buffers at this pH, such as phosphate, in that the anions do not form insoluble salts with Cd$^{2+}$. Unless otherwise indicated, nitrate and nitrite reduction were studied by adding solutions of either KNO$_3$ (Fisher) or NaNO$_2$ (Fisher) in the mM range to the base electrolyte containing 1 mM Cd(ClO$_4$)$_2$ (Alfa Aesar). A carbon rod and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The GC disk electrode was modified with hemin (Hm) by placing a drop of a 1 mM Hm (Porphyrin Products Inc.) aqueous solution in 0.1 M Na$_2$B$_4$O$_7$ (Fisher) on the surface and then allowing it to dry in air. Gold nanoparticles ca. 18 nm in diameter (determined by transmission UV-visible spectroscopy) devoid of surfactant were prepared following literature procedures, and then dispersed on GC by adding one drop of an aqueous Au(np) suspension on the GC disk surface and allowing it to dry in air. The cyclic voltammograms of Au(np)|GC displayed features ascribed to the oxidation of Au during the scan in the positive direction, and its subsequent reduction upon reversing the
scan at the positive limit. Coulometric analysis of the oxide reduction peak allowed for the area of Au in contact with the electrolyte to be determined. This overall dispersion procedure was repeated several times until the Au area was found to be equivalent to half of the total projected area of the composite Au(np)|GC electrode. Afterwards, the Au(np)|GC electrode was rinsed and later modified with Hm following the same method described above to yield Au(np)|Hm|GC electrodes. All electrochemical measurements were performed with a conventional rotator and bipotentiostat (Pine Instruments, Model AFCBP1). Detection of hydroxylamine was effected using a rotating Au(ring)|Au(disk) electrode (Pine Instruments).

5.4 RESULTS AND DISCUSSION

Shown in Fig. 5-1 are polarization curves recorded at a scan rate, $\nu = 10 \text{ mV/s}$, with a Au RDE in base electrolyte containing 1 mM Cd(ClO$_4$)$_2$ and either 1 mM KNO$_3$ (black curve) or 1 mM NaNO$_2$ (red) at a rotation rate $\omega = 2500 \text{ rpm}$. Corresponding data for bare GC and Hm|GC electrodes in the same supporting electrolyte containing 1 mM NaNO$_2$ under otherwise the same conditions are given in the grey and blue curves in the same figure, respectively. No changes in the voltammetric curves for Hm|GC recorded in quiescent base electrolyte containing 1 mM NaNO$_2$ could be discerned upon adding 1 mM Cd(ClO$_4$)$_2$. Furthermore, Hm|GC displayed no activity for nitrate reduction under the same conditions.

Several conclusions can be drawn based on these results:
i. The currents observed on the Au electrode at the more negative potentials can be attributed predominantly to the Cd(UPD)|Au catalyzed reduction of $\text{NO}_3^-$ (black curve, Fig. 5-1)) and $\text{NO}_2^-$ (red curve in the same figure).

ii. The currents associated with the reduction of $\text{NO}_3^-$ on Cd(UPD)|Au are larger than those observed for the reduction of $\text{NO}_2^-$ at the same concentration over the entire potential range examined.

iii. Bare GC surfaces display no activity for the reduction of $\text{NO}_2^-$ (grey curve, Fig. 5-1)

iv. Hm|GC is a far more potent electrocatalyst (blue curve) than Cd(UPD)|Au for the reduction of $\text{NO}_2^-$ (red curve)

The onset for the reduction of $\text{NO}_2^-$ on Hm|GC (blue curve) occurs at a potential more positive than that found for the reduction of $\text{NO}_3^-$ on Cd(UPD)|Au (black curve). On this basis, it might be expected that electrode surfaces incorporating both Au and Hm|GC polarized at potentials at which $\text{NO}_3^-$ is reduced in solutions containing Cd$^{2+}$ would yield higher currents than those observed on Cd(UPD)|Au in the same media due to the ability of adsorbed Hm on GC to reduce $\text{NO}_2^-$. To test this hypothesis, Au(np) were first dispersed on the GC RDE and then a few drops of a Hm solution placed on the Au(np)|GC surface and allowed to dry. It should be stressed that Hm adsorbed on Au shows no activity for nitrite reduction beyond that of the bare substrate in the same media. In fact, the current observed in the cyclic voltammograms ($v = 10 \text{ mV/s}$) for Au recorded with a RDE in base electrolyte in the presence of 1 mM Cd(ClO$_4$)$_2$ and 1 mM
NaNO$_2$ at $\omega$ = 2500 decreased following adsorption of Hm. This behavior could be caused by the blocking of Au sites due to the presence of the macrocycle.

Shown in Fig. 5-2 are polarization curves for a Au(np)|GC (black curve) and a Hm|Au(np)|GC (red curve) RDE in base electrolyte containing 1 mM Cd(ClO$_4$)$_2$ and 1 mM KNO$_3$ at $\omega$ = 2500 rpm. Also displayed for comparison is the corresponding curve for Au(np)|GC in the presence of 1 mM Cd(ClO$_4$)$_2$ and 1 mM NaNO$_2$ under otherwise the same conditions (blue), which yielded qualitatively similar results as those found with Au RDE in Fig. 5-1. As clearly evidenced from these data, the currents observed for Hm|Au(np)|GC are significantly larger than those for Au(np)|GC in solutions containing KNO$_3$, and thus consistent with the subsequent reduction of NO$_2^-$ generated by Cd(UPD)|Au on the Hm modified GC.

A more quantitative measure of these effects can be gleaned from a plot of the ratio of the average currents observed in the scans in the negative and positive directions (to minimize double layer charging contributions) for the two interfaces, $\xi = i_{T}(Hm|GC)/i_{T}(GC)$, shown in the insert in this figure, which yielded monotonically increasing values as the potential was made more negative, ranging from ca. 1.2 at $E$ = -0.55 up to ca. 1.34 at $E$ = -0.7 V vs SCE.

Insight into the nature of the product generated by the reduction of nitrite was obtained using rotating ring-disk electrode (RRDE) techniques. Prior to these experiments the electrochemical properties of hydroxylamine and nitrite on Au were carefully examined. Shown in Panel A, Fig. 5-3 are cyclic voltammograms ($\nu$ = 10 mV/s) obtained with a Au RDE in base electrolyte in the presence of either 1 mM
NH$_2$OH (red) or 1M NaNO$_2$ (blue). Also shown for comparison is the corresponding curve in the neat base electrolyte (black curve). The data in Panel B was acquired in the same solution with the RDE rotating at rate $\omega = 2500$ rpm. In stark contrast with reports published in the literature,$^9$ Au is active for the oxidation of hydroxylamine, a reaction for which the onset potential is found at about 0.45 V vs SCE. This value is more negative than that associated with the oxidation of nitrite in the same media (see Panel A, blue curve). Based on the results in Panel B, Fig. 5-3, the oxidation of hydroxylamine is not purely diffusion controlled as judged from the non-Levich behavior of the limiting currents. In fact, the current for sufficient high rotation rates seems to be independent of $\omega$ for $\omega > 1600$ rpm. The results of these experiments provide solid bases for detection of hydroxylamine generated by the reduction of nitrite.

Shown in Panel A, Fig. 5-4 are polarization curves obtained for a Au(ring)|Hm|GC(disk) RRDE in base electrolyte and 1 mM Cd(ClO$_4$)$_2$ in the presence of 1 mM NaNO$_2$ recorded at $\omega = 900$ rpm. For these measurements, the disk electrode was polarized at either 0.1 (black curve) and -0.7 V (red), while the Au ring was scanned at $\nu = 10$ mV/s over the potential range specified. Similar data involving a Au(ring)|Au(disk) RRDE acquired under otherwise identical conditions are shown in Panel B in the same figure. For both RRDE arrangements, the onset potential associated with the oxidation of the product of nitrite reduction occurs precisely at the value at which oxidation of hydroxylamine ensues, providing unambiguous evidence that hydroxylamine is indeed one of the products of nitrite reduction at these interfaces under the conditions of these experiments.
Finally, polarization curves \( (v = 10 \text{ mV/s}) \) obtained for a Au(ring)|Au(np)|GC(disk) RRDE in base electrolyte in the presence of 1 mM Cd(ClO₄)₂ and also 1 mM KNO₃ recorded at \( \omega = 900 \text{ rpm} \) are given in Panel B, Fig. 5-5. Also shown in Panel A in this figure are the corresponding curves recorded with a Au(ring)|Au(np),Hm|GC(disk). It may concluded based on these results that although nitrite is detected for both types of disk electrodes, only the Hm-modified surface yields hydroxylamine as one of the products. Insight into quantitative aspects of these results was gained from numerical simulations performed with COMSOL in which the bifunctional electrocatalytic interface was regarded as a hexagonal array of Au disks of radius, \( r \), surrounded by concentric Hm|GC rings of thickness \( d \) with no insulating gap. This axisymmetric geometry has been successfully implemented by other workers to treat similar types of disk arrays uniformly distributed over a (continuous) flat surface.¹⁰ Within this framework, the problem reduces to that of a single ring-disk arrangement with a zero flux boundary condition normal to the wall of the cylinder with radius \( R = r + d \). Calculations were performed for a fixed \( R \) (see below) and various values of \( r \). For simplicity, all redox reactions were assumed to be first order in each of the reactants involved, i.e. A and B in Scheme 5-1 below,
where A represents nitrate, B nitrite and C, without loss of generality, either a two-electron or a four-electron product for the reduction of nitrite, i.e. n = 2 and n = 4. The latter step in this simplified reaction scheme may not be correct as the nature of other possible products of nitrite reduction is not known with certainty. Nevertheless, as we will show, the results obtained provide a primitive model which approximates rather well semi-quantitative aspects of the experimental data. The actual value of the (potential dependent) rate constant $k_3$ was extracted directly from the (negative going) polarization curves in Fig. 5-1 (see blue curve) assuming full kinetic control, whereas $k_1$ and $k_1$ were determined by solving the rate equations at steady state including contributions due to diffusion for both nitrate and nitrite. The values of the (potential dependent) rate constants obtained are given in Table 5-1 both for $E = -0.7$ and -0.55 V vs SCE. The boundary conditions involved in the COMSOL simulations are given in the Appendix.

Shown in Table 5-1 are values of the fraction of the total current, $i_T$, associated with the generation of C, $i_C$, obtained for a single disk-ring element for two different potentials, i.e. $E = -0.7$ and -0.55 V vs SCE, and two different values of n associated with the B $\rightarrow$ C step, where the columns, denoted as GC and Hm|GC represent an inactive and
an active ring, respectively. As noted in the table, the rate constants evaluated assuming \( n = 2 \) are larger than those with \( n = 4 \). Values of \( i_C/i_T \) were calculated for different disk radii, i.e. \( r = 20 \text{ nm}, 200 \text{ nm} \) and \( 2 \mu\text{m} \), keeping the outer radius of the ring fixed, i.e. \( R = 20 \mu\text{m} \). The effect of Hm adsorbed on the GC on the overall catalytic process can be expressed in terms of a parameter \( \xi = i_T(Hm|GC)/i_T(GC) \). Based on the \( \xi \) values listed in Table 5-1, the presence of Hm gives rise to a sizable increase in the total current, i.e. ca. 25% and 14% for \( E = -0.55 \text{ V} \) and 40% and 25% for \( E = -0.70 \text{ V} \) for \( n = 2 \) and \( n = 4 \), respectively, for all values of \( r \) selected, which is well within the range of those found experimentally lending strong support for the simple mathematical model herein presented. Also noteworthy is the fact that \( \xi \) was not very sensitive to \( r \) nor to \( r/R \) within the range of values of \( r \) and \( R \) selected.

In summary, an electrode incorporating two electrocatalysts acting in series specifically designed to promote the reduction of nitrate beyond the nitrite stage in pH 3 aqueous buffered solutions containing \( \text{Cd}^{2+} \) was assembled and tested. This bifunctional interface consisted of Au nanoparticles Au(np) dispersed on a hemin modified glassy carbon (Hm|GC) surface, where the reduction of nitrate is catalyzed by underpotential deposited Cd on Au(np) to yield nitrite which is then further reduced on Hm|GC to yield hydroxylamine as one of the products. Support for this mechanism was provided by numerical simulations in which the electrode was regarded as an array of Au(Cd|UPD) disks surrounded by Hm|GC rings yielding results in fairly good agreement with those observed experimentally.
REFERENCES


Fig. 5-1. Polarization curves for a Au RDE recorded at a scan rate of $\nu = 10$ mV/s and a rotation rate $\omega = 2500$ rpm in base electrolyte containing 1 mM Cd(ClO$_4$)$_2$ in the presence of either 1 mM KNO$_3$ (black) or 1 mM NaNO$_2$ (red). The curves in grey and blue were obtained using a GC (grey) and Hm|GC RDE (blue) RDE in the presence of 1 mM NaNO$_2$, respectively, under otherwise the same experimental conditions.
Fig. 5-2. Polarization curves (ν = 10 mV/s) for a Au(np)|GC (black) and a Hm|Au(np)|GC (red) RDE in base electrolyte containing 1 mM Cd(ClO$_4$)$_2$ and 1 mM KNO$_3$ at ω = 2500 rpm. The curve in blue was recorded with a Au(np)|GC disk electrode in base electrolyte containing 1 mM Cd(ClO$_4$)$_2$ and 1 mM NaNO$_2$ under otherwise the same conditions. Insert: Plot of the ratio of the average currents observed for the Hm|Au(np)|GC (red) and Au(np)|GC (black) curves in the main figure, $\eta = \frac{i_T(Hm|GC)}{i_T(GC)}$ as a function of the applied potential.
Fig. 5-3. A. Cyclic voltammograms ($v = 10$ mV/s) for a Au disk electrode in a quiescent base electrolyte in the presence of either 1 mM NH$_2$OH (red, b) or 1 mM NaNO$_2$ (blue, c). The curve in black (a) was recorded in the base electrolyte. B. Polarization curve obtained with the same solution as in the red curve in Panel A at $\omega = 2500$ rpm.
Fig. 5-4. A. Polarization curves obtained for a Au(ring)|Hm|GC(disk) RRDE in base electrolyte and 1 mM Cd(ClO₄)₂ in the presence of 1 mM NaNO₂ recorded at ω = 900 rpm. For these measurements, the disk electrode was polarized at either 0.1 (black curve) or -0.7 V (red) while the Au ring was scanned at ν = 10 mV/s over the potential range specified. B. same as Panel A for a Au(ring)|Au(disk) RRDE under otherwise identical conditions.
Fig. 5-5. **A.** Polarization curves ($v = 10$ mV/s) for a Au(ring)|Au(np),Hm|GC(disk) RRDE in base electrolyte in the presence of 1 mM Cd(ClO$_4$)$_2$ and also 1 mM KNO$_3$ recorded at $\omega = 900$ rpm. For these measurements, the disk electrode was polarized at either 0.1 (blue curve) or -0.7 V (black), while the Au ring was scanned at $v = 10$ mV/s over the potential range specified. **B.** Same as Panel A for a Au(ring)|Au(np)|GC(disk) RRDE under otherwise identical conditions.
Table 5-1

Ratio of the currents associated with the generation of C, $i_C$, and total current, $i_T$, on the ring-disk electrode and ratio of the total currents for a Hm|GC and GC rings, $\xi$, for two different potentials, for $n = 2$ and $n = 4$ and three different disk radii.

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APPENDIX. Boundary Conditions

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CHAPTER 6: THE OXIDATION OF HYDROXYLAMINE ON GOLD ELECTRODES IN MILDLY ACIDIC AQUEOUS ELECTROLYTES: ELECTROCHEMICAL AND IN SITU DIFFERENTIAL REFLECTANCE STUDIES
6.1 ABSTRACT

The oxidation of hydroxylamine (HAM) on polycrystalline Au electrodes in aqueous acetate buffer (pH = 4) has been examined, using electrochemical and in situ reflectance spectroscopy methods. Cyclic voltammograms recorded under quiescent conditions in the potential region negative to the onset of Au oxidation were characterized by two clearly defined peaks centered at ca. 0.42 V and ca. 0.76 V vs SCE. Corresponding polarization curves obtained with a Au rotating disk electrode (RDE) as a function of rotation rate, \( \omega \), yielded two rather well defined plateaus. However, plots of the limiting currents, \( i_{\text{lim}} \), as a function of \( \sqrt{\omega} \) (Levich) and of the reciprocal of the observed currents vs \( 1/\sqrt{\omega} \) (Koutecky-Levich) based on these data were found to be non linear. Also non linear were plots of \( i_{\text{lim}} \) as a function of the concentration of HAM, \([\text{HAM}]\), at fixed \( \omega \). These observations clearly indicate that the reaction mechanism is far from trivial. Experiments involving dual electrode techniques including rotating ring disk electrodes (RRDE) afforded evidence that the two consecutive redox waves are associated primarily with oxidation of HAM to nitrite and nitrate, respectively. Normal incidence differential reflectance spectroscopy measurements, \( \Delta R/R \), on a Au RDE performed at high \( \omega \) or large \([\text{HAM}]\) failed to detect the presence of Au oxide during HAM oxidation in the potential region in which Au is known to form oxides. This behavior is analogous with that found earlier in our laboratories for the oxidation of bisulfite on Au.
6.2 INTRODUCTION

Conflicting results have been reported in the literature regarding the electrocatalytic properties of Au electrodes toward hydroxylamine (HAM) oxidation in aqueous electrolytes. Whereas Piela and Wrona found no detectable activity over the pH range 0.6 - 5.6,\textsuperscript{1} a clear oxidation wave was observed in linear voltammetric scans in phosphate buffer solutions by Li and Lin (4.0 ≤ pH ≤ 10.0)\textsuperscript{2} and later by Kannan and John (5.2 ≤ pH ≤ 9.2).\textsuperscript{3} Insight into some aspects of this reaction was gained more recently in our laboratories using a combination of electrochemical and \textit{in situ} surface enhanced Raman scattering (SERS) on roughened Au electrodes in aqueous phosphate buffer (pH = 3).\textsuperscript{4} Specifically, the voltammetric curves showed two well-defined oxidation waves within the double layer region of Au in the neat, i.e. HAM-free, electrolyte, and the \textit{in situ} SERS spectra of roughened Au electrodes displayed two clear features ascribed to adsorbed nitrite and adsorbed NO$_2$ over two distinct potential ranges.

The present contribution expands the scope of our earlier investigations by examining in more detail various aspects of the electrochemical properties of Au for HAM oxidation using cyclic voltammetry and rotating disk (RDE) and ring-disk electrode (RRDE) techniques and normal incidence differential reflectance spectroscopy. Experiments were performed in acetate buffer solutions (pH = 4) to allow introduction of soluble salts of Cd$^{2+}$ (which otherwise forms phosphates of very low solubility in mildly acidic aqueous solutions) and thus implement methods that exploit the ability of Cd underpotential deposition (UPD) on Au for the \textit{in situ} electrochemical detection of nitrate and nitrite. Advantage was also taken of the electrocatalytic properties of hemin (HM)-modified glassy carbon (GC) electrodes to monitor \textit{in situ} the presence of solution phase
nitrite, yet another expected product of HAM oxidation, as a function of the applied potential on Au. Additional insight into the reaction mechanism in the potential region in which Au oxides are known to form in the neat electrolyte was gained by using in situ normal incidence differential reflectance spectroscopy, ΔR/R, coupled to a RDE.

6.3 EXPERIMENTAL

Most of the measurements were performed using a Au ring-Au disk rotating ring-disk electrode, Au|Au RRDE, (disk area, $A_{disk} = 0.164 \text{ cm}^2$; ring area, $A_{ring} = 0.037 \text{ cm}^2$; gap, $G = 180 \text{ μm}$; collection efficiency, $N = 22\%$, Pine Instruments) in 0.1 M acetate buffer (pH = 4) solution prepared from glacial acetic acid (Fisher) and sodium acetate (Fisher) in 0.1 M NaClO$_4$ (Aldrich), denoted hereafter as the base electrolyte, containing either NH$_2$OH (Aldrich), Cd(ClO$_4$)$_2$ (Alfa Aesar), or NaCl (Fisher). Experiments were performed in a conventional all-glass, three-compartment cell with a carbon rod and a saturated calomel (SCE) as counter and reference electrodes, respectively, using a commercial rotator (Pine Instruments, Model AFMSRX) and a bipotentiostat (Pine Instruments, Model AFCBP1).

Solution phase nitrite generated during HAM oxidation on Au was detected using a static GC RDE ($A_{disk} = 0.164 \text{ cm}^2$, Pine Instruments) modified with a monolayer of irreversibly adsorbed hemin (Hm|GC) prepared by placing the electrode in contact with a Hm (Porphyrin Products Inc.) solution in aqueous 0.1 M Na$_2$B$_4$O$_7$ (Fisher), as described by Tao et al.$^5$ Although the activity of Hm for nitrite reduction either in the form of electropolymerized Hm films or layers of monomers mixed with didodecyldimethylammonium bromide (DDAB) has been well documented,$^6$ the present study appears to be the first involving a simple Hm monolayer spontaneously adsorbed
on a carbonaceous surface for studies of this specific reaction. As will be shown, Hm|GC is inactive toward reduction of both HAM and nitrate and, therefore, affords a highly specific means for monitoring solution phase nitrite without interference from those species. For these experiments, the Hm|GC disk electrode polarized at a potential negative enough for nitrite reduction to ensue, was placed directly in front of a Au disk electrode of much smaller area (A = 0.02 cm², Bioanalytical System) as shown in Scheme 6-1. This arrangement made it possible to record using a bipotentiostat the current associated with nitrite reduction at the Hm|GC electrode as the potential of the Au disk was scanned within the region in which HAM oxidation was found to occur.

**SCHEME 6-1**

Cross section of the dual disk electrode arrangement employed for the in situ detection of nitrite on a Hm modified GC disk electrode generated during the oxidation of HAM on the surface of the Au disk electrode of smaller area.

The instrumental array employed for collecting in situ normal incidence differential reflectance spectroscopy (ΔR/R) on a RDE was very similar to that developed earlier in our laboratories which included a CW laser (HeNe, 633 nm, JDS Uniphase 1144P, 15 mW) and a Si detector (ThorLabs PDA155), and a SCE reference electrode connected to the main cell compartment via a Teflon tubing.

**6.4 RESULTS AND DISCUSSION**

**6.4.1 Oxidation of hydroxylamine on gold electrodes**
Shown in Fig. 6-1 are cyclic voltammetric curves recorded at a scan rate of $\nu = 10$ mV/s with the Au disk electrode of the Au|Au RRDE in 1 mM NH$_2$OH (HAM) in the base electrolyte under quiescent conditions, in the potential ranges $-0.1 \leq E \leq 0.9$ V (double layer region, blue) and $-0.1 \leq E \leq 1.4$ V vs SCE (magenta). Also displayed therein is the corresponding voltammogram obtained in the neat base electrolyte under otherwise identical conditions (see thin black curve). As reported in a previous communication,$^4$ the oxidation of HAM in the potential range negative to the onset of Au oxide formation is characterized by two clearly defined waves centered at ca. 0.42 V and at ca. 0.76 V vs SCE, labeled as I and II in this figure, respectively. The third peak centered at ca. 1.05 V is due to the pseudocapacitance associated with the formation of Au oxide (see thin black curve). Upon reversing the scan at 1.4 V the current decreased monotonically reaching a minimum at $E$ ca. 0.95 V, a value just positive to the onset of Au oxide reduction in the base electrolyte. As the scanning was further continued, the current increased yielding a peak centered at $E$ ca. 0.75 V associated with II, followed by another sharp peak pointing in the opposite direction ascribed to the reduction of Au oxide. Lastly, for $E < 0.5$ V, the curve was very similar to that observed in the scan toward positive potentials. Additional insight into the interplay between Au oxide formation and reduction and HAM oxidation was gained from the analysis of in situ normal incidence reflectance spectroscopy to be discussed later in this work.

Monotonic increases in the current were observed upon increasing the concentration of HAM, [HAM], in the electrolyte in the range $0.2 \leq [\text{HAM}] \leq 2$ mM (see Fig. 6-2). In fact, plots of the peak currents, $i_{\text{peak}}$, as a function of [HAM] were found to
be linear with rather small intercepts (see insert, Fig. 6-2 and statistical parameters in the caption).

Dynamic polarization curves for the Au RDE acquired at fixed rotation rates, $\omega$, in 1 mM NH$_2$OH solution in the base electrolyte in the potential region negative to the onset of Au oxide formation (see Fig. 6-3) were characterized by two rather well-defined plateaus labeled, in accordance with Figs. 6-1 and 6-2, as I and II. Although the overall currents increased with rotation rate ($\omega$) in the range examined, i.e. 100 $\leq \omega \leq$ 2500 rpm, plots of the limiting currents, $i_{\text{lim}}$, vs $\omega^{1/2}$ were found to deviate from the linear behavior predicted by the Levich equation (see Panel A, Fig. 6-4) and the Koutecky-Levich plots (Panel B in this figure) were also found to be non linear. This behavior is indicative that that under the conditions selected for these studies, the reactions involved are not strictly diffusion controlled. In addition, the currents recorded initially from lower to higher $\omega$ (see black curves) were found to be a bit larger than those acquired subsequently in decreasing order (see red curves) for the same rates, particularly for large $\omega$.

As expected, the currents also increased with [HAM] under forced convection, in the range 0.2 to 2 mM (see Fig. 6-5). However, plots of $i_{\text{lim}}$ vs [HAM] recorded at fixed $\omega = 900$ (black symbols) and 1600 rpm (red symbols) were found to be non linear both for I and II (see insert, Fig. 6-5) suggesting once again that the mechanism involved may not be straightforward.

It is interesting to note that the hysteresis observed at constant $\omega$ both in Figs. 6-3 and 5 (see arrows) is not due to capacitive effects, as the currents increased in the scan in the negative direction.
6.4.2 Mechanistic Aspects

6.4.2.1 In situ Electrochemical Detection of Nitrate and Nitrite

A. Cd(UPD) on Au

Insight into the nature of the products generated during HAM oxidation on Au as a function of the applied potential was gained in part from experiments involving the use of a Au(ring)|Au(disk) RRDE in solutions containing 1 mM Cd(ClO₄)₂. As has been well established, Cd underpotential deposition, Cd(UPD), on Au promotes reduction of nitrate and nitrite in aqueous acidic electrolytes. This effect is illustrated in Fig. 6-6, which displays cyclic voltammetric curves recorded in the base electrolyte containing 1 mM Cd(ClO₄)₂ before (blue) and after addition of 1 mM KNO₃ (red). Also shown therein are data collected in 1 mM NaNO₂ (black) under otherwise identical conditions indicating not only that Cd(UPD) displays electrocatalytic activity for the reduction of nitrite, but also that the onset for this reaction is about 50 mV more negative than that associated with the reduction of nitrate.

It should be stressed that the presence of Cd²⁺ in the solution does not affect HAM oxidation to any significant extent. This is clearly evidenced by comparing the curves in red (no Cd²⁺) and in blue (1 mM Cd(ClO₄)₂ ) in Fig. 6-7. Furthermore, as shown in the insert in this figure, the double layer capacity of Au in the region 0.1 - 0.2 V is virtually identical in solutions with and without HAM, regardless of the presence of Cd²⁺ in the media. This may not be surprising, as Cd UPD occurs in a potential range negative to the onset of HAM oxidation.

Shown in Panel A, Fig. 6-8, are plots of the ring currents, i_{ring}, recorded in 1 mM NH₂OH in the base electrolyte containing 1 mM Cd(ClO₄)₂ at ω = 900 rpm, while
scanning the ring potential, \(E_{\text{ring}}\), at 10 mV/s in the range \(-0.75 \leq E_{\text{ring}} \leq 0.2\) vs SCE, at various fixed disk potentials, \(E_{\text{disk}} = 0.2\), and in 0.1 V intervals thereafter up to 1 V in the sequence indicated by the arrow. For each of these \(E_{\text{disk}}\) values, the disk current, \(i_{\text{disk}}\), was found to remain virtually steady (see solid circles in panel B, Fig. 6-8) yielding values very similar to those measured under dynamic polarization (see solid line in this panel).

Cursory inspection of these data reveals that:

i. \(\text{Cd(UPD) on Au is completely inactive toward HAM reduction in the potential region examined, as evidenced by the absence of any detectable ring currents when no current flows through the disk.}\)

ii. \(|i_{\text{ring}}|\) increases monotonically with \(E_{\text{disk}}\) (and, correspondingly, with \(i_{\text{disk}}\)) over the potential range \(-0.75 \leq E_{\text{ring}} \leq -0.45\) V vs SCE and thus consistent with the generation of a much larger amount of reducible products at the disk as \(E_{\text{disk}}\) becomes more positive or, equivalently, as the overpotential for HAM oxidation is increased.

A rather crude measure of the relative electrocatalytic activity of Au for the oxidation of HAM can be made based on the magnitudes of \(i_{\text{ring}}\) at an arbitrary value of \(E_{\text{ring}}\), such as those shown in Panel C, Fig. 6-8 for \(E_{\text{ring}} = -0.75\) V vs SCE (see solid black circles). Also included in the latter panel are similar data collected in solutions devoid of HAM (see solid red circles), which provides a measure of the potential independent background current, ca. \(-11\) \(\mu\)A.
A more careful examination of the data in Fig. 6-8 revealed that the onset of \( i_{\text{ring}} \) for values of \( E_{\text{disk}} \) within wave I occurs at potentials more negative than those associated with the corresponding values of \( E_{\text{disk}} \) within wave II. Since the onset of nitrite reduction is more negative than that of nitrate reduction (see Fig. 6-6), it is reasonable to surmise that nitrite and nitrate are predominantly generated over the potential ranges associated with waves I and II, respectively. Support for this view was obtained from experiments employing a Hm modified GC electrode (Hm|GC) to be described next.

**B. Hemin-modified Glassy Carbon (Hm|GC)**

Shown in Fig. 6-9 are polarization curves obtained with a Hm|GC RDE electrode prepared by spontaneous adsorption (see Experimental Section) in the base electrolyte in the presence of 1 mM NaNO₂ for \( \omega \) in the range 100 - 2500 rpm. Also given in this figure (see grey curve) is the voltammogram obtained for the (Hm|GC) electrode in the same electrolyte devoid of nitrite under stagnant conditions for which the observed currents were negligible. As evidenced from these data, the onset for nitrite reduction occurs at ca. \(-0.45 \) V vs SCE. This value is close to that found by Younathan et al. in the cyclic voltammogram of an electropolymerized film of iron(III) protoporphyrin IX dimethyl ester complex formed on GC and In-doped tin oxide (ITO) in 10 mM nitrite solutions in aqueous phosphate buffer pH 2.49.\(^9\) Furthermore, the currents in Fig. 6-9, increased monotonically as the potential was made more negative and also as \( \omega \) was increased for all potentials over the entire range examined. Also noteworthy is the emergence of a clearly defined shoulder for high values of \( \omega \) in the range \(-0.6 \leq E \leq -0.55 \) V vs SCE. In fact, a well defined plateau has also been reported by Mimica et al. for Hm embedded in
DDBA films supported on carbon.\textsuperscript{6} It must be emphasized that Hm|GC electrodes display no activity toward the reduction of neither nitrate nor hydroxylamine (not shown) at this pH, and as such are ideal for detection of nitrite without interference from these species. These special attributes are illustrated in Fig. 6-10, which displays current vs time (or Au disk potential) curves acquired for experiments using the arrangement depicted in Scheme 6-1. For these measurements, the Hm|GC electrode polarized at $E_{\text{Hm|GC}} = -0.7$ V vs SCE (see Panel A in this figure), while the potential of Au electrode, $E_{\text{Au}}$, was scanned at 10 mV/s between 0 to 0.9 V vs SCE (see Panel B) in a 1 mM NH$_2$OH solution in the base electrolyte. The negative current flowing through the Hm|GC disk, $i_{\text{Hm|GC}}$, observed for values of $E_{\text{Au}}$ at which no current is detected on the Au disk, is due primarily to the reduction of residual oxygen in the solution, for which the current is enhanced owed to the electrocatalytic activity of adsorbed Hm toward this reaction, and remains constant up to about 0.5 V, i.e. slightly positive to maximum in peak I. As $E_{\text{Au}}$ is further scanned in the positive direction, $i_{\text{Hm|GC}}$ increases in magnitude consistent with the reduction of nitrite being generated at the Au disk via HAM oxidation. At $E_{\text{Au}}$ ca. 0.74 V, which is very close to the onset of peak II, $|i_{\text{Hm|GC}}|$ reaches a maximum and decreases thereafter signaling a decrease in the local concentration of nitrite next to the Hm|GC disk. As the direction of the scan is reversed, the current due to nitrite reduction increases reaching a peak at ca. 0.63 V and decreases steadily thereafter. These results are consistent with those found with the Au|Au RRDE (vide supra). Specifically, peak I is due predominantly to the oxidation of HAM to nitrite, and peak II to its further oxidation to nitrate and also to the possible direct oxidation of without formation of nitrite as a
solution phase intermediate. The observed lag in the response of the Hm|GC disk is most likely due to the finite time required for material to diffuse between the two disks.

6.4.2.2 In situ Normal Incidence Differential Reflectance

Shown in Panel A, Fig. 6-11 are a series of dynamic polarization curves recorded at $\nu = 20$ mV/s at various rotation rates in a 2 mM NH$_2$OH solution in the base electrolyte over a potential range wide enough to encompass oxide formation and reduction. As evidenced from these data, an additional peak is clearly observed for $E_{\text{disk}} > 1.0$ in the scan toward positive potentials, the magnitude of which increased monotonically with $\omega$. Also shown for completeness is the corresponding curve (black line) recorded under stagnant conditions. Upon reversing the scan at the positive limit, i.e. 1.4 V, the current decreased down to about $E$ ca. 0.8 V vs SCE and later increased at a potential very close to the onset of oxide reduction on Au in the absence of the reactant in solution (see black curve, Fig. 6-1). Finally, for even lower potentials the curves virtually retraced those recorded during the scan in the positive direction.

Insight into the large hysteresis observed in the higher potential range was gained by monitoring simultaneously the current and the normal incidence differential reflectance data, $\Delta R/R$ (see Panel B, Fig. 6-11). As has been well documented in the literature,$^{10}$ the rather pronounced change in the slope of $\Delta R/R$ as the potential is scanned in the positive direction beyond 1 V, is associated with the formation of one or more forms of Au oxide. This effect is reversible in that $\Delta R/R$ returns to its original values once the oxide is reduced which is signaled by the increase in the optical signal at about 0.75 V. Careful examination of the curves as a function of $\omega$ reveal that the onset for
oxide formation is not only shifted toward positive values with respect to that found under stagnant conditions, but also that the extent of shift becomes larger as $\omega$ is increased. Also noteworthy is the fact that the overall magnitude of the change was smaller than that observed for quiescent conditions. In fact, no changes in the optical signal other than those associated with the intrinsic properties of the Au|electrolyte interface, i.e. a close to linear drop with potential, could be found when the concentration of HAM was increased to 5 mM over the entire potential range selected for rotation rates higher than 900 rpm (see Fig. 6-12). This behavior is very similar to that found earlier in our research group for the oxidation of bisulfite on Au in mildly acidic buffered aqueous electrolytes using the same exact techniques\(^8\) and strongly suggests that in analogy with the mechanism proposed therein conditions can be found under which the oxidation of HAM and/or its intermediates react with the nascent oxide preventing its further growth.

6.4.2.3 Role of Chloride

An important aspect that requires special attention is the possible role of impurities on the reaction pathway(s) of HAM oxidation on Au. Attention in what follows will focus on chloride, which is present in the chemicals employed in this study in amounts as high as tens of ppm. As reported in our recent publication,\(^4\) addition of chloride to the base electrolyte under quiescent conditions shifts the onset for HAM oxidation, $E_{\text{onset}}^{\text{HAM}}$, on roughened Au electrodes toward more positive potentials, but, at the same time, increases the peak currents associated I and II. The same effect was found in this work for smooth Au disk electrodes, as judged by a comparison between voltammetric data obtained in the base electrolyte before (see black curve) and after
introducing a 1 mM NaCl solution (see red and green curves in Fig. 6-13, respectively). Increasing the concentration of chloride to 5 mM led to further shifts in $E_{\text{onset}}^\text{HAM}$ albeit without gains in activity (see blue curve). Highly detrimental effects were found, however, as the concentration was further increased to 10 mM NaCl, namely, $E_{\text{onset}}^\text{HAM}$ shifted to even more positive values and the peak currents decreased. The same general trend was observed in experiments involving the same electrolytes for a Au RDE at $\omega = 1600$ rpm (see Fig. 6-14). Small differences, particularly for the first voltammetric wave, were observed in curves recorded after the experiments under forced convection were completed compared to the original ones. Whether such changes are due to the buildup of an adsorbed layer of a yet to be identified intermediate, or to impurities present in the electrolyte remains to be established.

6.5 CONCLUSIONS

The oxidation of hydroxylamine (HAM) on polycrystalline Au electrodes has been examined in aqueous acetate buffer (pH = 4), with electrochemical and in situ reflectance spectroscopy methods yielding a number of interesting results. In particular,

i. Conventional voltammetric experiments under quiescent conditions yielded two clearly defined peaks in the double layer region of Au in this electrolyte. Plots of the peak currents as a function of the concentration of HAM were found to be linear with very small intercepts.

ii. Analyses of polarization curves obtained as a function of rotation rate, $\omega$, yielded non linear Levich and Koutecky-Levich plots. Also non linear were plots of the limiting currents as a function of the concentration of HAM,
[HAM], for fixed $\omega$ providing evidence that the reaction does not follow a simple mechanism. This behavior could be due to contributions due to reactions involving the reactant and products of the electrochemical process including HAM and nitrite which produce electrochemically unreactive $\text{N}_2\text{O}$ as well as the decomposition of nitrite which yields NO which is also expected to be redox in the potential range involved.

iii. Experiments involving RRDE and dual electrode techniques afforded evidence that the two consecutive redox waves are associated primarily with oxidation of HAM to nitrite and nitrate, respectively. Normal incidence normalized reflectance spectroscopy, $\Delta R/R$, on a rotating Au disk electrode failed to detect the presence of Au oxide during HAM oxidation in the potential region in which Au is known to form oxides for sufficiently high $\omega$ or large [HAM]. This behavior is analogous with that found earlier in our laboratories for the oxidation of bisulfite on Au and provides a second illustration of the interplay between oxide formation and oxygen transfer directly from Au oxide to HAM.

REFERENCES


Fig. 6-1. Cyclic voltammograms (ν = 10 mV/s) recorded with a Au disk electrode under stagnant conditions in the base electrolyte in the presence of 1 mM NH$_2$OH in the potential ranges 0.1 – 0.9 V (blue) and 0.1 – 1.4 V vs SCE (magenta). Also shown in this figure (see thin black curve) is the corresponding voltammogram obtained for the same electrode in the absence of HAM under otherwise identical conditions.
Fig. 6-2. Cyclic voltammograms (ν = 10 mV/s) for a Au disk electrode in the base electrolyte in the presence of 0.2 to 2 mM NH₂OH as specified in the figure. Insert: Plots of the peak currents, i_{peak}, as a function of the concentration of hydroxylamine, [HAM] based on the data in the figure for the first (solid circles) and second (open circles) voltammetric peaks. The straight lines represent best linear fits to the data. Peak II: Intercept, I = 0.00948 ± 0.0044; Slope, S = 0.23769 ± 0.00358; R² = 0.99909; Peak I: I = 0.01037 ± 9.936E-4; S = 0.13532 ± 8.0910E-4; R² = 0.99986.
Fig. 6-3. Dynamic polarization curves recorded for a Au RDE ($\nu = 10 \text{ mV/s}$) in 1 mM NH$_2$OH for various rotation rates as specified (in rpm) recorded in increasing (black) and subsequently decreasing values of $\omega$ (red). The small arrows indicate the direction of the potential scan (see text).
Fig. 6-4. Plots of the limiting currents, $i_{lim}$ vs $\omega^{1/2}$ (Panel A) and $i_{lim}^{-1}$ vs $\omega^{-1/2}$ (Panel B) based on the data in Fig. 6-3.
Fig. 6-5. Dynamic polarization curves ($\nu = 10$ mV/s) for a Au RDE in base electrolyte containing 0.1 M NaClO$_4$ in the presence of 0.2 (black), 0.5 (red) and 1.0 (green), 1.5 (blue) and 2 mM NH$_2$OH (magenta) recorded at $\omega = 900$ rpm. Insert: Plots of the limiting currents, $i_{lim}$ recorded at 0.6 V (solid circles) and 0.9 V (open circles) as a function of the concentration of NH$_2$OH for $\omega = 900$ rpm (black circles) and $\omega = 1600$ (red circles) rpm.
Fig. 6-6. Cyclic voltammograms ($\nu = 10$ mV/s) recorded with a Au disk electrode in the base electrolyte containing 1 mM Cd(ClO$_4$)$_2$ before (blue) and after addition of either 1 mM NaNO$_2$ (black) or 1 mM KNO$_3$ (red).
Fig. 6-7. Cyclic voltammograms ($\nu = 10$ mV/s) for a Au disk in a quiescent base electrolyte containing 1 mM NH$_2$OH in the absence (red) and the presence (blue) of 1 mM Cd(ClO$_4$)$_2$. The insert displays an enlarged version of these curves in the potential region between 0.1 and 0.3 V vs SCE.
Fig. 6-8. Panel A. Plots of the Au ring currents, $i_{\text{ring}}$, of the Au|Au RRDE collected while scanning $E_{\text{ring}}$ at 10 mV/s in the base electrolyte in the presence of 1 mM NH$_2$OH and 1 mM Cd(ClO$_4$)$_2$ in the range $-0.75 \leq E_{\text{ring}} \leq 0.2$ vs SCE for $E_{\text{disk}} = 0.2$ and in 0.1 V intervals thereafter up to 1 V in the direction specified by the arrow. Data were acquired at $\omega = 900$ rpm. Panel B. Plots of the steady state disk current (scattered solid circles), $i_{\text{disk}}$, as a function of the disk potential, $E_{\text{disk}}$, recorded in the solution specified in Panel A in this figure where the solid line is dynamic polarization curve recorded at 10 mV s$^{-1}$ under otherwise the same conditions. Panel C. Plots of $i_{\text{ring}}$ @ $E_{\text{ring}} = -0.75$ V vs SCE vs $E_{\text{disk}}$ (solid black circles) based on the data in Panel A in this figure. Also shown for completeness are values of $i_{\text{ring}}$ collected under otherwise identical conditions in the absence of HAM in the media (see solid red circles) in this panel.
Fig. 6-9. Dynamic polarization curves recorded with a Hm(GC) RDE in 1 mM NaNO₂ solutions in the base electrolyte at \( \omega = 100, 400, 900, 1600 \) and 2500 rpm in the sequence specified by the arrow. Also shown in this figure (see grey curve) is the cyclic voltammogram obtained for the Hm|GC electrode in the neat base electrolyte under stagnant conditions.
Fig. 6-10. Cyclic voltammogram (ν = 10 mV/s) of a Au disk electrode (Panel B) in 1 mM NH₂OH in the base electrolyte under stagnant conditions. The Panel A shows the current collected with a Hm|GC disk electrode polarized at -0.7 V while the Au electrode was being scanned with the two electrodes very close to each other (< 1 mm, see Scheme 6-1).
Fig. 6-11. Dynamic polarization curves ($v = 20$ mV/s, Panel A) and normal incidence $\Delta R/R$ vs $E$ ($\lambda = 632$ nm, Panel B, $E_{\text{ref}} = 0.0$ V) recorded simultaneously with a Au RDE in the base electrolyte in the presence of 2 mM NH$_2$OH at various rotation rates, $\omega = 0$ (black, Acq = 6), 400 (red, Acq = 11), 900 (green, Acq = 10), 1600 (blue, Acq = 7) and 2500 (magenta, Acq = 6) rpm.
Fig. 6-12. Same as Fig. 6-11 for 5 mM NH$_2$OH at various rotation rates, $\omega = 0$ (black, Acq = 9), 900 (red, Acq = 14), 1600 (green, Acq = 15) and 2500 rpm (blue, Acq = 13).
Fig. 6-13. Cyclic voltammograms ($\nu = 10 \text{ mV/s}$) recorded with Au disk electrode in the base electrolyte containing 1 mM NH$_2$OH before (red) and after adding 1 (green), 5 (blue) and 10 mM NaCl (magenta). The curve in black represents the linear voltammetric scan toward positive potentials in the base electrolyte before addition of HAM and chloride.
Fig. 6-14. Dynamic polarization curves ($\nu = 10$ mV/s) recorded with a Au RDE in the base electrolyte containing 1 mM NH$_2$OH in the absence (dotted curve) and presence of 1 (black), 5 (red) and 10 mM NaCl (blue) at a rotation rate $\omega = 1600$ rpm (solid lines).


