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APPLICATION OF MODULATED HYDRODYNAMIC VOLTAMMETRY TO THE STUDY OF ANODIC ELECTROCATALYSIS

Iowa State University

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Ph.D. 1984
Application of modulated hydrodynamic voltammetry
to the study of anodic electrocatalysis

by

Deborah S. Austin

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For the Graduate College

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1984
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DEDICATION

In memory of my grandfather-R. H. Engle
who inspired me to explore the wonders of science.
I. INTRODUCTION

The development of new electroanalytical techniques evolves from the limitations of existing techniques. The progression of polarographic techniques from conventional dc polarography to normal pulse polarography to differential pulse polarography is a prime example. With each advance, the interference from charging current, which flows as the electrode area increases, was minimized further. Although Hg has an excellent cathodic potential range, the anodic potential range is limited by dissolution of Hg. Solid electrodes, e.g., Pt and Au, have wide anodic potential ranges. Therefore, voltammetric techniques utilizing solid electrodes were introduced, but their use is not without inherent limitations. Double-layer charging and oxidation/reduction of the surface atoms result from changes in the applied electrode potential. Surface reactions, such as the anodic formation and cathodic dissolution of oxide, cause substantial current to flow which often obscures the analytical signal of interest. Hydrodynamically modulated voltammetry was developed to overcome these limitations by effectively isolating the signal of interest, i.e., the mass-transport coupled component of the total signal, from the background current components.

Although background currents produced by the oxidation of the metal surface are viewed as an interference when attempting to measure the mass-transport coupled current by conventional cyclic voltammetry, surface oxides in the early stage of formation have been found to catalyze many anodic reactions. However, as growth of the oxide film proceeds, loss of catalytic activity is observed. A catalytically active surface can
be continually regenerated by modulating the applied electrode potential. Simultaneous modulation of the electrode potential and the rotational velocity allows one to investigate the effect that the potential-dependent surface state has on anodic reactions which are coupled to the mass-transport of the analyte from the bulk solution.

The objectives of this research project included the development of the software necessary for modulated hydrodynamic voltammetric techniques and their application to the study of surface-catalyzed reactions. Based on preliminary results, the oxidation of I⁻ in acidic media at a Pt electrode was chosen to be studied in further detail.
II. LITERATURE REVIEW

A. Anodic Electrocatalysis and the Role of Surface Oxides in Oxygen-transfer Reactions

Electrochemical reactions are influenced markedly by the applied electrode potential. The potential-dependent rate constant \( k \) for electrochemical reactions is given by the equation (1):

\[
k = k^0 \exp\left\{-\alpha n FE/RT\right\}
\]

where \( k^0 \) is the standard rate constant, \( \alpha \) is the transfer coefficient, \( n \) is the number of electrons, \( F \) is the Faraday constant, \( E \) is potential, \( R \) is the gas constant, and \( T \) is temperature. Also significant in electrochemical reactions are the choice of electrode material and the properties of the electrode surface, i.e., surface morphology and the presence of oxides. Electrochemical reactions can be catalyzed, thus, the term electrocatalysis was coined. Appleby (2) defined electrocatalysis as "the study of heterogeneous catalytic reactions that involve reactant and product species transferring electrons through an electrolyte-catalyst interface". Electrocatalytic effects were reported first in the literature in 1928 by Bowden and Rideal (3). They observed, for reactions such as the deposition of H, differences in the exchange current density for different electrodes at the same potential. Presently, interest in electrocatalysis is in the area of energy conversion devices. Electrocatalyzed reactions directly convert combustion energy into electricity. The major objective is to develop a system
which produces the maximum reaction rates at potentials close to the reversible potential, thereby minimizing cost.

The catalytic participation of surface oxygen at a Pt electrode in electro-oxidative processes was implicated by Russian scientists in the early 1950's (4-6). In the early to mid-1960s, surface oxides on noble metal electrodes were demonstrated to affect the mechanism of a reaction in addition to the kinetics of the reaction (7-10). Numerous examples of anodic oxidation of inorganic compounds are cited in Table II-1 in which the involvement of surface oxides at metal electrodes has been suggested. Note that the oxidation products of the species listed in Table II-1 have a greater oxygen content than the reactant species, e.g., \( H_2AsO_3 \rightarrow H_3AsO_4 \), \( I^- \rightarrow IO_3^- \), and \( SO_3^{2-} \rightarrow SO_4^{2-} \), thereby inferring that the electrode serves as an O-transfer catalyst. Since the involvement of surface oxides is apparently an integral part of the electrocatalytic process, the formation of oxides on noble metal electrodes, in particular Pt, merits discussion.

An excellent survey of literature pertaining to the formation of oxides on noble metal electrodes prior to 1965 was presented by Gilman (46). Recent reviews of literature were reported by Belanger and Vijh (47) and Cabelka (48). The evolution of \( O_2 \) at noble metal electrodes was reviewed by Hoare (49). The intention of this discussion is to summarize those conclusions most widely accepted among present-day researchers.

Angerstein-Kozlowska et al. (50), Conway and Gottesfeld (51), and Tilak et al. (52) have studied extensively the formation of surface
Table II-1. Evidence of electrocatalysis by surface oxide

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oxides on Pt in acidic solutions. They concluded that the initial step involves the production of adsorbed OH radicals by the reaction

\[ \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ + \text{e}^- \]

They also demonstrated that the formation of the equivalent of a monolayer of lower surface oxide occurs in a stepwise manner: the anodic wave can be deconvoluted into three peaks corresponding to oxides with surface stoichiometry of \( \text{Pt}_4\text{OH} \) (ca. 0.89 V vs. NHE), \( \text{Pt}_2\text{OH} \) (ca. 0.95 V vs. NHE), and \( \text{PtOH} \) (ca. 1.05 V vs. NHE). The "lower oxide" will be designated as "PtOH". The initial PtOH produced with low surface coverage can be reduced by a nearly reversible cathodic process. The reversible PtOH has only transient existence; however, with time, as well as a result of local potential fields, the adsorbed OH radicals and Pt atoms undergo place-exchange to produce "OH\text{Pt}" which is more stable than PtOH. The reduction of this oxide species occurs at a more negative reduction potential. For \( E > 1.0 \text{ V} \) in acidic media, a monolayer of adsorbed OH is formed rapidly with subsequent conversion by oxidation to the "higher oxide" designated as "PtO". Place-exchange also occurs with the PtO species to form "OPt".

Angerstein-Kozlowska et al. (53) also investigated the effect of adsorbed ions on the initial stage of oxide formation. As a result of competition between the ions and the OH radicals for adsorption sites on the electrode surface, the potential at which oxide formation commences is shifted to more positive values. Adsorbed ions also facilitate place-exchange between Pt atoms and adsorbed OH, thereby
decreasing the number of OH species available on the surface for reaction with the analyte. As mentioned previously, place-exchange is promoted at higher potential values. Therefore, the combination of adsorbed ions and higher potential values contribute to the shortening of the potential range over which PtOH exists for a significant period of time.

The electrochemical evolution of O₂ at Pt anodes has been investigated by several researchers (54-57). Damjanovic and Jovanovic (54) proposed that the process involves the direct participation of O-atoms in the oxide film. The participation of the surface oxygen is supported by the work of Rozental and Veselovskii (55) and Churchill and Hibbert (56) using a tracer technique. The Pt surface oxide was formed by anodic polarization in an 18O-enriched aqueous solution followed by the evolution of O₂ from the enriched oxide surface in an unlabeled aqueous solution. The initial gas evolved was rich in the dimer 18O₁⁶O resulting in the progressive depletion of 18O from the surface oxide. Damjanovic and Jovanovic (54) postulated that the evolution of O₂ proceeds according to the scheme:
The first step in the mechanism involves the generation of OH radicals on the PtO surface. When O₂ molecules leave the surface of the electrode, the oxide must be reformed which involves OH radicals as an intermediate product:

\[
\begin{align*}
-\text{Pt} - \text{O} - \text{Pt} & \quad \overset{\dots}{\text{O-}0^-} + \text{H}^+ \\
-\text{Pt} & \quad \overset{\dots}{\text{O-}0^-} + \text{H}^+ + \text{e}^- + \text{O}_2
\end{align*}
\]

The apparent abundance of OH radicals present on the electrode surface during O₂ evolution and the fact that catalysis is observed in the presence of the lower oxide (i.e., PtOH) causes one to suspect that O₂ evolution may also exhibit an electrocatalytic effect on many anodic
reactions.

The potential for onset of surface oxidation at a Au electrode has been widely disputed. Hoare (58), using double-layer capacitance measurements, first observed the possible existence of adsorbed oxygen at $E < 1.06$ V vs. SCE which greatly influences the electrochemical properties of the electrode. For example, the electro-oxidation of organic molecules presumably requires a surface oxygen loosely bound to the metal substrate. Maximum oxidation rates for olefins at Au electrodes are observed in the region $0.95 \, V < E < 1.1 \, V$ (59). Other researchers (60-63) maintain that no Au oxidation occurs until $E > 1.06$ V, and they attribute the change in capacitance at $E < 1.06$ V to impurities in the electrode material or in the electrolyte solution. Results of recent studies utilizing ellipsometry (59, 64), reflectance spectroscopy (59, 64, 65), and a photochemical method (66, 67) support the existence of adsorbed oxygen, presumably as AuOH, at $E < 1.06$ V as proposed by Hoare (58). The onset of AuO formation occurs at $E > 1.06$ V with monolayer coverage attained at ca. 1.2 V. For $E > 1.2$ V, further oxidation of the surface occurs producing $\text{Au}_2\text{O}_3$ up to ca. 1 nm in thickness. Application of $E > 1.8$ V leads to the formation of a highly-hydrated, highly-colored (reddish brown), surface layer with the dominant species being $\text{Au(OH)}_3$ (68). The latter two oxides differ in electronic and ionic conductivity; $\text{Au}_2\text{O}_3$ is a semiconductor whereas $\text{Au(OH)}_3$ is a conductor.

Gold(III) oxide, loosely held on the electrode surface, flakes off exposing Au sites (69-71). Oxygen evolution and continued formation of


$\text{Au}_2\text{O}_3$ can occur at the exposed Au sites, both reactions involving intermediate production of an OH species (70-72).

Literature pertaining to the anodic oxidation of Pd is limited (47, 69, 73-76). The stability and reactivity of surface oxides on Pd are highly dependent upon the electrode history. Palladium dissolution occurs at a freshly polished electrode during the initial scans of potential which results in roughening of the electrode surface hence, an increase in the real area of the electrode. However, after repetitive potential cycling, surface roughening ceases, the electrode stabilizes, and activity toward oxygen adsorption increases. Palladium oxide formation occurs in a stepwise fashion during the positive scan of potential by a mechanism similar to oxide formation on Pt. Initially, a PdOH species is formed at $E > 0.48$ V, reaching monolayer coverage at ca. 0.7 V, followed by the formation of the more stable oxide PdO. With time, place-exchange of Pd and O occurs. Formation of PdO$_2$ begins at a potential corresponding to the evolution of O$_2$ on Pd (ca. 1.2 V). Since PdO$_2$ is known to be unstable in acid, Hoare (77) proposed that O$_2$ evolution at a Pd electrode occurs by decomposition of PdO$_2$ in the reaction $\text{PdO}_2 \rightarrow \text{PdO} + \frac{1}{2}\text{O}_2$. Hence, the anodic current observed is the result of regeneration of PdO$_2$ by the reaction $\text{PdO} + \text{H}_2\text{O} \rightarrow \text{PdO}_2 + 2\text{H}^+ + 2\text{e}^-$.  

The anodic behavior of an Ir electrode displays unique characteristics in comparison with that of other noble metal electrodes (46, 76, 78). Voltammograms recorded in an electrolyte of 1 M H$_2$SO$_4$ are fairly symmetrical about the potential axis in the region of oxygen adsorption
and oxygen desorption indicating reversibility of the electrode reaction. A continual increase in the anodic oxide formation current and the cathodic oxide dissolution current is observed upon repetitive potential cycling owing to the buildup of oxide on the electrode surface. The extent of continuous oxide buildup decreases as the concentration of the acidic electrolyte solution increases. In 5 M H₂SO₄, current does not change significantly with continuous potential cycling; however, reversible behavior is not observed. Irreversibility of oxygen adsorption and oxygen desorption increases as the potential scan is reversed at more positive potential values. The surface oxidation of Ir occurs with initial formation of IrOH at E > 0.16 V, and further oxidation to IrO at E > 0.95 V. At E > 1.15 V, IrO is converted to IrO₂. Initially, O₂ evolution takes place at a potential where a mixture of IrO and IrO₂ sites exist. A decrease in the anodic current for O₂ evolution occurs at ca. 1.4 V as a result of a change in the properties of the metal ions in the anodic film. The existence of an IrO₃ species has been observed at high potentials by Frazier and Woods (79), and Kim et al. (68). The former authors speculated also that IrO₃ participates directly in the O₂ evolution reaction as represented by the equations:

\[
\text{IrO}_3 \rightarrow \text{IrO}_2 + \text{O}_2
\]

\[
2\text{O}_2 \rightarrow 0_2
\]

The electrocatalytic activity of the oxide toward O₂ evolution depends upon the number of sites within the oxide that can react according to the above equations. Hence, the activity is proportional to the
quantity of IrO$_3$. Gottesfeld and Srinivasen (80) reported that the rate of O$_2$ evolution is 5-10 times faster on a well-developed oxide layer than on a freshly polished electrode at which the oxide layer is not yet well-developed.

B. Hydrodynamically Modulated Voltammetry

Miller, Bellavance, and Bruckenstein (81) examined the feasibility of hydrodynamically modulated voltammetry at rotating disk electrodes based on the application of sine-wave and square-wave modulations about a nonzero, average rotational velocity. An important experimental advantage which resulted from the use of superimposed modulations on a steady speed was the ability to separate the convective-diffusion controlled component of the total current from background components, which result from surface processes and decomposition of the supporting electrolyte and are not influenced by variation in the rotational velocity. Subsequent investigations (82-87) have focused on the sinusoidal version of hydrodynamically modulated voltammetry (SHMV). The theoretical basis of the technique has been developed extensively. Although SHMV has been applied for the determination of heterogeneous kinetic parameters for quasi-reversible and irreversible systems and the determination of diffusion coefficients, major emphasis has been placed on application of SHMV for trace analysis. Recent advances in SHMV include amplitude enhancement (88) and operation in the derivative mode (89). Both modifications were developed to increase the sensitivity of the extracted signal, thus extending the analytical applicability for
submicromolar electroanalysis. Miller and Bruckenstein (84) concluded that SHMV "... can frequently overcome severe complications arising from interfering discharge of supporting electrolyte and thereby extract serviceable voltammetric waves ..."; however, no specific examples have been reported which exploit this advantage. Blaedel and coworkers (90-92) investigated the square-wave version of hydrodynamically modulated voltammetry, which they referred to as "pulsed rotation voltammetry". The determination of reaction rate constants and transfer coefficients, and application to trace analysis have been emphasized. In addition, Engstrom and Blaedel (93) recognized the advantages of automating the square-wave technique through use of small computers. The theory and application of hydrodynamically modulated voltammetric techniques have been reviewed by Wang (94).

Both the sine-wave and square-wave versions of hydrodynamically modulated voltammetry are capable of extracting the convective-controlled faradaic signal from a total current dominated by surface-controlled processes, however, the interest in this research project focused on square-wave hydrodynamically modulated voltammetry (QHMV) under computer control. The choice to apply QHMV for the study of electrocatalysis was based on the following factors: 1) Instrumentation is simplified since no filtering device or lock-in amplifier is required. 2) The technique is automated easily with control of the experiment and data acquisition provided by a small computer. 3) Under computer control and the use of a staircase potential waveform, the time necessary to complete an experiment is relatively short. 4) All instrumentation is commercially
available, allowing researchers to assemble the instrumentation quickly and focus their attention on the data produced. Furthermore, emphasis on application of QHMV in this project was shifted from a quantitative interest in trace analysis to a qualitative interest in the characterization of reactions under mixed surface and transport control. Application of hydrodynamically modulated voltammetry for micro- and submicromolar analysis has been given considerable attention, however, the technique will never compete successfully with other electroanalytical techniques available for trace analysis. The complexity of real-life samples mandates the use of chromatography for separation of components thus eliminating the practicality of analysis in a batch cell which is required for rotational velocity modulations. Even though a pulsed-flow technique has been investigated (95), this detection system is not feasible in conjunction with chromatography.

The ability to observe mass-transport controlled current occurring simultaneously with $O_2$ evolution is by far the most salient feature of QHMV. There is a wealth of information available in a potential region previously inaccessible by conventional voltammetry. Anodic reactions once avoided due to the complexity of the anodic signal now can be studied. Future research with hydrodynamically modulated voltammetric techniques may provide further extension of the available potential range which is limited by dissolution of the electrode material, not the production of $O_2$. 
III. EXPERIMENTAL

A. Chemicals

All solutions were prepared from reagent grade chemicals and triply distilled water. The water was passed through an ion-exchange column following the first distillation, distilled from an alkaline permanganate solution (0.1 M KMnO₄/0.1 M KOH), and finally distilled from a 1 M H₂SO₄ solution. Dissolved O₂ was removed from all solutions by saturation with N₂. A blanket of N₂ was maintained above the solution throughout experimentation.

B. Instrumentation

1. Voltammetric studies

a. Electrodes  The rotating disk and ring-disk electrodes (RDE and RRDE) (Pine Instrument Co., Grove City, PA) are listed in Table III-1.

<table>
<thead>
<tr>
<th>Model</th>
<th>Type</th>
<th>Electrode Material</th>
<th>Area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFMD28</td>
<td>RDE</td>
<td>Pt</td>
<td>0.166</td>
</tr>
<tr>
<td>AFMD28</td>
<td>RDE</td>
<td>Au</td>
<td>0.162</td>
</tr>
<tr>
<td>AFMD19</td>
<td>RDE</td>
<td>Pd</td>
<td>0.197</td>
</tr>
<tr>
<td>AFDT06</td>
<td>RRDE</td>
<td>Pt,Pt</td>
<td>0.459, 0.059</td>
</tr>
<tr>
<td>AFMDI1980</td>
<td>RDE</td>
<td>RuO₂/TiO₂</td>
<td>0.201</td>
</tr>
</tbody>
</table>

⁠^a Anode material supplied by Dow Chemical Co. (Freeport, TX).
An Ir electrode (0.496 cm²) was fabricated in the machine shop in the Department of Chemistry, Iowa State University. Prior to each use, the electrodes (except for RuO₂/TiO₂) were polished with 0.05 µm Buehler Alumina on microcloth then thoroughly rinsed with triply distilled water.

b. Rotators The model PIR rotator (Pine Instrument Co.) was used with the AFDT06 electrode for ring-disk studies. This rotator had nine fixed speeds between 400 and 10,000 rpm. The rotator model MSR (Pine Instrument Co.) was used with the model AFMD electrodes and the Ir electrode. This rotator was a solid-state, servo-controlled system capable of rapid acceleration and deceleration. The speed could be set from 100 to 10,000 rpm within 1% accuracy. Acceleration from 1000 rpm to 4000 rpm occurred in 22 ms. An external analog signal applied to the input jack on the speed control box made possible the application of modulated waveforms.

c. Potentiostats Potentiostatic control for application of triangular and staircase potential waveforms was achieved by the model RDE-3 potentiostat (Pine Instrument Co.). The faster potentiostatic response necessary for application of the triple-step potential waveform was achieved with a PAR-174A potentiostat (EG&G Princeton Applied Research Corp., Princeton, NJ). A miniature, saturated calomel electrode (SCE) served as the reference electrode and all potentials are reported as volts vs. SCE.

d. Computer system External signals for control of rotational velocity and electrode potential were generated, and data were acquired, under computer control. The computer (model 6800, Southwest Technical
Products Corp., San Antonio, TX) was equipped with 32-K bytes of memory, four 12-bit digital/analog (D/A) converters, and eight multiplexed 12-bit analog/digital (A/D) converters. Peripheral devices included a Beehive International B-150 computer terminal (Salt Lake City, UT), a Centronics microprinter P-1 (Hudson, NH), and floppy disk storage. Programming was done in BASIC. Program listings are given in the Appendix.

e. Miscellaneous. Current-potential (I-E and ΔI-E) and current-time (I-t) curves were recorded on a X-Y recorder (model 7035B, Hewlett Packard, San Diego, CA; or model Omnigraphic 100 Recorder, Houston Instruments, Bellaire, TX). An oscilloscope (model 122A, Hewlett Packard) was used in preliminary experiments to optimize conditions for QHMV by observing the time required for the rotation speed to be established following a step change in the external analog input. Also, the response of the electrode current following a step change in the rotation speed was monitored.

2. Flow injection system

The flow injection apparatus was assembled as described by Hsi (96). The flow-through cell was constructed by the machine shop of the Department of Chemistry, Iowa State University, and is illustrated in Figure III-1. A 25-gauge Pt wire (3 mm long) served as the working electrode. The cell was submerged in a beaker filled with supporting electrolyte. A Pt-wire counter electrode and the reference electrode were also placed in the beaker. The dispersion constant for this flow injection system was 0.45. A microprocessor-controlled potentiostat (model UEM detector, Dionex, Inc., Sunnyvale, CA) was utilized for the
Figure III-1: Flow-through cell utilized for constant potential and multi-step potential amperometric detection
Cross-Sectional View

- contact wire
- glass
- outlet
- Pt working electrode

inlet

Kel-F
- o-ring

Side View
application of double-step and triple-step potential waveforms. Data were recorded using a stripchart recorder (model 250-1, Curken, Inc., Lincoln, NE).
IV. SQUARE-WAVE HYDRODYNAMICALLY MODULATED VOLTAMMETRY

A. Theory

The theoretical basis of QHMV is relatively straightforward. Total current \( I_{\text{tot}} \) observed at a solid electrode is expressed as follows:

\[
I_{\text{tot}} = I_{\text{conv}} + I_{\text{solv}} + I_{\text{surf}} + I_{\text{ch}} \tag{1}
\]

where \( I_{\text{conv}} \) is the convective-coupled component of current, \( I_{\text{solv}} \) is the current produced by electrolysis of the solvent, \( I_{\text{surf}} \) is the faradaic current from surface-controlled processes such as the formation or reduction of oxide and reactions involving adsorbed species, and \( I_{\text{ch}} \) is the double-layer charging current. The transient currents, \( I_{\text{surf}} \) and \( I_{\text{ch}} \) are independent of mass transport. Since the concentration of \( \text{H}_2\text{O} \) at the electrode surface is not a function of the rotational velocity, \( I_{\text{solv}} \) is not dependent upon mass transport. Therefore, isolation of \( I_{\text{conv}} \) from \( I_{\text{tot}} \) can be achieved by modulating the rate of convective transport of electroactive species to the electrode surface, i.e., by variation of the rotational velocity of the electrode. The value of \( I_{\text{tot}} \) is measured at two rotational velocities (i.e., the upper (u) and lower (l) velocity) and the difference is computed. The resultant signal (\( \Delta I \)) is a function solely of the mass-transport component of total current at the two velocities (equation 2).

\[
\Delta I = I_{\text{tot},u} - I_{\text{tot},l}
\]
ΔI = (I_{conv,u} + I_{solv} + I_{surf} + I_{ch}) - 
(I_{conv,l} + I_{solv} + I_{surf} + I_{ch})

ΔI = I_{conv,u} - I_{conv,l} \tag{2}

If the mass-transport coupled reaction behaves according to the Levich equation, the theoretical limiting signal, ΔI_{lim} (coul/s) can be calculated by equation 3,

ΔI_{lim} = 0.62 \cdot \frac{nFAD^{2/3}v^{-1/6}}{\omega_0^{1/2} - \omega_1^{1/2}}c^b \tag{3}

where \(n\) is the number of electrons (eq/mol), \(F\) is the Faraday constant (96,484 coul/eq), \(A\) is the area of the electrode (cm²), \(D\) is the diffusion coefficient (cm²/s), \(v\) is the kinematic viscosity (cm²/s), \(\omega\) is the angular velocity (rad/s), and \(C^b\) is the bulk concentration of analyte (mol/cm³).

B. Experimental Procedure

1. Staircase potential waveform

QHMV, utilizing a staircase potential waveform (Figure IV-1), was performed according to the following sequence: 1) Experimental parameters were specified, including the cathodic (E_c) and anodic (E_a) limits for the potential scan, the potential step increment (∆E), the lower (W_l) and upper (W_u) rotation speeds, the time delay (t_d) required after application of a change in rotation speed (∆W) to allow current stabilization prior to the measurement of current, and the number of data points (N) to be collected at each rotation speed. 2) The average
Figure IV-1: Staircase potential waveform

Arrow indicates point at which measurement of current commences.
$E$ (step)
of the N values of current measured at \( W_1 \) and \( W_u \) was calculated for each value of potential, and the difference between the two average current values (\( \Delta I \)) was computed. 3) Finally, the data were plotted as \( \Delta I \) vs. \( E \).

2. Triple-step potential waveform

QHMV was applied also utilizing the triple-step potential waveform illustrated in Figure IV-2. The waveform consisted of an initial potential value \( (E_1) \) which resulted in reduction of PtOH and PtO, an oxidizing potential \( (E_2) \) for which surface oxidation was initiated, and a sampling potential \( (E_3 < E_2) \) at which the faradaic signal was measured. The triple-step waveform was applied at both \( W_1 \) and \( W_u \) during each modulation cycle of rotation speed, and \( \Delta I \) was calculated corresponding to \( \Delta W \). Potential \( E_3 \) was incremented by \( \Delta E \) after completion of each modulation cycle. The time spent at each potential is designated by \( t_1 \), \( t_2 \), and \( t_3 \), respectively.

A plot of \( \Delta I \) vs. \( t_2 \) was generated for a series of \( E_2 \) values by holding \( E_2 \) constant and incrementing \( t_2 \) following each modulation cycle of rotation speed. Similarly, plots of \( \Delta I \) vs. \( t_3 \) were constructed for several values of \( E_2 \) by holding \( E_3 \) constant and incrementing \( t_3 \) at the completion of each modulation cycle of rotation speed.

C. Optimization of Parameters

The time required for relaxation of the hydrodynamic boundary layer to a steady-state value following a step-wise change in the disk speed has been discussed in detail by Albery, Hillman, and Bruckenstein (97). The relaxation time is dependent upon the final rotation speed and the
Figure IV-2: Triple-step potential waveform

Arrow indicates point at which measurement of current commences.
Schmidt number (the dimensionless ratio \( v/D \)), and has been shown to occur within 4% of the time required for a single rotation.

The time required for the rotation speed to be established following a step change in the voltage applied to the speed controller is given in Table IV-1. Note that the time required to achieve the final speed upon deceleration is longer than the time required to establish the final speed upon acceleration for equal values of \( |\Delta W| \).

Table IV-1. Time response of the MSR to a voltage step

<table>
<thead>
<tr>
<th>Initial Speed (rpm)</th>
<th>Final Speed (rpm)</th>
<th>Time to achieve 95% of final speed (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>2000</td>
<td>20</td>
</tr>
<tr>
<td>1000</td>
<td>3000</td>
<td>30</td>
</tr>
<tr>
<td>1000</td>
<td>4000</td>
<td>30</td>
</tr>
<tr>
<td>2000</td>
<td>1000</td>
<td>30</td>
</tr>
<tr>
<td>3000</td>
<td>1000</td>
<td>40</td>
</tr>
<tr>
<td>4000</td>
<td>1000</td>
<td>60</td>
</tr>
</tbody>
</table>

When stepping from \( W_l \) to \( W_u \), the thickness of the diffusion layer \( (\delta) \) decreases and any excess reactant in the hydrodynamic layer is depleted quickly as it diffuses to the electrode. The time required for this process is determined by the distance through which the reactant must diffuse. The thickness of the diffusion layer is given approximately by \( \delta = 1.61 \sqrt[3]{\omega} \cdot \frac{1}{6} \). Because of the reciprocal dependence of \( \delta \) on \( \omega \), \( \delta \) at 4000 rpm is less than \( \delta \) at 1000 rpm. Therefore, one would expect the current to stabilize faster when stepping
from 1000 rpm to 4000 rpm than when stepping from 4000 rpm to 1000 rpm. This expected behavior was verified experimentally. In addition, the time required for the total current to stabilize following deceleration to the same rotation speed was found to be independent of the value of the upper rotation speed.

To produce a well-defined $\Delta I$-$E$ curve for a staircase potential waveform, especially in the regions of rapidly changing current, the potential increment should be small. The resolution of a 12-bit D/A converter is 5 mV. Therefore, an analog scaling device was constructed to increase the resolution of the D/A converter so that the potential could be set accurately even at small values of $\Delta E$. The potential range of the D/A converter was $-10$ V to $9.995$ V, whereas for most electrode materials, a potential range of $-2.0$ V to $2.0$ V is sufficient. The full range of the D/A converter was utilized with the analog scaling device, thus increasing resolution. For example, if a potential of 1.0 V was to be applied at the electrode, the computer was programmed to output a signal of $1.0 \text{ V}/DV$ ($DV$ is the deamplification factor). If $DV = 0.2$, the potential output by the computer was 5.0 V. The signal output by the computer was passed through a variable deamplifier ($E_{\text{out}} = DV E_{\text{in}}$) then applied to the potentiostat. The actual potential applied was measured by passing the potential signal from the potentiostat through a variable amplifier ($E_{\text{out}} = E_{\text{in}}/DV$) to the A/D converter. The computer was programmed to account for the scaling factor when storing the measured potential values. For the case where $DV = 0.2$, the resolution of the D/A converter was 1 mV. By making the deamplification factor variable,
one could choose the factor which provided maximum resolution for each system being investigated.

Following a time delay \( t_d \), the current, measured at each rotation speed, was sampled \( N \) times and the values were averaged to minimize the effect of current fluctuations (i.e., noise). Each current measurement required 10 ms. Typical values of \( t_d \) and \( N \) were 150 ms and 10. Upon completion of each modulation cycle, the \( \Delta I \) value was calculated and stored.

Each of the parameters discussed (i.e., \( \Delta E \), \( t_d \), \( N \)) and data manipulation affects the total time required to complete an experiment, which in turn affects the value of \( \Delta W \) and the frequency of modulation which can be applied. A thermal circuit breaker protected the motor of the rotator from overheating; therefore, if the \( \Delta W \) was too large, and/or the frequency was too high, the experiment could not be completed without triggering the circuit breaker. Consequently, a compromise between \( \Delta W \) and frequency was made. For example, the rotator could not be modulated between 1000 rpm and 5000 rpm at 1 Hz for a 20-min period without tripping the circuit breaker. However, modulation between 1000 rpm and 4000 rpm at 1 Hz could be applied for successive 20-min periods over 6-8 hr with minimal shutdown. Modulation between 1000 rpm and 4000 rpm was applied typically.
V. SURVEY OF ANODIC REACTIONS USING CYCLIC VOLTAMMETRY AND SQUARE-WAVE HYDRODYNAMICALLY MODULATED VOLTAMMETRY

A. Introduction

Numerous anodic reactions were examined by the application of cyclic voltammetry (CV) and square-wave hydrodynamically modulated voltammetry (QHMV). Current-potential (I-E) curves were recorded as a function of rotational velocity (ω) or potential scan rate (φ). The current produced by a mass-transport limited reaction increases as ω is increased according to the Levich equation

\[ I = 0.62 nFAD^{2/3} \nu^{-1/6} \omega^{1/2} C_b \]

Mass-transport limited current is independent of φ. On the other hand, the current produced by surface-controlled reactions, i.e., current limited by the area of the electrode, is dependent on φ and independent of ω. The dependence on φ is observed since the amount of charge (q) is constant for the scan of potential between two potential values. Hence, when φ is increased, the time necessary to pass through the potential region decreases and the instantaneous current (I = dq/dt) must increase. The study of electrochemical reactions is complicated when mass-transport and surface reactivity contribute simultaneously to the control of the reaction rate. The development of QHMV has made possible the extraction of the convective-coupled component from the total current. Hence, current-potential curves (ΔI-E) are simplified and the study of electrochemical reactions is facilitated. A significant advantage of QHMV is
the ability to observe mass-transport coupled reactions occurring simultaneously with \( O_2 \) evolution as well as oxide formation.

The investigation of anodic reactions electrocatalyzed by an intermediate stage of noble metal oxides was of major interest in this research project. Anodic reactions involving O-transfer mechanisms derived the most benefit from the oxide layer. Six anodic reactions will be discussed in some detail. The results obtained for the remainder of the analytes investigated are summarized briefly at the end of this section.

B. Residual Curves

The characteristic I-E and \( \Delta I-E \) curves obtained for Pt, Au, Pd, and Ir electrodes in the absence of electroactive species will be described briefly. The so-called "residual curves" in acidic media are shown in Figures V-1, V-2, V-3, and V-4. The curves for Pt and Au in basic media are similar in appearance to those in acidic media, except that the potential at which reactions such as oxide formation and reduction, \( O_2 \) evolution, and \( H_2 \) evolution are observed to shift 59 mV negative per unit of \( pH \). The practical anodic limit (\( E_a \)) of the potential scan in CV is usually considered to be that value for which the current from \( O_2 \) evolution has risen to become a significant fraction (ca. 0.2-0.5) of the analytical signal for faradaic reactions under study. The practical limit for QHMV is that value for which the error in computing \( \Delta I \) is a significant fraction of the transport coupled signal of interest. The practical anodic limits observed in this research for CV and QHMV for
Figure V-1: I-E and ΔI-E curves of Pt in 0.5 M H_2SO_4

----- I-E curve
Electrode rotation speed (W): 1000 rpm
Potential scan rate (φ): 6 V/min

----- ΔI-E curve
Lower rotation speed (W_L): 1000 rpm
Upper rotation speed (W_U): 4000 rpm
Potential step increment (ΔE): 5 mV
Time delay (t_d): 150 ms
Number of data points (N): 10
Figure V-2: I-E and ΔI-E curves of Pd in 0.5 M H$_2$SO$_4$

----- I-E curve

Electrode rotation speed ($W$): 1000 rpm
Potential scan rate ($\phi$): 6 V/min

----- ΔI-E curve

Lower rotation speed ($W_1$): 1000 rpm
Upper rotation speed ($W_U$): 4000 rpm
Potential step increment (ΔE): 5 mV
Time delay ($t_d$): 150 ms
Number of data points (N): 10
Figure V-3: I-E and ΔI-E curves of Au in 0.5 M H$_2$SO$_4$

---- I-E curve

Electrode rotation speed (W): 1000 rpm
Potential scan rate (φ): 6 V/min

---- ΔI-E curve

Lower rotation speed (W$_L$): 1000 rpm
Upper rotation speed (W$_U$): 4000 rpm
Potential step increment (ΔE): 5 mV
Time delay (t$_d$): 150 ms
Number of data points (N): 10
Figure V-4: I-E and ΔI-E curves of Ir in 5.0 M H₂SO₄

----- I-E curve

Electrode rotation speed (W): 1000 rpm
Potential scan rate (ψ): 6 V/min

ΔI-E curve

Lower rotation speed (W₁): 1000 rpm
Upper rotation speed (Wₚ): 4000 rpm
Potential step increment (ΔE): 5 mV
Time delay (tₖ): 200 ms
Number of data points (N): 25
each electrode are listed in Table V-1. Note that for QHMV, the anodic potential limit is extended approximately 150-400 mV beyond the limit for CV depending upon the electrode material.

Table V-1. Practical anodic potential limits for CV and QHMV.

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Electrolyte</th>
<th>Anodic Potential Limit (V vs. SCE)</th>
<th>Extension of $E_a$ by QHMV (^a) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>1.3</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>0.1 M NaOH</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Au</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>1.6</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>0.1 M NaOH</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Pd</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Ir</td>
<td>5 M H$_2$SO$_4$</td>
<td>1.3</td>
<td>1.45</td>
</tr>
</tbody>
</table>

^a The potential at which the current from $O_2$ evolution is a significant fraction (ca. 0.2-0.5) of the analytical signal for faradaic reactions under study.

^b The potential for which the error in computing $\Delta I$ is a significant fraction of the transport coupled signal of interest.

The residual I-E curve for a Pt electrode in 0.5 M H$_2$SO$_4$ is shown in Figure V-1. The small anodic current observed in the region 0.1 V < E < 0.55 V during the positive scan of potential is due to charging of the double-layer. At $E > 0.55$ V, surface oxide is formed: PtOH in the region 0.55 V < E < 0.81 V and PtO at $E > 0.81$ V. Appreciable $O_2$ evolution occurs at $E > 1.25$ V. During the negative scan of potential,
reduction of the surface oxide occurs yielding the large cathodic peak at \( E_p = 0.48 \) V. The formation and dissolution of adsorbed atomic H occurs on the cathodic and anodic scans, respectively, for \( 0.1 \) V > \( E \) > -0.2 V. Molecular H\(_2\) is evolved at \( E < -0.2 \) V.

The processes occurring at a Pd electrode parallel those on Pt; however, the shape of the I-E curve is unique to Pd (Figure V-2). Double-layer charging current occurs in the region \( 0.2 \) V < \( E < 0.5 \) V followed by formation of Pd oxide at \( E > 0.5 \) V. The evolution of O\(_2\) commences at \( E > \text{ca.} \ 1.15 \) V. Reduction of Pd oxide occurs at \( E_p = 0.41 \) V producing a sharper peak than observed for Pt. No characteristic peaks are observed for the adsorption of H on Pd owing to the complicating factor that H atoms not only adsorb on Pd but also absorb into the metal.

The useful potential range for CV at Au is broader than for either Pt or Pd (Figure V-3). The double-layer region extends from \(-0.4 \) V < \( E < 0.8 \) V during the positive scan of potential. Oxidation of the Au surface occurs at \( E > \text{ca.} \ 0.8 \) V. The anodic wave produced by oxidation of Au to AuOH in the potential region \( 0.80 \) V < \( E < 1.06 \) V is observed only at high current sensitivities. The conclusion that AuOH is produced is supported by results obtained utilizing nonelectrochemical methods (64, 65, 68). The anodic wave observed at \( E > 1.06 \) V is produced by the formation of AuO. Oxygen evolution begins at ca. \( 1.5 \) V. The Au oxide is reduced rapidly with \( E_p = 0.88 \) V. Continuing the negative potential scan, only double-layer charging current is observed in the region \( 0.7 \) V > \( E > -0.4 \) V and reduction of H\(^+\) occurs at \( E < -0.4 \) V. Adsorption of H atoms on Au is minimal; therefore, cathodic and anodic waves for
generation and dissolution of adsorbed H are not observed.

An electrolyte solution of 5 M H₂SO₄ was utilized for voltammetric studies at an Ir electrode. The highly acidic electrolyte minimizes the continuous buildup of oxide which occurs in less-concentrated acidic electrolytes with each subsequent cycle of potential. The residual I-E curve for Ir is shown in Figure V-4. The anodic dissolution of adsorbed H from the surface produces the current peaks at -0.08 V and 0.06 V on the anodic scan of potential. At E > 0.16 V, oxidation of the Ir surface occurs. Evolution of O₂ begins at ca. 1.25 V. During the negative scan of potential, no sharp peak is observed for cathodic dissolution of oxide. Instead, reduction of the oxide occurs over a broad range of potential overlapping with the region of the H adsorption wave.

C. Anodic Reactions

1. Arsenic(III)

The electro-oxidation of As(III) at a Pt electrode has been studied in detail by several researchers (23-25, 48, 98, 99). Arsenic ions adsorb on Pt and exhibit an inhibitory effect on the anodic formation of surface oxide (25, 48). Arsenic(III) is oxidatively desorbed as As(V). Zakharov and Songina (23), Lown and Johnson (24), and Cabelka et al. (25) reported that the mechanism of As(III) oxidation involves the transfer of an O-atom from the oxide to the As(III) species as indicated schematically by

\[ \text{PtO[0]} + \text{As(OH)}_3 \rightarrow \text{PtO} + \text{OAs(OH)}_3 \]
The I-E curve recorded for As(III) is shown in Figure V-5a. Although the oxidation of As(III) is thermodynamically allowed at \( E > 0.32 \) V, no current was observed until ca. 0.75 V. An anodic, peak-shaped wave (A) was produced at \( E > 0.75 \) V and is attributed to three concurrent processes: 1) oxidation of the Pt surface, 2) oxidation of adsorbed As(III), and 3) oxidation of As(III) transported to the electrode surface by convective-diffusion. Note that oxide formation was suppressed by ca. 150 mV due to the presence of adsorbed As(III). Maximum current was obtained during the positive scan of potential at ca. 0.85 V. A steady decrease in anodic current was observed for \( E > 0.85 \) V owing principally to the loss of current produced by the oxidation of adsorbed As(III). Upon reversal of the potential scan at \( E_a = 1.3 \) V, an anodic current plateau was observed in the region \( 1.2 \) V < \( E < 0.7 \) V. Peak B corresponds to the reduction of Pt oxide. The shoulder on the falling edge of the oxide reduction peak (C) is due to the underpotential deposition of As(V).

Current-potential curves recorded as a function of \( \omega \) at a constant value of \( \phi \) indicated that the oxidation of As(III) was dependent upon \( \omega \), although plots of \( I \) vs. \( \omega^2 \) were nonlinear. A series of I-E curves was recorded while varying \( \phi \) at a constant value of \( \omega \). The height of peak A varied with changes in \( \phi \); hence, surface-controlled reactions, i.e., oxide formation and oxidative desorption of As(III), are occurring simultaneously with the transport-coupled oxidation of As(III). The magnitude of the current plateau observed in the region \( 1.2 \) V < \( E < 0.7 \) V during the negative scan of potential was independent of \( \phi \); however, the
Figure V-5: I-E and ΔI-E curves of 0.5 mM As(III) in 0.5 M H₂SO₄ at a Pt RDE

a. I-E curve
   Electrode rotation speed (W): 1000 rpm
   Potential scan rate (ϕ): 6 V/min

b. ΔI-E curve
   Lower rotation speed (W_l): 1000 rpm
   Upper rotation speed (W_u): 4000 rpm
   Potential step increment (ΔE): 5 mV
   Time delay (t_d): 150 ms
   Number of data points (N): 10
current magnitude was much less than the predicted transport-limited value. Hence, the reaction is under mixed transport and kinetic control.

Wave A is comprised of three simultaneous processes, two of which are independent of $\omega$; hence, the transport-coupled component of total current can be extracted by the application of QHMV (Figure V-5b). During the positive scan of potential, a large anodic wave (A) was observed corresponding to the oxidation of As(III) to As(V) with a maximum value attained in the region $0.8 \, V < E < 0.9 \, V$. As the positive scan of potential continued, $\Delta I$ decreased steadily; however, as the potential was increased beyond $1.25 \, V$, $\Delta I$ in region B increased and approached the maximum value observed for wave A. Upon reversal of the potential scan, the mass-transport coupled oxidation of As(III) continued as long as $O_2$ was being evolved. A $\Delta I$ plateau was observed in the region $1.2 \, V < E < 0.9 \, V$ for the oxidation of As(III). The magnitude of $\Delta I$ in this region was dependent upon $E_a$; as $E_a$ became more positive, $\Delta I$ decreased.

The rising portion of the anodic wave was analyzed by measuring the value of $E_{2/3} - E_{1/3}$. The predicted value for a reversible reaction is $E_{2/3} - E_{1/3} = 0.0356/n$. Therefore, if $n = 2$, a value of $17.8 \, mV$ is expected. The observed value of $E_{2/3} - E_{1/3}$ was $20 \, mV$; hence, the reaction of As(III) to As(V) is virtually reversible. However, recall that the theoretical $E^0$ for the As(V)/As(III) half reaction is $0.32 \, V$. A reaction appearing to be reversible but occurring at an overpotential ($\eta$) of $400 \, mV$ can only be rationalized in terms of electrocatalysis caused by a potential dependent change in activity of the electrode.
surface. The anodic formation of surface oxide is inhibited by the presence of adsorbed As(III). Adsorbed As(III) is oxidatively desorbed by a mechanism concluded to involve O-atom transfer from PtOH to the As-species (25, 48). When a small amount of the adsorbed As(III) is desorbed, corresponding bare Pt sites are rapidly converted to PtOH which has a consequential accelerating effect on the reaction of the remainder of adsorbed As(III). Furthermore, oxidation of As(III) from the bulk solution is initiated also by the production of PtOH.

The oxidation of As(III) at a Au electrode has been examined by Zakharov et al. (41) and Loucka (99). Arsenic(III) adsorbs on Au; however, not to the extent of the adsorption on Pt. The I-E curve for As(III) on Au is shown in Figure V-6a. Wave A ($E_z = 0.82$ V) was the result of oxidation of As(III) to As(V). A limiting current plateau was observed in the region $0.9 < E < 1.1$ V. The small peak observed at $E_p = 0.85$ V was the result of the oxidative desorption of As(III). At $E > 1.1$ V, oxidation of the Au surface, i.e., the formation of AuO, occurred followed by a decrease in anodic current below the limiting value for As(III). When the scan direction was reversed, anodic current rapidly decreased; no current plateau was observed for As(III) oxidation on Au as was observed for As(III) oxidation during the negative scan on Pt. Reduction of Au oxide commenced at ca. 0.95 V.

The $\Delta$I-E curve obtained for As(III) oxidation at a Au electrode is shown in Figure V-6b. During the positive scan of potential, an anodic wave (A) was observed. A limiting value of current was attained in the region $0.95 < E < 1.15$ V. At $E > 1.15$ V, $\Delta$I decreased rapidly to a
Figure V-6: I-E and ΔI-E curves of 0.5 mM As(III) in 0.5 M H₂SO₄ at a Au RDE

a. I-E curve

Electrode rotation speed (W): 1000 rpm
Potential scan rate (χ): 6 V/min

b. ΔI-E curve

Lower rotation speed (Wₗ): 1000 rpm
Upper rotation speed (Wᵤ): 4000 rpm
Potential step increment (ΔE): 5 mV
Time delay (t₅): 150 ms
Number of data points (N): 10
near-zero value. However, at $E > 1.40 \, V$, $\Delta I$ increased linearly with potential (region B). The maximum $\Delta I$ attained at 1.85 V was ca. 23% of the theoretical value of $\Delta I_{\text{lim}}$ observed in region A. Upon reversal of the potential scan, $\Delta I$ decreased rapidly to zero. Anodic $\Delta I$ was observed following the reduction of Au oxide, the magnitude of which was dependent upon $E_a$.

The electro-oxidation of As(III) at a Au electrode produced an anodic wave with $E_{2/3} - E_{1/3} = 10 \, mV$; hence, the reaction was concluded to be virtually reversible. However, the reaction does not occur until the potential is 150 mV more positive than the $E^0$ for this reaction. Once again, electrocatalysis of the reaction is concluded to occur, presumably through the involvement of adsorbed OH radicals on Au. The formation of AuOH proceeds at $E > 0.8 \, V$. The value of $\Delta I$ remained at the mass-transport limited value until the formation of AuO occurred at $E > \text{ca.} \, 1.1 \, V$. The inhibitory effect exhibited by AuO is much greater than the inhibitory effect observed for As(III) oxidation at a Pt electrode. The observed difference in behavior of As(III) at Au and Pt may be attributed to a low surface density of OH species adsorbed on AuO. Also, the strength of the Au-O bond may preclude direct O-atom transfer and AuO cannot participate in the oxidation of As(III). An increase in $\Delta I$ was observed concurrently with an increase in surface density of $(OH)_{\text{ads}}$, i.e., as $O_2$ evolution commenced at ca. 1.4 V and subsequently, as the formation of a highly hydrated Au(III) species, Au(OH)$_3$, occurred. Upon scan reversal, $\Delta I$ rapidly diminished to zero and remained at zero until Au oxide was reduced ca. 0.88 V, giving a
small anodic $\Delta I$.

2. Nitrite

The I-E curves for $\text{NO}_2^-$ at Pt and Au (Figures V-7 and V-8) appear, at first glance, quite similar to the I-E curves obtained for As(III) at Pt and Au (see Figures V-5 and V-6). Further voltammetric investigation of $\text{NO}_2^-$ oxidation demonstrated both similarities and differences with the anodic behavior of As(III). Nitrite oxidation during the positive scan of potential occurred concomitantly with the initial stage of surface oxidation. No mass-transport coupled oxidation of $\text{NO}_2^-$ occurred simultaneously with $O_2$ evolution on Pt; however, renewal of the oxidative process for $\text{NO}_2^-$ occurred concurrently with $O_2$ evolution at a Au electrode. The literature available for the electro-oxidation of $\text{NO}_2^-$ on Pt and Au is sparse. However, Guidelli et al. (100), who examined the oxidation of $\text{NO}_2^-$ on Pt, and Erlikh et al. (42), who studied $\text{NO}_2^-$ on Au, concluded that $\text{NO}_2^-$ oxidation involves the interaction of active surface oxygen (PtOH and AuOH) and passivation is due to further oxidation of the oxides to a less active form (PtO and AuO).

No current was observed for oxidation of $\text{NO}_2^-$ for $E < 0.8$ V at a Pt electrode (Figure V-7a) due to the suppression of oxide formation caused by the presence of adsorbed $\text{NO}_2^-$. At $E > 0.8$ V on the positive scan, a large, anodic, peak-shaped wave (A) was observed with maximum current at $E = \text{ca. } 1.03$ V. The anodic wave is comprised of three components: 1) oxidation of the Pt surface, 2) oxidation of adsorbed $\text{NO}_2^-$, and 3) oxidation of $\text{NO}_2^-$ transported to the electrode by convective-diffusion. As the positive scan of potential was continued,
Figure V-7: I-E and ΔI-E curves of 0.5 mM NO$_2^-$ in 0.5 M H$_2$SO$_4$ at a Pt RDE

a. I-E curve
   
   Electrode rotation speed ($W$): 1000 rpm
   Potential scan rate ($\phi$): 6 V/min

b. ΔI-E curve
   
   Lower rotation speed ($W_L$): 1000 rpm
   Upper rotation speed ($W_U$): 4000 rpm
   Potential step increment (ΔE): 5 mV
   Time delay ($t_d$): 150 ms
   Number of data points (N): 10
Figure V-8: I-E and ΔI-E curves of 0.5 mM NO$_2^-$ in 0.5 M H$_2$SO$_4$ at a Au RDE

a. I-E curve
   
   Electrode rotation speed (W): 1000 rpm
   
   Potential scan rate (ϕ): 6 V/min

b. ΔI-E curve
   
   Lower rotation speed (W$_l$): 1000 rpm
   
   Upper rotation speed (W$_u$): 4000 rpm
   
   Potential step increment (ΔE): 5 mV
   
   Time delay (t$_d$): 150 ms
   
   Number of data points (N): 10
anodic current decreased steadily caused by the loss of the contribution from the oxidation of adsorbed NO$_2^-$.

The anodic current observed in the region $1.2 \, V > E > 1.0 \, V$ during the negative scan of potential was less than the value predicted by the Levich equation.

A series of I-E curves was recorded as a function of $\omega$ at a constant value of $\phi$. The oxidation of NO$_2^-$ was dependent upon the value of $\omega$; however, a plot of I vs. $\omega^{1/2}$ was not linear. Current-potential curves were also recorded at various values of $\phi$ for a given value of $\omega$. Wave A was dependent upon $\phi$, as well as $\omega$, indicating that surface-controlled reactions were occurring simultaneously with NO$_2^-$ oxidation.

The $\Delta I$-E curve obtained by QHMV is shown in Figure V-7b. A large anodic wave was observed during the positive scan of potential which reached a maximum value at $E = \text{ca.} \, 1.0 \, V$. At $E > 1.0 \, V$, $\Delta I$ steadily decreased, reaching zero at ca. $1.5 \, V$. No additional transport-coupled current occurred during the remainder of the positive potential scan. The magnitude of $\Delta I$ observed during the subsequent negative scan was highly dependent upon $E_a$. For $E_a > 1.45 \, V$, $\Delta I$ was zero throughout the negative potential scan. For $E_a < 1.45 \, V$, an anodic $\Delta I$ was observed in the region $1.45 \, V > E > 0.90 \, V$. The value of $\Delta I$ increased as $E_a$ was made more negative.

The oxidation of NO$_2^-$ has been concluded to occur by the electrocatalytic involvement of OH radicals on the Pt surface. The $E^0$ value for the NO$_3^-$/NO$_2^-$ half reaction is $0.70 \, V$. No appreciable current was observed until $\eta > 150 \, \text{mV}$. Nitrite ions adsorb on Pt and inhibit the formation of surface oxides. Adsorbed NO$_2^-$ is oxidatively desorbed by
a mechanism concluded to involve 0-atom transfer from PtOH to the NO\textsubscript{2}⁻ species. When a small amount of adsorbed NO\textsubscript{2}⁻ is desorbed, the associated Pt sites are rapidly converted to PtOH. An accelerating effect then is exhibited on the reaction of the remainder of adsorbed NO\textsubscript{2}⁻. In addition, the oxidation of NO\textsubscript{2}⁻ from the bulk solution is initiated by the presence of PtOH. Conversion of PtOH to PtO results in a decrease of NO\textsubscript{2}⁻ oxidation at E > ca. 1.0 V. Oxygen evolution appears to have no catalytic effect on the mass-transport coupled anodic reaction of NO\textsubscript{2}⁻.

The I-E curve obtained for NO\textsubscript{2}⁻ at a Au electrode is shown in Figure V-8a. An anodic wave (A) was produced during the positive scan at E > 0.9 V, as the result of the oxidation of NO\textsubscript{2}⁻ to NO\textsubscript{3}⁻, and a limiting current plateau was attained in the region 0.95 V < E < 1.1 V. At E > 1.1 V, bulk oxidation of the Au surface occurred simultaneously with NO\textsubscript{2}⁻ oxidation. Upon reversal of the potential scan, the anodic current steadily decreased. The Au oxide was reduced with E_p = 0.88 V.

A series of curves recorded as a function of ω at a given value of φ demonstrated that the anodic current plateau was dependent upon ω; however, the plot of I vs. ω\textsuperscript{1/2} was not linear. Variation of φ at a constant value of ω demonstrated that the anodic current plateau was independent of φ.

Two anodic waves were observed upon application of QHMV (Figure V-8b). The first wave (A) corresponded to the production of NO\textsubscript{3}⁻; however, the predicted ΔI\textsubscript{lim} was not attained. At E > 1.25 V, ΔI decreased; however, at E > 1.45 V an increase in ΔI was observed (B)
but which did not exceed 23% of the value for wave A. For $E = 1.85 \text{ V}$, no $\Delta I$ was observed during the negative scan of potential; however, at less positive $E_a$ values, a small increase in anodic $\Delta I$ was observed at $E < 0.95 \text{ V}$, i.e., $\text{NO}_2^-$ oxidation was renewed upon reduction of Au oxide.

The $E^0$ for the $\text{NO}_3^-/\text{NO}_2^-$ half reaction is 0.70 V. No current for the oxidation of $\text{NO}_2^-$ was observed, however, until $E > 0.8 \text{ V}$ which corresponds with the potential at which the formation of AuOH proceeds. Hence, $\text{NO}_2^-$ oxidation is concluded to be catalyzed by AuOH. The formation of AuO at ca. 1.1 V inhibits the oxidation of $\text{NO}_2^-$. This observation is in agreement with the results reported by Erlikh et al. (42). In contrast to the behavior observed at a Pt electrode, renewed oxidation was observed at a Au electrode simultaneously with $\text{O}_2$ evolution. Furthermore, an interesting similarity was observed in comparison to As(III) oxidation at a Au electrode. The anodic $\Delta I$ observed for both $\text{NO}_2^-$ and As(III) concomitantly with $\text{O}_2$ evolution was 23% of the anodic $\Delta I$ value attained in the region $0.95 \text{ V} < E < 1.1 \text{ V}$. The resulting increase in anodic $\Delta I$ may be attributed to flaking of $\text{Au}_2\text{O}_3$ from the electrode surface exposing Au metal sites. Reformation of $\text{Au}_2\text{O}_3$ and/or evolution of $\text{O}_2$ would occur at these sites which would be expected to have a similar catalytic effect on the oxidation of $\text{NO}_2^-$ and As(III).

3. Iodide

Since the oxidation of $\text{I}^-$ at a Pt electrode was chosen to be studied in greater detail, only a brief summary will be presented here to facilitate the discussion of results obtained for $\text{I}^-$ at other noble
metal electrodes. For I-E and ΔI-E curves, see Figures VI-2 and VI-5; for a complete discussion see section VI.

The mass-transport limited production of I₂ occurs with apparent reversibility at $E_\text{eq} = 0.48 \text{ V}$, as predicted thermodynamically. The anodic formation of surface oxide on a Pt electrode during the positive scan of potential is significantly inhibited by the presence of adsorbed I (see Figure VI-1). Adsorbed I is oxidatively desorbed as IO₃⁻ in the region $1.0 \text{ V} < E < 1.2 \text{ V}$ by a mechanism concluded to involve O-atom transfer from PtOH to the I species. When a small amount of adsorbed I is desorbed, the corresponding bare Pt sites are rapidly converted to more PtOH which has a consequential accelerating effect on the reaction of the remaining adsorbed I. Furthermore, oxidation of I⁻ from the bulk solution to IO₃⁻ is initiated by the production of PtOH. Unfortunately, the potential range is quite narrow over which the oxidation of I⁻ to IO₃⁻ is thermodynamically allowed, and in which PtOH exists in an appreciable quantity at the electrode surface. Rearrangement of PtOH to OHPt and further oxidation to PO₂ occur rapidly at $E > 1.2 \text{ V}$ and IO₃⁻ production is sharply suppressed. As the potential is increased beyond 1.25 V, the mass-transport limited production of IO₃⁻ proceeds simultaneously with O₂ evolution. The formation of IO₃⁻ at $E > 1.25 \text{ V}$ is attributed to the catalytic involvement of OH radicals produced on the electrode surface during O₂ evolution. Upon reversal of the potential scan, IO₃⁻ production proceeds as long as O₂ was evolved. At $E < 1.3 \text{ V}$, only the transport-limited oxidation of I⁻ to I₂ occurs.

The oxidation of I⁻ in basic media at a Pt electrode was investi-
gated briefly. No anodic wave was observed for the oxidation of I\textsuperscript{−} to I\textsubscript{2}. The simultaneous formation of IO\textsubscript{3}\textsuperscript{−} and surface oxide produced a peak at $E_\text{p} = 0.37$ V. The height of this peak varied nonlinearly with $\omega^{1/2}$ as the result of surface-controlled reactions, i.e., the formation of surface oxide and the possible oxidative desorption of I occurring concomitantly with the mass-transport coupled production of IO\textsubscript{3}\textsuperscript{−}. A small, single, anodic peak ($E_\text{p} = 0.37$ V) was observed upon application of QHMV for I\textsuperscript{−} in basic media. However, no mass-transport coupled formation of IO\textsubscript{3}\textsuperscript{−} was observed simultaneously with O\textsubscript{2} evolution.

No study of the voltammetric response of I\textsuperscript{−} at Au, Ir, or Pd electrodes has been reported in the literature. The initial observations obtained upon application of CV and QHMV will be described briefly. Of major significance is the mass-transport coupled production of IO\textsubscript{3}\textsuperscript{−} occurring simultaneously with O\textsubscript{2} evolution.

The I-E and ΔI-E curves for I\textsuperscript{−} at a Au electrode are shown in Figure V-9. Several anodic waves and peaks were observed during the positive scan of potential. The oxidation of I\textsuperscript{−} to I\textsubscript{2} proceeds with the thermodynamically predicted value of $E_\text{p} = 0.48$ V to yield an anodic current plateau (A) in the region $0.58$ V $< E < 0.88$ V. The second anodic wave (B) was observed in the region $0.88$ V $< E < 1.12$ V and is attributed to the oxidation of I\textsuperscript{−} to HI\textsubscript{O}. Peak C is produced as the result of the anodic formation of Au oxide and, possibly, the formation of a gold-iodide surface species. Peak D is attributed to the formation of IO\textsubscript{3}\textsuperscript{−} concomitantly with surface oxidation. Current in the region $1.4$ V $< E < 1.6$ V corresponds to the formation of IO\textsubscript{3}\textsuperscript{−} (E). Oxygen
Figure V-9: I-E and ΔI-E curves of 0.5 mM I\textsuperscript{-} in 0.5 M H\textsubscript{2}SO\textsubscript{4} at a Au RDE

a. I-E curve
   
   Electrode rotation speed (W): 1000 rpm
   Potential scan rate (ϕ): 6 V/min

b. ΔI-E curve
   
   Lower rotation speed (W\textsubscript{L}): 1000 rpm
   Upper rotation speed (W\textsubscript{U}): 4000 rpm
   Potential step increment (ΔE): 5 mV
   Time delay (t\textsubscript{d}): 150 ms
   Number of data points (N): 10
a.

b.

E (V vs. SCE)

I (μA)

A

B

C

D

E

F

G

ΔI (μA)

1.5

0.9

0.3

-0.3

-100

-200

-300

-400
evolution increased rapidly at $E > 1.6 \text{ V}$; therefore, the potential scan was reversed at $E = 1.6 \text{ V}$. Upon reversal of the potential scan, the formation of $\text{IO}_3^-$ was observed in the region $1.6 \text{ V} > E > 1.45 \text{ V}$. At $E < 1.45 \text{ V}$, current decreased to the current plateau value attained for the oxidation of $\text{I}^- \text{ to } \text{I}_2$ (A). The reduction of Au oxide (F) occurred with $E_p = 0.88 \text{ V}$. Peak G is attributed to the reduction of reversibly adsorbed $\text{I}_2$.

Results for the variation of $\omega$ at a constant value of $\phi$ demonstrated that the anodic current plateau (A) varied linearly with $\omega^{3/2}$, as predicted by the Levich equation; hence, $\text{I}_2$ formation is a mass-transport limited reaction. Current owing to the oxidation of $\text{I}^- \text{ to } \text{HIO}$ (B) reached a plateau value at progressively more positive values of $E_{1/2}$ as $\omega$ was increased. Current in the region $1.15 \text{ V} < E < 1.6 \text{ V}$ increased nonlinearly with $\omega^{3/2}$ due to the surface-controlled oxidation of Au which occurred simultaneously with the transport-coupled formation of $\text{IO}_3^-$. A series of I-E curves was recorded as a function of $\phi$ at a constant value of $\omega$. Wave A was independent of $\phi$ which is the expected behavior of a mass-transport limited reaction. The $E_{1/2}$ of wave B shifted to more positive potential values at low $\omega$. The height of peaks C and D varied with $\phi$ which is the typical response for reactions under surface control. At $\phi < 0.5 \text{ V/min}$, peak D was not observed. Current in the region of wave E was dependent upon $\phi$ because of the simultaneous formation of $\text{Au}_2\text{O}_3$.

The application of QHMMV produced a $\Delta$I-E curve less complex than
the corresponding I-E curve for CV. Three anodic waves were observed during the positive scan of potential. The mass-transport limited formation of $I_2$ (A) was observed in the region $0.55 \, V < E < 0.95 \, V$. The oxidation of $I^-$ to HIO produces wave B. Wave C was observed for the oxidation of $I^-$ to $IO_3^-$. A limiting value of $\Delta I$ was attained in the region $1.55 \, V < E < 1.75 \, V$. The ratio of $\Delta I_C/\Delta I_A$ is 6.0 as expected based on the assigned reactions. Upon reversal of the potential scan, $\Delta I$ decreased to the limiting value observed for wave A. The limiting $\Delta I$ value for the production of $I_2$ was observed in the region $1.5 \, V > E > 0.55 \, V$. As in the case of Pt, $I_2$ formation is not inhibited by the presence of surface oxides.

The oxidation of $I^-$ at an Ir electrode was examined briefly. An electrolyte solution of 5 M $H_2SO_4$ was utilized to minimize the continuous buildup of oxide with repetitive potential scanning that is observed in less concentrated acidic solutions. The I-E curve obtained is shown in Figure V-10a. The anodic formation of Ir oxide commenced at $E = 0.16 \, V$. The anodic wave (A), $E_{1/2} = 0.37 \, V$, is attributed to the oxidation of $I^-$ to $I_2$. Zakharov and Songina (101) also observed that the oxidation of $I^-$ to $I_2$ occurred at $E < E^0$ in highly acidic media at a Pt electrode; however, they did not offer an explanation for the phenomenon. Since this behavior is not unique to the Ir electrode, it is concluded that the highly acidic media is responsible for the observed anodic response. The cause of this behavior requires further investigation. The large residual current obscured the observation of a limiting current plateau for the production of $I_2$ at this concentration.
Figure V-10: I-E and ΔI-E curves of 0.5 mM I⁻ in 5.0 M H₂SO₄ at an Ir RDE

a. I-E curve

Electrode rotation speed (W): 1000 rpm
Potential scan rate (ψ): 6 V/min

b. ΔI-E curve

Lower rotation speed (W₁): 1000 rpm
Upper rotation speed (W₂): 4000 rpm
Potential step increment (ΔE): 5 mV
Time delay (tₓ): 200 ms
Number of data points (N): 25
of $I^-$. At $E > 1.0$ V, anodic current increased producing peak B which corresponds to the oxidation of $I^-$ to a mixture of HIO and $IO_3^-$. At $E > 1.28$ V, anodic decomposition of the solvent became significant, therefore, the anodic potential limit was established.

Current-potential curves, recorded as a function of $\phi$ while holding $\omega$ constant, were not particularly informative for the evaluation of the surface dependence of the oxidative reactions of $I^-$ since Ir oxidation occurred over the whole potential range of $I^-$ oxidation. A series of I-E curves was recorded as a function of $\omega$ at a constant value of $\phi$. Although both anodic waves were dependent upon $\omega$, precise rotation speed data could not be obtained due to the large contribution to the total current from the formation of Ir oxide.

The application of QHMV was advantageous since the contribution to the total current from the mass-transport coupled oxidation of $I^-$ could be isolated from the large background current produced during the formation of Ir oxide. The $\Delta I$-E curve is shown in Figure V-10b. During the positive scan of potential, an anodic $\Delta I$ plateau (A) was observed in the region $0.3 \, V < E < 1.0 \, V$ corresponding to the oxidation of $I^- \to I_2$. At $E > 1.0 \, V$, $\Delta I$ decreased; however, $\Delta I$ increased abruptly at $E > 1.05 \, V$. A limiting $\Delta I$ plateau was attained in the region $1.25 \, V < E < 1.45 \, V$ (B). The ratio of $\Delta I_B/\Delta I_A$ was 4.26. The ratio of $\Delta I$ values was less than 6, as predicted for the formation of $IO_3^-$, and was concluded to be the result of the concomitant formation of $IO_3^-$ and an I species with a lower oxidation state than $IO_3^-$, presumably HIO. Upon reversal of the potential scan, the limiting value of $\Delta I$ was observed in the region...
1.45 V > E > 1.3 V. The value of ΔI decreased to a minimum at ca. 1.15 V. The limiting ΔI value for the formation of \( I_2 \) was observed during the negative scan of potential in the region 1.0 V > E > 0.9 V. For E < 0.9 V, ΔI decreased to zero current at 0.6 V.

Anodic response of \( I^- \) at a Pd electrode was observed, as shown in Figure V-IIa (curve 1), provided that the electrode was not anodized at E > 1.3 V. The oxidation of \( I^- \) to \( I_2 \) (A) occurred at E > 0.45 V with a limiting current plateau attained in the region 0.55 V < E < 0.9 V during the positive scan of potential. At E > 1.05 V, a sharp increase in current was observed which reached a maximum value at \( E_p = 1.19 \) V (B). This peak is produced by the concurrent oxidation of Pd and the oxidative desorption of I. Oxygen evolution was significant at E > 1.25 V. Upon reversal of the potential sweep, current decreased to a plateau in the region 1.1 V > E > 0.7 V which corresponds to the oxidation of \( I^- \) to \( I_2 \). The reduction peak (C) observed at \( E_p = -0.05 \) V is due to the reduction of irreversibly adsorbed \( I_2 \).

Current-potential curves were recorded as a function of \( \omega \) while holding \( \phi \) constant. Anodic current observed in the region of wave A increased linearly with \( \omega^{1/2} \); therefore, the production of \( I_2 \) is a mass-transport limited reaction. The anodic current observed for E > 0.9 V was dependent upon \( \omega \) as the result of the mass-transport limited formation of \( I_2 \) which occurred simultaneously with the surface-controlled formation of Pd oxide and oxidative desorption of I. Peak C was independent of \( \omega \) which is indicative of a surface-controlled process.

A series of I-E curves was also recorded as a function of \( \phi \) at a
Figure V-11: I-E and ΔI-E curves of 0.5 mM \( \text{I}^- \) in 0.5 M \( \text{H}_2\text{SO}_4 \) at a Pd RDE

a. I-E curves

- Electrode rotation speed \((W)\): 1000 rpm
- Potential scan rate \( (\phi) \): 6 V/min
  1) Electrode anodized at \( E \leq 1.3 \ V \)
  2) Electrode anodized at \( E > 1.3 \ V \)

b. ΔI-E curve

- Lower rotation speed \( (W_L) \): 1000 rpm
- Upper rotation speed \( (W_U) \): 4000 rpm
- Potential step increment \( (\Delta E) \): 5 mV
- Time delay \( (\tau_d) \): 150 ms
- Number of data points \((N)\): 10
constant value of \( \omega \). Wave A, produced as the result of the formation of \( I_2 \), was independent of \( \phi \) as expected for a mass-transport limited reaction. The height of peak B decreased rapidly as \( \phi \) was decreased and, appeared only as a small shoulder on a rising wave at \( \phi < 0.5 \) V/min. Hence, the reaction producing \( IO_3^- \) in the potential region of peak B is a surface-controlled reaction. The height of peak C decreased and the value of \( E_p \) shifted more positive as \( \phi \) was decreased.

The \( \Delta I-E \) curve recorded for \( I^- \) at a Pd electrode is shown in Figure V-11b. A \( \Delta I \) plateau (A) was observed in the region \( 0.55 \) V < \( E < 1.1 \) V which corresponds to the production of \( I_2 \). At \( E > 1.1 \) V, \( \Delta I \) increased to a plateau \( \Delta I \) value (B) in the region \( 1.4 \) V < \( E < 1.55 \) V. The ratio of \( \Delta I_B/\Delta I_A \) was 4.74 indicating that a mixture of \( IO_3^- \) and an I species with a lower oxidation state is produced simultaneously with \( O_2 \) evolution. This behavior is similar to that observed for the further oxidation of \( I^- \) at an Ir electrode.

The anodic response of \( I^- \) at a Pd electrode is highly dependent upon the pretreatment of the electrode. If the Pd electrode was anodized at \( E > 1.3 \) V prior to cycling the potential \((-0.2 \) V < \( E < 1.3 \) V), the I-E curve shown in Figure V-11a (curve 2) was obtained. The mass-transport limited oxidation of \( I^- \) to \( I_2 \) was not observed in the region \( 0.55 \) V < \( E < 0.9 \) V during the positive scan of potential. However, a peak (D) was produced at \( E_p = 0.95 \) V which corresponds, presumably, to the formation of \( PdI_2 \). Peak D increased with each repetitive scan of potential as the result of continuous roughening of the electrode surface through the oxidation and desorption of Pd metal which produced Pd black and thereby
increased the effective surface area of the working electrode. Anodization at \( E > 1.3 \, \text{V} \) provided the initial Pd black. Evidently, the mechanism of reaction changed in the presence of Pd black and the formation of PdI\(_2\) is favored over the production of I\(_2\). The position of peak B shifted 35 mV more positive and the height of this peak decreased gradually with repetitive scans of potential. During the negative scan of potential, peak E was observed as the result of the reduction of Pd oxide. Peak C, produced by the reduction of irreversibly adsorbed I\(_2\), was not observed. Rotation speed and scan rate studies did not provide useful information since the height of peaks B and D changed with each consecutive scan of potential even at constant \( \omega \) and \( \phi \).

4. **Chloride**

The industrial interest in chlor-alkali technology has prompted the study of the electrocatalytic effect of various noble metals and noble metal oxides on the Cl\(_2\) evolution reaction \((15, 102-117)\). The fundamental and applied aspects of anodic Cl\(_2\) production are discussed by Novak, Tilak, and Conway \((118)\). Chlor-alkali technology is reviewed by Caldwell \((119)\), and by Venkatesh and Tilak \((120)\).

Chloride ions strongly adsorb on Pt \((15, 103, 104, 121)\) with retention of the negative charge. Adsorbed ions have been shown to exhibit an inhibitory effect on the anodic formation of surface oxide on Pt \((53, 122, 123)\). Novak and Conway \((104)\) observed that the adsorption of Cl\(^-\) preferentially blocks the formation of PtOH by competing with hydroxyl radicals for adsorption sites on the electrode surface. However, at chloride concentrations greater than \(10^{-4.8} \, \text{M} \), competitive
adsorption is observed at $E > 0.86$ V where the second stage of Pt oxidation occurs, i.e., the formation of PtO.

Two mechanisms have been proposed for the evolution of Cl$_2$:

I. $\text{Cl}^-_{(aq)} + S \rightarrow \text{SCl}^*_{(ads)} + e^-$ (Volmer)

$2\text{SCl}^*_{(ads)} \rightarrow 2S + \text{Cl}_2^+$ (Tafel)

II. $\text{Cl}^-_{(aq)} + S \rightarrow \text{SCl}^*_{(ads)} + e^-$ (Volmer)

$\text{SCl}^*_{(ads)} + \text{Cl}^-_{(aq)} \rightarrow S + \text{Cl}_2^+ + e^-$ (Heyrovsky)

where $S$ designates an oxidized or partially oxidized Pt surface. The second step in each mechanism is the rate determining step. Most researchers agree that Cl$_2$ evolution occurs by a recombination-controlled mechanism (mechanism I). A nondiffusion limited current ($I_{ndl}$) is attained as the coverage of Cl$^-$ approaches unity. Since no oxide formation occurs on Pt in anhydrous trifluoroacetic acid (TFA), the evolution of Cl$_2$ has been investigated in TFA/H$_2$O mixtures (0-100% H$_2$O) to evaluate the effect which surface oxides exhibit on the production of Cl$_2$ (102, 124). In all TFA/H$_2$O mixtures, Cl$_2$ evolution proceeds by a recombination-controlled mechanism; therefore, solvation effects are secondary. For the case of anhydrous TFA, S (mechanism I) represents an unoxidized Pt electrode surface. The limiting current ($I_{ndl}$) obtained at an oxide-covered surface is 45 times larger than that observed at an unoxidized Pt surface. Since the mechanism is the same in both solvents, the observed increase in current indicates that substantial electrocatalytic
enhancement of the recombination rate for Cl\textsuperscript{-}(ads) exists for an oxidized Pt surface. The increase in the rate of recombination is due to weaker binding of Cl\textsuperscript{-} on an oxidized Pt surface than on the Pt metal surface; consequently, a lower activation energy exists for the recombination step.

The I-E curve recorded for Cl\textsuperscript{-} at a Pt electrode is shown in Figure V-12a. The anodic formation of surface oxide on a Pt electrode during the positive scan of potential is inhibited by the presence of adsorbed Cl\textsuperscript{-}. The formation of Cl\textsubscript{2} commenced at the thermodynamically predicted value of 1.11 V. A decrease in the height of the oxide reduction peak was observed during the negative scan of potential in the presence of Cl\textsuperscript{-} indicating that adsorbed Cl\textsuperscript{-} influences not only the potential at which oxide formation begins but also the quantity of oxide which forms. Adsorbed Cl\textsuperscript{-} also affects the adsorption of H on Pt. Although a monolayer of H is adsorbed regardless of the coverage by Cl\textsuperscript{-}, the adsorbed Cl\textsuperscript{-} affects the energy distribution of adsorbed H by decreasing the Pt-H bond energy (121). Therefore, the H adsorption waves were shifted to more negative potentials.

Current-potential curves recorded at different values of $\phi$, while holding $\omega$ constant, indicated that the evolution of Cl\textsubscript{2} is a surface-dependent process. The anodic production of Cl\textsubscript{2} exhibited minimal dependence upon $\omega$ as observed by recording I-E curves at different $\omega$ while holding $\phi$ constant. Hence, the evolution of Cl\textsubscript{2} occurs predominantly by a surface-controlled process which is consistent with the proposed recombination-controlled mechanism.
Figure V-12: I-E and $\Delta$I-E curves of 0.5 mM Cl$^{-}$ in 0.5 M H$_2$SO$_4$ at a Pt RDE

a. I-E curves

- Electrode rotation speed ($W$): 1000 rpm
- Potential scan rate ($\phi$): 6 V/min
- $\cdots \cdots$ Pt residual
- $\cdots \cdots$ 0.5 mM Cl$^{-}$

b. $\Delta$I-E curve

- Lower rotation speed ($W_l$): 1000 rpm
- Upper rotation speed ($W_u$): 4000 rpm
- Potential step increment ($\Delta E$): 5 mV
- Time delay ($t_d$): 150 ms
- Number of data points (N): 10
The ΔI-E curve obtained by QHMV is shown in Figure V-12b. There is a finite contribution to the total current by a mass-transport coupled process during the positive scan of potential. Perhaps, the formation of Cl₂ occurs to a small extent by an alternate pathway (mechanism II) as proposed by Burrows, Entwisle, and Harrison (111). Since the rate determining step involves the reaction of Cl⁻(aq) with Cl⁻(ads), the reaction is dependent upon the transport of Cl⁻ to the surface; therefore, current is a function of ω. The anodic current will become limiting provided the kinetics of the second step is fast. The observed ΔI₁lim was approximately 5% of the theoretical ΔI₁lim therefore, the kinetics of the second step are quite slow. The anodic formation of Cl₂ occurs predominately by a surface-controlled reaction.

Currently, the anode material of choice in the chlor-alkali industry is a mixed oxide electrode of RuO₂ and TiO₂ coated on a Ti substrate. This electrode was first patented by Beer (125) in the late 1950s. Although the exact composition of commercial cells is proprietary, increased production of Cl₂ is observed upon doping the electrode with various nonnoble metals e.g., Sn, Bi, or Co. The composition of the coating also affects the rate of undesired side reactions such as O₂ evolution or the formation of ClO₃⁻. The RuO₂/TiO₂ anode has a low overpotential for Cl₂ evolution; commercial chlorine cells operate at an anodic overpotential of ca. 50 mV (119). Unlike the graphite anode, which is consumed by physical wear and electrochemical oxidation (service time of 6-24 months), the RuO₂/TiO₂ anode has a service time of 8-10 years.
Because RuO$_2$/TiO$_2$ is an efficient electrocatalyst for Cl$_2$ evolution, the reaction mechanism has been investigated by numerous researchers (111, 113, 116, 126, 127). Comparison of results must be done cautiously due to the variation in coating composition and the difficulty in reproducibly preparing the electrode surface. Both the Volmer-Heyrovsky and Volmer-Tafel mechanisms have been proposed for Cl$_2$ evolution on RuO$_2$/TiO$_2$ electrodes. Ardizzone et al. (127) reported that the mechanism is dependent upon the macroscopic defect structure of the electrode surface. At highly compact electrodes, the Volmer-Heyrovsky mechanism predominates (113, 127) whereas at highly cracked electrodes, the mechanism changes to the Volmer-Tafel pathway. The slow step in both pathways is the removal of the adsorbed intermediate therefore the transition between mechanisms implies an increase in the metal-halogen surface bond strength. Burke and O'Neill (128) suggest that the reaction mechanism may involve the participation of surface oxygen species although the precise nature of the surface species is uncertain. Based on the results obtained for Cl$_2$ evolution at a Pt electrode in mixtures of TFA/H$_2$O (0-100% H$_2$O) (102, 124), which demonstrate the enhanced electrocatalysis of Cl$_2$ evolution at an oxide covered electrode, the participation of a surface oxygen species is not an unreasonable hypothesis.

Preliminary results obtained by QHMV indicate that the production of Cl$_2$ is occurring by a surface-controlled mechanism since no mass-transport dependent current was observed in either acidic or basic media at concentrations as high as 0.1 M Cl$^-$. Gold is not a practical anode for Cl$_2$ evolution owing to the
corrosive nature of the chloride solution; however, electrolytic refining of Au by the Wohlwill process takes advantage of the increased rate of dissolution of the metal through the formation of stable chloro-gold complexes. Therefore, the anodic dissolution of Au in Cl\textsuperscript{−} solutions has been the subject of fundamental electrochemical studies (129-137). Chloride ions adsorb on Au at a diffusion-limited rate (134). Dissolution of Au occurs at $E > 0.8$ V and approaches the theoretical limiting value. The formation of AuCl\textsubscript{2}\textsuperscript{−} proceeds by the mechanism (137)

\[
\begin{align*}
\text{Au} + \text{Cl}^\text{−}(\text{aq}) & \rightarrow \text{AuCl}^\text{−}(\text{ads}) \\
\text{AuCl}^\text{−}(\text{ads}) & \rightarrow \text{AuCl}(\text{ads}) + e^\text{−} \\
\text{AuCl}(\text{ads}) + \text{Cl}^\text{−} & \rightarrow \text{AuCl}_2^\text{−}(\text{aq})
\end{align*}
\]

where the third step is the rate determining step. Removal of an AuCl(ads) species exposes a bare metal site where adsorption of Cl\textsuperscript{−} occurs rapidly. However, if the Cl\textsuperscript{−} ions in the diffusion layer are consumed faster than they are replenished, i.e., the rate of transport becomes limiting, oxide formation is initiated. Passivation of the Au dissolution reaction occurs concomitantly with the formation of surface oxide (136). The potential at which the onset of passivation is observed corresponds to the potential at which sudden changes are observed by ellipsometry (135). As the Cl\textsuperscript{−} concentration increases, the potential at which passivation occurs shifts to more positive values.

The I-E curve obtained for Cl\textsuperscript{−} at a Au electrode is shown in Figure V-13a. Wave A corresponds to the formation of AuCl\textsubscript{2}\textsuperscript{−}. The formation of
Figure V-13: I-E and ΔI-E curves of 0.5 mM Cl\(^-\) in 0.5 M H\(_2\)SO\(_4\) at a Au RDE

a. I-E curve
   
   Electrode rotation speed (\(W\)): 1000 rpm
   
   Potential scan rate (\(\phi\)): 6 V/min

b. ΔI-E curve
   
   Lower rotation speed (\(W_l\)): 1000 rpm
   
   Upper rotation speed (\(W_u\)): 4000 rpm
   
   Potential step increment (ΔE): 5 mV
   
   Time delay (\(t_d\)): 150 ms
   
   Number of data points (N): 10
Au oxide was observed at ca. 1.2 V producing wave B. At \( E > 1.2 \) V, current sharply decreased owing to the passivation of Au dissolution which occurs as the formation of surface oxide commences.

Variation of the \( \phi \) at a constant \( \omega \) indicated that the formation of \( \text{AuCl}_2^- \) is independent of \( \phi \). Current in the region \( 1.2 \) V < \( E < 1.6 \) V was dependent upon \( \phi \); therefore, surface-controlled processes are occurring at \( E > 1.2 \) V. The magnitude of waves A and B increased with increased \( \omega \) at a constant \( \phi \). Since wave A was dependent solely upon \( \omega \), the formation of \( \text{AuCl}_2^- \) is a mass-transport coupled process. Current in the region \( 1.2 \) V < \( E < 1.6 \) V was independent of \( \omega \); therefore, only surface-controlled processes are occurring. There was no evidence of \( \text{Cl}_2 \) evolution occurring at a Au electrode prior to the evolution of \( \text{O}_2 \).

The potential region over which corrosion of the Au surface occurs is clearly defined by the application of QHMV (Figure V-13b). A single, narrow anodic peak, corresponding to the production of \( \text{AuCl}_2^- \), was observed during the positive scan of potential. The magnitude of \( \Delta I \) rapidly declined to zero at \( E > 1.15 \) V. No transport-coupled current was observed throughout the remainder of the triangular potential sweep. If \( \text{Cl}_2 \) evolution occurs at an oxide covered Au electrode simultaneously with the evolution of \( \text{O}_2 \), the mechanism involves a surface-controlled rate determining step perhaps analogous to the mechanism on Pt, i.e., a recombination-controlled mechanism.

5. Bromide

The investigation of halide ions utilizing QHMV is completed with the discussion of the results obtained for the anodic oxidation of \( \text{Br}^- \).
at Pt and Au electrodes. The I-E and ΔI-E curves obtained for Br⁻ at Pt and Au are shown in Figures V-14 and V-15. The contribution to total current by the mass-transport coupled current is dramatically different for these electrode materials; however, the ΔI response can be rationalized based on specific properties of the surface oxides formed on Pt and Au.

Bromide ions adsorb on Pt in the H region (-0.2 V < E < 0.1 V) with substantial retention of charge (104, 121, 122). The adsorption of Br⁻ alters the energy distribution of adsorbed H; however, the total amount of H adsorbed does not change regardless of the extent of coverage by Br⁻ (104, 122). Partial charge transfer occurs as the potential is scanned in the positive direction (138). Unlike Cl⁻ which blocks the initially deposited OH monolayer at Pt, adsorbed Br⁻ blocks the formation of the surface oxide nonselectively over a wide potential range (0.55 V < E < 1.25 V) (104).

The mechanism for Br₂ evolution on Pt is dependent upon the oxidation state of the electrode surface (139). The change in mechanism is attributed to the ease of Br⁻ adsorption on an oxide-free or oxide-covered surface. Although Br⁻ strongly adsorbs on Pt metal, adsorption of Br⁻ on an oxide-covered Pt surface does not occur (20, 121, 140). The evolution of Br₂ was proposed to occur on a reduced Pt electrode by the mechanism:

\[
\begin{align*}
\text{Br}^- (aq) & \rightarrow \text{Br}^- (ads) \\
\text{Br}^- (ads) & \rightarrow \text{Br} (ads) + e^-
\end{align*}
\]
Figure V-14: I-E and ΔI-E curves of 0.5 mM Br⁻ in 0.5 M H₂SO₄ at a Pt RDE

a. I-E curve
   
   Electrode rotation speed (W): 1000 rpm
   Potential scan rate (φ): 6 V/min

b. ΔI-E curve
   
   Lower rotation speed (W₁): 1000 rpm
   Upper rotation speed (Wₚ): 4000 rpm
   Potential step increment (ΔE): 5 mV
   Time delay (tₜ): 150 ms
   Number of data points (N): 10
Figure V-15: I-E and ΔI-E curves of 0.5 mM Br⁻ in 0.5 M H₂SO₄ at a Au RDE

a. I-E curve
   
   Electrode rotation speed (W): 1000 rpm
   
   Potential scan rate (φ): 6 V/min

b. ΔI-E curve
   
   Lower rotation speed (W₁): 1000 rpm
   
   Upper rotation speed (W₂): 4000 rpm
   
   Potential step increment (ΔE): 5 mV
   
   Time delay (tₓ): 150 ms
   
   Number of data points (N): 10
with the rate determining step being the charge transfer from an adsorbed Br⁻ ion to form an adsorbed Br atom. If the rate determining step is fast, a limiting current will be observed. The mechanism for the production of Br₂ on an oxidized electrode occurs according to the scheme

\[
2\text{Br}^{\text{(ads)}} \rightarrow \text{Br}_2^{\text{(aq)}} \quad \text{or} \quad \text{Br}^-^{\text{(aq)}} + \text{Br}^{\text{(ads)}} \rightarrow \text{Br}_2^{\text{(aq)}} + e^- 
\]

The rate determining step involves the discharge of Br⁻ from the solution. The anodic formation of Br₂ proceeds at a faster rate on a reduced Pt surface in comparison with an oxidized Pt surface (139), i.e., the discharge of Br⁻ from the solution occurs at a slower rate than the charge transfer from an adsorbed Br⁻ to form an adsorbed Br atom.

The I-E response of Br⁻ at a Pt electrode has been examined in detail by Johnson and Bruckenstein (20). Three anodic waves were observed when scanning the potential in the positive direction (Figure V-14a). The first anodic wave (A) is attributed to the oxidation of Br⁻ to Br₂ (Eₐ = 0.90 V). The formation of Pt oxide during the positive scan of potential is inhibited by the presence of adsorbed Br⁻ and no oxide reduction peak was observed until E > 1.0 V. Wave B corresponds to the formation of Pt oxide. As Eₐ was increased beyond 1.0 V, the height of the oxide reduction peak increased and it was concluded that surface oxidation is occurring simultaneously with the production of HOBr (C). The small reduction peak D observed during the negative scan
of potential is attributed to the reduction of Br\textsubscript{2} present in the convective-diffusion layer. At higher \( \omega \) and/or lower \( \phi \), peak D was not observed. The reduction of Pt oxide (E) occurred with \( E_p = 0.48 \) V.

Current-potential curves recorded as a function of \( \omega \) at a low \( \phi \) demonstrated that \( I_{\text{lim}} \) vs. \( \omega^{1/2} \) is linear for wave A, i.e., the production of Br\textsubscript{2} is a mass-transport limited reaction. The height of waves B and C increased in a nonlinear fashion with increasing \( \omega \) indicating that surface-controlled reactions are occurring or that the kinetics of a mass-transport coupled reaction are slow.

A single anodic wave was observed upon application of QHMM to a study of the oxidation of Br\textsuperscript{-} at a Pt electrode (Figure V-14b). In the region \( 1.05 \ V < E < 1.4 \) V, the value of \( \Delta I \) is the theoretical value predicted from the Levich equation. However, at \( E > 1.4 \) V, \( \Delta I \) decreased steadily. The decrease in \( \Delta I \) corresponds to an increasing amount of surface oxidation. Upon reversal of the potential scan, \( \Delta I \) decreased to a value less than the \( \Delta I \) observed during the positive scan of potential; the value of \( \Delta I \) is a function of \( E_a \). The observed behavior of Br\textsubscript{2} production by QHMM is consistent with the results of mechanistic and kinetic studies reported by Rubenstein (139). At a reduced electrode, the charge transfer from an adsorbed Br\textsuperscript{-} ion to an adsorbed Br atom occurs rapidly and the predicted value of \( \Delta I_{\text{lim}} \) is attained for the formation of Br\textsubscript{2}. However, as the potential increases and the degree of surface oxidation increases, the reaction mechanism changes. The discharge of Br\textsuperscript{-} from solution is now the rate controlling step which proceeds more slowly than the charge transfer step at a reduced
electrode. Consequently, mass-transport coupled current is less than the predicted $\Delta I_{\text{lim}}$ value. There was no evidence of the transport-coupled production of H\text{OB}r or Br\text{O}_3^- occurring simultaneously with the evolution of O\text{2}. Hence, H\text{OB}r is generated only by a surface-controlled reaction, i.e., the oxidative desorption of Br^-.

The $E^0$ value for the Br\text{O}_3^-/Br^- half reaction in base is 0.37 V. An I-E curve was recorded for Br^- in 0.1 M NaOH; however, no change in the response of current was observed. Nevertheless, QHMV was applied to determine if any transport-coupled reaction occurs simultaneously with O\text{2} evolution. No transport-coupled current was observed in the region of O\text{2} evolution.

The anodic reactions occurring at a Au electrode in the presence of Br^- have not been studied in detail. The formation of Br_2 is thermodynamically predicted to occur with $E_2 = 0.94$ V vs. SCE which is close to the values for the formation of the gold-bromo complexes AuBr_2^- ($E_2 = 0.92$ V) and AuBr_4^- ($E_2 = 0.80$ V). Early investigation of the oxidation of Br^- at a Au electrode by Gaur and Schmid (133) indicated that Au is dissolved and passivated in a dilute Br^- solution similarly to the dissolution and passivation of Au in Cl^- solutions. However, Gaur and Schmid did not consider the possible evolution of Br_2 until $E > 1.0$ V. More recently, Nicol (129) has reported preliminary results for the anodic behavior of Br^- at a Au electrode which were obtained by cyclic voltammetry at a RRDE. Experiments utilizing a RRDE provide additional information about the reactions occurring at the disk electrode (1, 141, 142). Soluble electroactive species which are
produced at the disk electrode, as well as electroactive species which are present in the bulk solution, are transported to the ring electrode where they can be detected at a constant potential value ($E_r$). By appropriate selection of the value of $E_r$, electroactive species can be detected selectively. Current produced at the ring electrode ($I_r$) is recorded as a function of the potential of the disk electrode ($E_d$). Hence, variations in $I_r$ reflect a change in reactions that are occurring at the disk electrode. To study the oxidation of Br$^-$ at a Au disk electrode, a Au electrode cannot be employed due to interfering reactions that occur at the Au electrode at potentials where the species of interest are detected. Therefore, a Au disk/Pt ring RRDE was utilized. Nicol observed that the quantity of Au(I), Au(III), and Br$_2$ produced at the anode was dependent upon potential and concentration of Br$^-$. The proportion of total current consumed in the production of Br$_2$ decreased with increasing Br$^-$ concentration. Therefore, the competing reaction, presumably the formation of a gold-bromo complex, is favored at higher concentrations of Br$^-$. Cadle and Bruckenstein (143) reported that the formation of soluble gold(I)-aquo species and gold(III)-aquo species occurs upon oxidation and reduction of the Au electrode in the absence of electroactive species. Nicol (129) did not specify the Au species detected as gold-aquo of gold-bromo species, nor did he report the potential region over which each of the Au species was detected. Unfortunately, no detailed report of the anodic behavior of Br$^-$ at a Au electrode or elucidation of the reaction mechanism has been found in the literature.
The I-E curve obtained in acidic solution at a Au electrode is shown in Figure V-15a. Three anodic waves were observed during the positive scan of potential. The production of Br$_2$ occurred with the thermodynamically predicted value of $E_{1/2} = 0.94$ V (A). Wave B was produced upon formation of a gold-bromo complex which was concluded to be AuBr$_4^-$ which has an $E^0$ value slightly more negative than the $E^0$ for the formation of AuBr$_2^-$. Peak C consists of current resulting from the anodic formation of Au$_2$O$_3$ and concomitant formation of Br$_2$ and AuBr$_4^-$. At E > 1.5 V, O$_2$ evolution commences. During the negative scan of potential, anodic current decreased rapidly to a small, yet finite, value in the region 1.35 V < E < 1.05 V. The reduction of Au oxide (D) occurred at $E_p = 0.95$ V; however, the quantity of oxide formed in the presence of Br$^-$ is diminished in comparison with the quantity formed in the absence of Br$^-$. 

A series of I-E curves was recorded as a function of $\phi$ at a constant value of $\omega$. The production of Br$_2$ (A) was independent of $\phi$ which is characteristic of a mass-transport coupled reaction, whereas, the height of peaks B and C varied with $\phi$ indicating that surface-coupled reactions are occurring in the potential region of peaks B and C. At high values of $\phi$, peak B was indistinguishable from peak C; hence, the formation of AuBr$_4^-$ is inhibited at high values of $\phi$.

Current-potential curves were recorded also as a function of $\omega$ while holding $\phi$ constant. All three anodic waves observed during the positive scan of potential increased with increasing $\omega$. Current due to the production of Br$_2$ (A) increased in a nonlinear fashion with
increasing $\omega$ indicating that the formation of $\text{Br}_2$ proceeds under mixed kinetic and convective-diffusion control. In effect, the kinetics of the reaction are sufficiently fast to produce the theoretical, transport-limited current at low values of $\omega$; however, at high values of $\omega$, the rate of $\text{Br}_2$ production is comparatively slow and, therefore, the theoretical limiting current is not observed. At higher values of $\omega$, peak B owing to the formation of $\text{AuBr}_4^-$ became more prominent and the $E_{1/2}$ shifted to less positive values. Formation of $\text{AuBr}_4^-$ occurred more readily than the production of $\text{Br}_2$ as the convective transport of $\text{Br}^-$ increased. The height of peak C increased with increasing $\omega$ due to the mass-transport coupled formation of $\text{Br}_2$ and production of $\text{AuBr}_4^-$ simultaneously with oxide formation. During the negative scan of potential, anodic current observed at $E < 1.15 \text{ V}$ increased due to the production of $\text{Br}_2$. The increase in anodic current in the region $1.15 \text{ V} < E < 0.85 \text{ V}$ produced an anomalous decrease in the height of the oxide reduction peak (D) at higher values of $\omega$.

The $\Delta I$-$E$ curve recorded for $\text{Br}^-$ at a Au electrode is shown in Figure V-15b. Wave A corresponds to the mass-transport coupled production of $\text{Br}_2$. In the region $1.2 \text{ V} < E < 1.3 \text{ V}$, there is an unresolvable, finite contribution to $\Delta I$, as the result of the production of $\text{AuBr}_4^-$ which is the kinetically favored reaction at the higher flux of $\text{Br}^-$. At $E > 1.3 \text{ V}$, oxide formation commences and the formation of $\text{AuBr}_4^-$ and $\text{Br}_2$ is inhibited; hence, $\Delta I$ decreased to a small value corresponding to the formation of only a small amount of $\text{Br}_2$. At ca. 1.5 V, $\text{O}_2$ evolution is initiated and renewed production of $\text{Br}_2$ was
observed. The theoretical $\Delta I_{\text{lim}}$ was observed in the region $1.7 \text{ V} < E < 1.85 \text{ V}$ (B). The renewed production of $\text{Br}_2$ which occurs simultaneously with $\text{O}_2$ evolution (B) resulted from the increased availability of Au metal sites. Gold(III) oxide, loosely held at the electrode surface, easily flakes off exposing bare Au sites (69-71). Bromide oxidation, as well as $\text{O}_2$ evolution and continued formation of Au$_2$O$_3$, can occur at the exposed Au sites (70-72). Upon reversal of the potential scan, $\Delta I$ decreased and a minimum value was attained in the region $1.4 \text{ V} > E > 1.2 \text{ V}$. At $E < 1.2 \text{ V}$, $\Delta I$ increased owing to the production of $\text{Br}_2$. No AuBr$_4^-$ was formed during the negative scan of potential. As the concentration of Br$^-$ was increased, the ratio $\Delta I_A/\Delta I_B$ decreased indicating that the production of $\text{Br}_2$, in the region $0.9 \text{ V} < E < 1.2 \text{ V}$, decreased and the formation of AuBr$_4^-$ increased as the concentration of Br$^-$ increased. The transport-limited production of $\text{Br}_2$ (B) was attained regardless of the Br$^-$ concentration since the formation of AuBr$_4^-$ is not a competing reaction at $E > 1.7 \text{ V}$.

6. Hydroquinone

The oxidation of hydroquinone (HQ) on Pt and Au does not involve O-atom transfer; nevertheless, a brief discussion of the anodic behavior of HQ is included because of the interesting results which were obtained, in particular, at a Au electrode. The adsorption of numerous aromatic compounds at Pt electrodes has been investigated utilizing thin-layer electrochemical techniques (144-148). The results demonstrated that aromatic molecules adsorb in specific molecular orientations. The molecular orientation is a function of the structure and the concen-
tration of the adsorbate, the strength of adsorption of the supporting electrolyte, and the pH of the solution. At millimolar concentrations in aqueous 0.1 M HClO₄, HQ adsorbs with the plane of the ring parallel to the electrode surface. At concentrations exceeding 10⁻³ M, HQ adsorbs with an edgewise orientation.

Hydroquinone adsorbs irreversibly on Pt (144, 148, 149) and is not removed upon rinsing with a HQ-free electrolyte solution. Oxidative desorption of the chemisorbed species occurs at E > 0.6 V. Complete conversion to CO₂ occurs if HQ is adsorbed in the parallel orientation whereas, if HQ is adsorbed in an edgewise manner, complete conversion to CO₂ does not occur. Minimal oxidation of the Pt surface occurs prior to the complete oxidative desorption of adsorbed HQ (150). Soriaga and Hubbard (151) concluded that Pt is ultimately oxidized to the same extent regardless of whether HQ had been previously adsorbed based on the observation that the area of the oxide reduction peaks is equal in the absence or presence of HQ. Adsorbed HQ suppresses the underpotential deposition of H in the region 0.15 V < E < -0.2 V (152). The adsorption of aromatic molecules is sufficiently strong to displace adsorbed HQ (145). Recently, Soriaga et al. (153) have examined the effects of halogens upon the adsorption of HQ. They observed that I⁻ quantitatively displaced HQ, on the other hand, HQ did not displace adsorbed I. Bromide and Cl⁻ displace HQ to some extent (Br⁻ > Cl⁻) whereas adsorbed -HQ is uneffected by F⁻. The oxidation of unadsorbed HQ has been observed to occur reversibly at a Pt electrode at E > 0.46 V vs. SCE (151).

The I-E curve obtained for HQ in 0.5 M H₂SO₄ at a Pt electrode is
shown in Figure V-16a. An anodic wave (A) was observed for the oxidation of HQ to quinone (Q) at the thermodynamically predicted value $E_{\text{f}} = 0.46$ V vs. SCE during the positive sweep of potential. The formation of Pt oxide was inhibited by the presence of adsorbed HQ. Wave B, observed at $E > 0.7$ V, consists of current produced as the result of the oxidation of adsorbed HQ and that which is transported to the electrode surface. At $E > 0.9$ V, the anodic formation of Pt oxide occurred concomitantly with the anodic reactions of HQ. Upon reversal of the potential scan, an anodic current plateau (C) was observed in the region $1.2$ V > $E > 0.8$ V for the oxidation of unadsorbed HQ. Reduction of Pt oxide occurred at $E_p = 0.45$ V. The characteristic H adsorption and H desorption peaks were not observed in the H region (0.1 V < E < -0.2 V) owing to the presence of adsorbed HQ which suppresses the underpotential deposition of adsorbed H.

A series of I-E curves were recorded as a function of $\phi$ at a constant value of $\omega$. After correcting for double-layer charging current, the anodic current produced upon oxidation of unadsorbed HQ (A) was independent of $\phi$ which is indicative of a mass-transport controlled reaction. Current in the region of peak B was dependent upon $\phi$. The variation in current with changes in $\phi$ is attributed to the surface-controlled reactions which occur at $E > 0.7$ V, i.e., the oxidation of adsorbed HQ and the oxidation of Pt. The current plateau (C) observed during the negative scan of potential was independent of $\phi$ which is characteristic of a convective-controlled reaction.

Current-potential curves were recorded at a constant value of $\phi$
Figure V-16: I-E and $\Delta$I-E curves of 0.5 mM hydroquinone in 0.5 M $\text{H}_2\text{SO}_4$ at a Pt RDE

a. I-E curve

Electrode rotation speed ($W$): 1000 rpm
Potential scan rate ($\phi$): 6 V/min

b. $\Delta$I-E curve

Lower rotation speed ($W_1$): 1000 rpm
Upper rotation speed ($W_u$): 4000 rpm
Potential step increment ($\Delta E$): 5 mV
Time delay ($t_d$): 150 ms
Number of data points (N): 10
while varying $\omega$. Both anodic waves observed during the positive scan of potential were a function of $\omega$ indicating that the transport-dependent oxidation of HQ is occurring in the region $0.46 \, V < E < 1.3 \, V$. During the negative scan of potential, the magnitude of the current plateau (C), observed in the region $1.2 \, V > E > 0.8 \, V$, increased linearly with $\omega^{1/2}$.

The $\Delta I$-$E$ curve recorded for HQ at a Pt electrode is shown in Figure V-16b. A $\Delta I$ plateau was observed in the region $0.6 \, V < E < 1.65 \, V$ during the anodic scan of potential corresponding to the transport-coupled oxidation of HQ. Upon reversal of the potential scan at $E_a = 1.65 \, V$, an anodic $\Delta I$ plateau was observed in the region $1.65 \, V > E > 1.05 \, V$. However, at $E < 1.05 \, V$, $\Delta I$ decreased to zero at ca. 0.6 V. The difference between the $E_{1/2}$ for the anodic wave observed during the positive scan of potential and the $E_{1/2}$ observed for the anodic wave during the negative scan decreased as the potential scan was reversed at successively less positive values of $E_a$. For $E_a < 0.9 \, V$, the $E_{1/2}$ values are equal for the two scan directions. No oxide formation occurred at $E < 0.9 \, V$, therefore, the observed irreversibility of HQ oxidation during the negative scan of potential is attributed to the presence of Pt oxide. The oxidation of HQ proceeded at a limiting value during the negative scan of potential provided that $n$ was sufficiently large.

In sharp contrast to the numerous investigations of the adsorption and oxidation of HQ on Pt, the characterization of the adsorption and anodic behavior of HQ on Au has not been described in the literature. The I-E curve recorded for HQ at a Au electrode is shown in Figure
V-17a. The oxidation of HQ to Q proceeded with the thermodynamically predicted value $E_{1/2} = 0.46$ V producing an anodic current plateau (A) in the region $0.55 \, V < E < 1.05 \, V$. The small peak (B) observed prior to the establishment of the limiting current plateau is attributed to the slow depletion of species in the diffusion layer. At $E > 1.05$ V, formation of Au oxide occurred simultaneously with the anodic oxidation of HQ. The formation of oxide was not inhibited in the presence of HQ nor does the formation of oxide exhibit an inhibitory effect on the oxidation of HQ. During the negative scan of potential, anodic current owing to the oxidation of HQ was observed in the region $1.6 \, V > E > 0.46 \, V$. The reduction of Au oxide occurred at $E_p = 0.88$ V concurrently with the oxidation of HQ.

Current-potential curves were recorded as a function of $\phi$ while holding $\omega$ constant. The magnitude of the anodic current plateau (A), corresponding to the oxidation of HQ, was independent of $\phi$ after correcting for double-layer charging current. This behavior is indicative of a mass-transport controlled process. At low values of $\phi$, peak B was not observed since the sufficient time elapsed at that scan rate for the depletion of species in the diffusion layer to occur during the rising portion of the oxidation wave. Current due to the formation of Au oxide and the reduction of Au oxide varied with $\phi$, which is characteristic of surface-controlled processes. Variation of $\omega$ at a constant value of $\phi$ demonstrated that the anodic plateau current increased nonlinearly with $\omega^{1/2}$. Since no surface-controlled reactions occurred simultaneously with HQ oxidation in the region $0.46 \, V < E <
Figure V-17: I-E and ΔI-E curves of 0.5 mM hydroquinone in 0.5 M \( \text{H}_2\text{SO}_4 \) at a Au RDE

a. I-E curve

Electrode rotation speed \( (W) \): 1000 rpm

Potential scan rate \( (\dot{\phi}) \): 6 V/min

b. ΔI-E curve

Lower rotation speed \( (W_l) \): 1000 rpm

Upper rotation speed \( (W_u) \): 4000 rpm

Potential step increment \( (\Delta E) \): 5 mV

Time delay \( (t_d) \): 150 ms

Number of data points \( (N) \): 10
a.

b.
1.05 V, it was concluded that the kinetics for the anodic oxidation of HQ at a Au electrode are the controlling factor at large ω.

The anodic oxidation of HQ at a Au electrode was investigated further by application of QHMV. For $E_a \leq 1.8$ V, a reversible anodic wave was observed for the mass-transport coupled oxidation of HQ. The $\Delta I$-$E$ curve obtained for $E_a = 1.85$ V is shown in Figure V-17b. An anodic current plateau was observed during the positive scan of potential; however, upon reversal of the potential scan direction, $\Delta I$ decreased linearly in the region $1.85$ V $> E > 0.9$ V at a rate of 31.2 $\mu A/V$. At $E < 0.9$ V, Au oxide was reduced and $\Delta I$ rapidly increased to the anodic value observed during the positive scan of potential. The linear decrease in $\Delta I$ in the region $1.85$ V $> E > 0.9$ V may be attributed to a change in the properties of the oxide-covered Au electrode upon anodization at $E > 1.8$ V. Kim et al. (68) reported that a highly-hydrated oxide Au(OH)$_3$ is formed at $E > 1.8$ V. Perhaps the formation of Au(OH)$_3$ forms a protective layer over the existing oxide; hence, less Au$_2$O$_3$ flakes off of the electrode surface. Since Au$_2$O$_3$ is known to be a poor electronic conductor, an ohmic drop may occur across the layer of Au$_2$O$_3$. It is also possible that by decreasing the amount of Au$_2$O$_3$ which flakes from electrode surface, the number of available oxide-free Au sites decreases; hence, the observed value of $\Delta I$ decreases. Cadle and Bruckenstein (143) have observed that anodization of a Au electrode at $E > 1.8$ V increases the surface roughness of the electrode. A two-fold increase in the roughness factor was observed upon potentiostating the electrode at $E = 1.9$ V for 2 min; whereas, no increase in
the roughness factor was observed upon potentiostating the electrode at 
$E = 1.7 \, V$ for as long as an hour even though Au dissolution occurred at 
$E = 1.7 \, V$. The rate of Au dissolution increased at $E > 1.8 \, V$ which 
corresponds to the potential at which Au(OH)$_3$ formation commences. 
Cadle and Bruckenstein concluded that the rate of dissolution, not the 
quantity of Au dissolved, controls the extent of roughening. The 
oxidation of HQ may be sterically hindered at a Au electrode roughened 
at the atomic level. Another possible explanation is that the reaction 
may be kinetically slower at an electrode which has been anodized at 
$E > 1.8 \, V$ until the oxide layer is reduced from the electrode surface. 
Further investigation of this phenomenon may provide novel information 
about the oxide which forms on Au at $E > 1.8 \, V$.

D. Summary

In this section, data obtained by CV and QHMV has been presented for 
several analyte/electrode combinations. The results demonstrate the 
complementary nature of the two techniques. The ability of QHMV to 
extract the mass-transport coupled current from the total current 
produced in the potential region of O$_2$ evolution has proven to be the 
most informative attribute of QHMV. Tables V-2 and V-3 summarize the 
results obtained by QHMV for the anodic reactions discussed. Table V-4 
summarizes the results obtained by QHMV at a Pt electrode for other 
-reactions briefly examined but not discussed here.
Table V-2. Mass-transport dependent reactions observed by QHME simultaneously with $O_2$ evolution

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Electrode Material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>$\text{As(III)} \rightarrow \text{As(V)}$</td>
<td>mtc</td>
</tr>
<tr>
<td>$\text{I}^- \rightarrow \text{IO}_3^-$</td>
<td>mtl</td>
</tr>
<tr>
<td>$\text{Br}^- \rightarrow \text{Br}_2$</td>
<td>mtc</td>
</tr>
<tr>
<td>$\text{Cl}^- \rightarrow \text{Cl}_2$</td>
<td>mtc</td>
</tr>
<tr>
<td>$\text{NO}_2^- \rightarrow \text{NO}_3^-$</td>
<td>nc</td>
</tr>
<tr>
<td>$\text{HQ} \rightarrow Q$</td>
<td>mtl</td>
</tr>
</tbody>
</table>

- **mtc**: mass-transport coupled current was observed
- **mtl**: mass-transport limited current was observed
- **nc**: no coupling of the reaction to mass-transport was observed
- **-**: reaction was not studied
Table V-3. General trends of electrocatalysis observed for mass-transport coupled reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Electrode Material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>As(III) → As(V)</td>
<td>1</td>
</tr>
<tr>
<td>I⁻ → IO₃⁻</td>
<td>1</td>
</tr>
<tr>
<td>Br⁻ → Br₂</td>
<td>4</td>
</tr>
<tr>
<td>Cl⁻ → Cl₂</td>
<td>2</td>
</tr>
<tr>
<td>NO₂⁻ → NO₃⁻</td>
<td>3</td>
</tr>
<tr>
<td>HQ → Q</td>
<td>4</td>
</tr>
</tbody>
</table>

1. catalyzed by lower oxide, inhibited by higher oxide, catalyzed during O₂ evolution
2. catalyzed only during O₂ evolution
3. catalyzed by lower oxide, inhibited by higher oxide, not catalyzed during O₂ evolution
4. the mass-transport coupled reaction does not involve electrocatalysis
- reaction was not studied
Table V-4. Mass-transport dependent reactions observed by QHMV occurring simultaneously with O$_2$ evolution at a Pt electrode

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Electrode Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(III) $\rightarrow$ Ce(IV)</td>
<td>1</td>
</tr>
<tr>
<td>Cr(III) $\rightarrow$ Cr(VI)</td>
<td>3</td>
</tr>
<tr>
<td>Mn(II) $\rightarrow$ Mn(III)</td>
<td>2</td>
</tr>
<tr>
<td>or</td>
<td></td>
</tr>
<tr>
<td>Mn(II) $\rightarrow$ Mn(VII)</td>
<td></td>
</tr>
<tr>
<td>Sb(III) $\rightarrow$ Sb(V)</td>
<td>3</td>
</tr>
<tr>
<td>Se(IV) $\rightarrow$ Se(VI)</td>
<td>3</td>
</tr>
<tr>
<td>Sn(II) $\rightarrow$ Sn(IV)</td>
<td>3</td>
</tr>
<tr>
<td>V(III) $\rightarrow$ V(V)</td>
<td>1</td>
</tr>
</tbody>
</table>

1 mass-transport limited reaction occurring simultaneously with O$_2$

2 mass-transport coupled reaction occurring simultaneously with O$_2$ evolution

3 no mass-transport coupled reaction observed
VI. THE ANODIC OXIDATION OF IODIDE IN ACIDIC MEDIA
AT A Pt ELECTRODE

A. Literature Review

The survey of anodic reactions utilizing CV and QHMV demonstrated
the complimentary nature of the two techniques and illustrated that
QHMV is an invaluable technique for the study of mass-transport coupled
reactions that are occurring simultaneously with surface oxidation and
O₂ evolution. Of particular interest are the results obtained for the
oxidation of I⁻ at a Pt electrode in acidic media. The following
observations promoted further study of the oxidation of I⁻ which
involves the uptake of O atoms: 1) The surface-coupled, oxidative
desorption of I to IO₃⁻ is initiated at the potential where PtOH
formation commences. 2) The transport-coupled oxidation of I⁻ to IO₃⁻
proceeds concomitantly with the formation of PtOH. 3) The transport-
limited production of IO₃⁻ occurs simultaneously with O₂ evolution.

Iodide is strongly adsorbed on an oxide-free Pt surface with
complete loss of the negative charge (16, 104, 122). Adsorption of
I⁻ as I₀ is irreversible and desorption does not occur upon thorough
rinsing with I⁻-free solutions. The maximum coverage by I atoms was
observed to be ca. θ = 0.5 (16), implying one adsorbed I per two Pt
surface atoms. Lane and Hubbard (16) suggested that the adsorption
of I⁻ proceeds through the formation of dissociated HI. However,
based on the results of recent studies utilizing low energy electron
diffraction (LEED), Auger electron spectroscopy (AES), and thermal
desorption mass spectrometry (TDMS), it has been concluded that the adsorption of I⁻ on Pt is limited only by the size of the I atom (154, 155). Felter and Hubbard (154) examined the adsorption of gaseous I₂ on Pt(100) and Pt(111) single crystals. They concluded that I₂ dissociatively adsorbs to form a hexagonal or near-hexagonal lattice with a maximum coverage of θ = 0.56. The adsorption of gaseous HI on Pt(100) and Pt(111) single crystals has been investigated by Garwood and Hubbard (155). The maximum coverage by I atoms on Pt(111) is θ = 0.43; whereas a maximum coverage of θ = 0.54 is attained on Pt(100). For θ < 0.50, at either Pt(111) or Pt(100), I atoms are desorbed exclusively. However, at Pt(100), HI is desorbed exclusively in the transition from θ = 0.54 to θ = 0.50; hence, adsorption in excess of θ = 0.50 occurs as HI. The stability of the Pt-I adsorption bond was demonstrated by the high temperature required for desorption to occur in vacuum. Thermal desorption of I from Pt(111) produced a peak at 735 K followed by a broad maximum for temperatures of 800-1000 K. At Pt(100), the transition from θ = 0.54 to θ = 0.50 produced a desorption peak at 620 K corresponding to the desorption of HI which is more weakly bonded than I atoms. Two desorption peaks were observed at temperatures of 735 K and 980 K, as the result of the desorption of I atoms from Pt(100). The contrasting thermal desorption behavior of I atoms from Pt(111) and Pt(100) parallels the dissimilar reactivity of these surfaces toward electrochemical oxidative desorption. Current-potential curves were recorded for the oxidative desorption of I which was deposited under vacuum on Pt(111) and Pt(100) single crystals.
The oxidative desorption of I from Pt(111) produced a single peak, whereas the oxidative desorption from Pt(100) produced two anodic peaks. Comparison of the I-E curve obtained for the oxidative desorption of I from Pt(100) deposited under vacuum with that for deposition from an aqueous solution indicated that the peak occurring at the more positive potential is unique to the adsorbed layer produced under vacuum. The differences in reactivity of adsorbed I are being investigated further by Felter and Hubbard (154).

The effects of adsorbed I upon the anodic formation of surface oxide and the underpotential deposition of H have been studied in detail (53, 104, 121, 122) and are illustrated in Figure VI-1. Adsorbed I suppresses the anodic formation of surface oxide on Pt nonselectively over the region 0.55 V < E < 1.0 V. However, at E > 1.0 V, adsorbed I is removed from the electrode surface by oxidative desorption to $\text{IO}_3^-$ with concurrent formation of surface oxide. No I adsorbs on an oxide-covered Pt surface (12, 17). Unlike adsorbed Br$^-$ and Cl$^-$, adsorbed I alters the quantity of H adsorbed in the region 0.1 V > E > -0.2 V; hence, the current observed progressively diminishes as the concentration of I$^-$ increases in the solution.

Iodine atoms adsorbed on a Pt surface influence the rate of many electrochemical reactions (14, 156-158). Upon adsorption of I, the electrostatic charge distribution of the solution-electrode interface is altered. Oppositely charged reactants are attracted to the diffuse layer, thus facilitating their reaction; whereas, the reaction of like-charged species is not facilitated by adsorbed I on a Pt surface. The
Figure VI-1: I-E curves of I⁻ in 0.5 M H₂SO₄ at a Pt RDE as a function of I⁻ concentration

Electrode rotation speed (W): 400 rpm
Potential scan rate (v): 4 V/min

0.0 μM I⁻

1.1 μM I⁻

3.1 μM I⁻

8.1 μM I⁻
following examples illustrate the affect which I adsorbed on a Pt substrate exhibits on several electrochemical reactions: 1) Adsorbed I accelerates the reaction of anionic Pt(II) complexes, e.g., PtCl$_4^{2-}$ (156). On the other hand, deceleration of the reaction of cationic Pt complexes, e.g., Pt(NH$_3$)$_4^{2+}$ (156) occurs, as expected from electrostatic considerations. 2) The oxidation of Sb(III) in acidic Cl$^-$ media is irreversible at a Pt electrode; however, upon pretreating the electrode with I, the oxidation of Sb(III) is reversible (157). 3) The *in vivo* voltammetric detection of catecholamines can be achieved without interference from oxide formation at a Pt electrode pretreated with I$^-$ (14). In the absence of adsorbed I, no oxidation peak is discernible for the catecholamines. 4) The reduction of Cr(VI), which is irreversible at a Pt electrode untreated with I, is reversible at a Pt electrode on which I is adsorbed (158).

The anodic behavior of I$^-$ on Pt in acidic media has been described previously (11, 12, 17, 101). The first step in the oxidation of I$^-$ is the production of I$_2$. The mechanism of this reaction, as proposed by Newson and Riddiford (159), Jordan and Javick (160, 161), and Dane et al. (162), involves the adsorption of I$^-$ . A more recent investigation by Osteryoung and Anson (11) indicated that the mechanism of I$_2$ formation does not require adsorbed I, e.g., when occurring at an oxide-covered electrode. However, they did not postulate specific mechanisms for the formation of I$_2$ at oxide-free or oxide-covered electrodes. The product of further oxidation of I$^-$ is IO$_3^-$ (12, 101, 163). Zakharov and Songina (101) concluded that the oxidation of I$^-$ to IO$_3^-$ takes place by the
direct participation of 0 atoms of the surface oxide of Pt as indicated schematically by

\[ \text{PtO}[0]_n + I^- \rightarrow \text{PtO}[0]_{n-3} + IO_3^- + 6e^- \]

No other mechanism has been reported in the literature.

A. Voltammetric Studies

1. Cyclic voltammetry

An I-E curve for 0.5 mM I\(^-\) in 0.5 M H\(_2\)SO\(_4\) is shown in Figure VI-2. During the positive scan of potential, I\(^-\) is oxidized to I\(_2\) (E\(_{1/2}\) = 0.48 V) to yield an anodic wave (A) with a limiting current plateau in the region 0.55 V < E < 0.95 V. Peak B, observed at E > 0.95 V, is the result of the production of IO\(_3^-\) and surface oxide. A significant part of the IO\(_3^-\) produced has been concluded to originate from adsorbed I with oxidative desorption occurring simultaneously with the anodic formation of surface oxide (12, 17). A limiting current plateau was not attained for the production of IO\(_3^-\) in the region of peak B; apparently, the production of IO\(_3^-\) is inhibited by the rapid conversion of the lower oxide (PtOH) to the higher oxide (PtO) in the potential region of peak B. At E > 1.3 V, the large current resulting from the anodic decomposition of the solvent to produce O\(_2\) serves as a practical limit for the positive scan of potential. Two cathodic peaks were observed during the subsequent negative scan of potential. Peak C at E\(_p\) = 0.45 V is the result of the reduction of the surface oxide formed during the positive scan for E > 1.0 V. The electrochemical reduction of I\(_2\) irreversibly adsorbed at
Figure VI-2: I-E curve of 0.5 mM I\textsuperscript{-} in 0.5 M H\textsubscript{2}SO\textsubscript{4}
at a Pt RDE

Electrode rotation speed (W): 1000 rpm

Potential scan rate (\psi): 6 V/min
the surface produces peak D at 0.0 V (17).

Current-potential curves were recorded as a function of $\phi$ for a constant value of $\omega$. The height of peak B varied with changes in $\phi$ as expected for a surface-controlled process. The faradaic signal corresponding to the oxidation of $I^- \rightarrow I_2$ (A) was independent of $\phi$ which is the typical behavior of a transport-controlled reaction. The I-E curves obtained at a single value of $\phi$, while varying $\omega$, demonstrated that the electrode current for both anodic reactions (A and B) increased as $\omega$ was increased. The oxidation of $I^-$ to $I_2$ (A) is a mass-transport limited reaction, i.e., a plot of $I_{\text{lim}}$ vs. $\omega^{1/2}$ is linear. The height of peak B varied nonlinearly with $\omega^{1/2}$, since peak B consists of currents resulting from the formation of surface oxide and the anodic production of $IO_3^-$ from $I$ (i.e., surface-controlled reactions), in addition to any transport-coupled oxidation of $I^-$ from the bulk solution.

A series of I-E curves was recorded as a function of $E_a$ (Figure VI-3). The anodic formation of surface oxide does not occur for $E_a \leq 1.0 \text{ V}$, because of the presence of adsorbed $I$. The reduction peak observed during the negative scan for $E_a \leq 1.0 \text{ V}$ (A) is attributed to the reduction of reversibly adsorbed $I_2$. For $E_a = 1.1 \text{ V}$, formation of PtOH proceeds with a minimal amount of place exchange to give OHPt or further oxidation to PtO. Therefore, upon reversal of the potential scan, PtOH is available to catalyze the oxidation of $I^-$ to $IO_3^-$. The $E_{1/2}$ observed for the formation of $IO_3^-$ during the negative scan of potential is 35 mV more negative than the $E_{1/2}$ observed for this reaction during the preceding positive scan of potential. In a thermodynamic
Figure VI-3: I-E curves of 0.5 mM I⁻ in 0.5 M H₂SO₄ at a Pt RDE as a function of $E_a$

Electrode rotation speed ($W$): 1000 rpm
Potential scan rate ($\phi$): 6 V/min

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>1.0 V</th>
<th>1.1 V</th>
<th>1.2 V</th>
<th>1.3 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>------</td>
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</tr>
<tr>
<td>Figure</td>
<td>------</td>
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</tbody>
</table>
sense, the oxidation reaction is more reversible in the presence of a small amount of surface oxide, specifically PtOH. At $E_a \geq 1.2\, \text{V}$, an anodic peak (B) was attained for the oxidation of $\text{I}^-$ to $\text{IO}_3^-$ during the positive scan of potential. The anodic formation of $\text{IO}_3^-$ did not occur during the negative scan of potential for $E_a \geq 1.2\, \text{V}$ because of the presence of OHPt and PtO on the electrode surface which do not catalyze the reaction.

The transition between reversibly adsorbed $\text{I}_2$ and irreversibly adsorbed $\text{I}_2$ was observed by close examination of the reduction reactions occurring in the region $0.7\, \text{V} > E > -0.22\, \text{V}$ (Figure VI-4). Peak A at $E_p = 0.45\, \text{V}$ corresponds to the reduction of reversibly adsorbed $\text{I}_2$ (17). As long as $E_a < 1.02\, \text{V}$, i.e., no oxide formation occurred, only peak A was observed. However, for $E_a > 1.02\, \text{V}$, a reduction peak at $E_p = 0.0\, \text{V}$ was produced which is attributed to the reduction of irreversibly adsorbed $\text{I}_2$ (17). The height of peak B, i.e., the amount of irreversibly adsorbed $\text{I}_2$, increased to a constant value as $E_a$ became more positive. Hence, the $\text{I}_2$, once reversibly adsorbed, is converted to irreversibly adsorbed $\text{I}_2$ as Pt oxide is formed on the electrode (17). The change in the height of peak A was obscured by the overlapping oxide reduction peak.

2. **Square-wave hydrodynamically modulated voltammetry**

   The investigation of the transport-coupled process of $\text{IO}_3^-$ formation required the measurement of the convective component of the total current, as can be achieved by QHMV. The production of $\text{IO}_3^-$ by oxidative desorption of adsorbed I does not contribute to the $\Delta I$ signal.
Figure VI-4: I-E curves of 0.5 mM I\textsuperscript{-} in 0.5 M H\textsubscript{2}SO\textsubscript{4} at a Pt RDE as a function of E\textsubscript{a}.

Electrode rotation speed (W): 1000 rpm
Potential scan rate (ϕ): 6 V/min

--- 1.0 V
----- 1.1 V
------ 1.2 V
----- 1.3 V
a. **Staircase potential waveform**  The electrochemical response of I⁻ at a Pt electrode was characterized by QHMV utilizing the staircase potential waveform illustrated in Figure IV-1. The resultant ΔI-E curve is shown in Figure VI-5. The reaction \( \text{I}^- \longrightarrow \frac{1}{2}\text{I}_2 + e^- \) occurred with the thermodynamically predicted value of \( E^\circ = 0.48 \) V and the transport-limited current was observed in the region \( 0.55 \) V < E < 0.95 V (A). The value of ΔI (67 μA) corresponds closely to the theoretical value (69 μA) predicted from the linear Levich plot (I vs. ω^½) constructed for this anodic process from data obtained by cyclic voltammetry. Peak B at ca. 1.05 V corresponds to the oxidation of I⁻ transported from the bulk solution to IO₃⁻. The height of peak B was significantly less than the transport-limited value predicted for this reaction (i.e., 6.69 μA); however, ΔI is greater than the value expected for the transport-limited oxidation of I⁻ to HIO (i.e., 2.69 μA). The appearance of a peak signal for the oxidation of I⁻ to IO₃⁻ can be explained on the basis of the catalytic properties of the surface oxide. Oxidation of I⁻ to IO₃⁻ is thermodynamically allowed in this solution for E > 0.84 V; however, the reaction was not observed to occur until E > 1.0 V, corresponding to the onset of the formation of surface oxide. It was concluded that the production of IO₃⁻ from I⁻, as well as adsorbed I, is initiated by the generation of PtOH as the first step in the formation of the surface oxide (PtO). Unfortunately, the adsorbed I suppresses the onset of oxide formation (see Figure VI-1); hence, the potential range is quite narrow over which the production of IO₃⁻ is thermodynamically allowed, and in which PtOH exists in an appreciable quantity at the electrode.
Figure VI-5: $\Delta I$-$E$ curve of 0.5 mM $I^-$ in 0.5 M $H_2SO_4$

at a Pt RDE

Lower rotation speed ($W_l$): 1000 rpm
Upper rotation speed ($W_u$): 4000 rpm
Potential step increment ($\Delta E$): 5 mV
Time delay ($t_d$): 150 ms
Number of data points ($N$): 10
The graph shows a redox reaction with three distinct regions labeled A, B, and C. The x-axis represents the electrode potential (E, V vs. SCE) ranging from 1.4 to 0.2 V, while the y-axis represents the change in current (ΔI, μA) ranging from -300 to -100 μA.
surface. Rearrangement of PtOH to the catalytically inactive OHPt, and further oxidation to PtO, occur rapidly for \( E > 1.2 \) V and the production of \( \text{IO}_3^- \) is suppressed sharply. As the potential increased beyond 1.3 V, \( \Delta I \) increased to a limiting current plateau for \( E > 1.5 \) V (C) and is attributed to the production of \( \text{IO}_3^- \). The ratio of \( \Delta I \) for the two limiting values of current for waves C and A (\( \Delta I_C/\Delta I_A \)) is 6.0 as expected on the basis of the assigned reactions. The renewed formation of \( \text{IO}_3^- \) occurring concomitantly with \( \text{O}_2 \) evolution is attributed to the catalytic involvement of the OH radical generated on the PtO surface as the first step in the production of \( \text{O}_2 \). In addition, the evolution of \( \text{O}_2 \) involves the abstraction of \( \text{O} \)-atoms in the oxide film (54, 56); therefore, when \( \text{O}_2 \) molecules leave the surface of the electrode, the oxide must be reformed. Since the formation of oxide involves OH radicals as an intermediate product, there is an abundance of OH radicals present on the electrode surface during \( \text{O}_2 \) evolution which exhibit an electrocatalytic effect on \( \text{IO}_3^- \) formation. Upon reversal of the potential scan, the transport-limited production of \( \text{IO}_3^- \) proceeded as long as \( \text{O}_2 \) was evolved. At \( E < 1.3 \) V, only the oxidation of \( \text{I}^- \) to \( \text{I}_2 \) occurred, since virtually no PtOH is generated during the negative scan of potential. These results are consistent with the conclusion that the oxidation of \( \text{I}^- \) to \( \text{IO}_3^- \) requires the electrocatalytic benefit of the OH radical, whether adsorbed on the metal surface (PtOH) or the oxide (PtOOH).

b. **Triple-step potential waveform** QHMV was applied utilizing the triple-step potential waveform illustrated in Figure IV-2. The potential waveform consisted of an initial potential value (\( E_1 \)) which
resulted in the reduction of PtOH and PtO on the electrode surface, an
oxidizing potential \( E_2 \) for which surface oxidation was initiated, and
a sampling potential \( E_3 < E_2 \) at which the faradaic signal was measured.
This particular sequence of potential values effectively "freezes" the
oxide layer, for the sampling period, in the state which is character­
istic of the oxide formed at \( E_2 \) for the time period \( t_2 \). For a small
value of \( t_2 \) (e.g., 50 ms), production of the catalytically active oxide
(PtOH) is maximized with relatively little conversion to the less active
OHPt and PtO. The driving force for the formation of additional oxide
no longer exists at \( E < E_2 \); therefore, anodic reactions which occur will
tend to be characteristic of the catalytic activity of the oxide formed
at \( E_2 \). It should be noted that catalytically active PtOH generated at
\( E_2 \) will undergo conversion to the inactive OHPt at \( E_3 < E_2 \). Since PtOH
is not reduced until \( E < 0.7 \) V, use of this waveform results in the
availability of PtOH produced at the electrode surface for a limited
time during the sampling period with \( E_3 > 0.7 \) V. The results for \( E_2 =
1.1 \) V, \( 1.2 \) V, and \( 1.6 \) V are shown in Figure VI-6. The oxidation of I
\( \text{to I}_2 \) (A) for \( 0.45 \) V < \( E < 0.95 \) V proceeded regardless of the value of
\( E_2 \), i.e., the formation of \( \text{I}_2 \) is not inhibited by the presence of
surface oxide. As \( E_2 \) was increased from \( 1.1 \) V to \( 1.2 \) V, the value of
\( \Delta I \) in the region of peak B decreased significantly and the \( E_{1/2} \) of the
wave shifted 25 mV in the positive direction; these changes demonstrate
that the formation of OHPt and PtO is more irreversible than the
formation of PtOH at less positive potentials. Current in the region of
peak B continued to decrease as \( E_2 \) was increased and the \( E_{1/2} \) of the
Figure VI-6: $\Delta I-E_3$ curve of 0.5 mM I$^-$ in 0.5 M H$_2$SO$_4$ at a Pt RDE utilizing the triple-step potential waveform illustrated in Figure IV-2

Lower rotation speed ($W_1$): 1000 rpm
Upper rotation speed ($W_u$): 4000 rpm
Potential step increment ($\Delta E$): 20 mV
Number of data points (N): 50

$E_1 = 0.0 \text{ V} \quad t_1 = 250 \text{ ms}$
$E_3 = \text{variable} \quad t_3 = 200 \text{ ms}$

Values of $E_2$ ($t_2 = 200 \text{ ms}$) were as follows:

- 1.10 V
- + 1.20 V
- + 1.60 V
reactions shifted to more positive values. However, values of $\Delta I$, obtained for $1.3 \, V < E < 1.6 \, V$ (C), correspond to the limiting current for the oxidation of $I^{-}$ to $IO_{3}^{-}$. The ratio of $\Delta I$ for the two limiting currents ($\Delta I_{C}/\Delta I_{A}$) is 6.0.

The time dependence for conversion of active PtOH to the inactive OHPt and PtO is illustrated by plots of $\Delta I$ as a function of $t_{2}$ for several values of $E_{2}$ in the range $1.1 \, V < E < 1.6 \, V$ (Figure VI-7). For $E_{2} = 1.1 \, V$, $\Delta I$ was essentially constant throughout the range of values of $t_{2}$ tested. For $E_{2} = 1.2 \, V$, the catalytic activity of the electrode surface, as measured by $\Delta I$, decreased with increasing $t_{2}$, approaching the limiting value for the oxidation of $I^{-}$ to $I_{2}$ observed for $t_{2} > ca. \, 400 \, ms$. For $E_{2} \geq 1.3 \, V$, $\Delta I$ corresponded approximately to the transport-limited value for the oxidation of $I^{-}$ to $I_{2}$ at all values of $t_{2}$.

3. **Summary**

The oxidative reactions of $I^{-}$ in acidic media at a Pt electrode were examined in detail. The convective components of the total electrode current include: 1) the mass-transport limited formation of $I_{2}$ at $E > 0.45 \, V$; 2) the mass-transport coupled oxidation of $I^{-}$ to $IO_{3}^{-}$, which is catalyzed by the anodic formation of PtOH; and 3) the mass-transport limited production of $IO_{3}^{-}$, which is concluded to be electrocatalyzed by OH, an intermediate product of $O_{2}$ evolution. Observation of the latter two components was possible only upon application of QHMV.
Figure VI-7: Plots of \( \Delta I \) vs. \( t_2 \) as a function of \( E_2 \) for 0.5 mM I\(^-\) in 0.5 M H\(_2\)SO\(_4\) at a Pt RDE

- Lower rotation speed \( (W_L) \): 1000 rpm
- Upper rotation speed \( (W_U) \): 4000 rpm
- Number of data points \( (N) \): 10

- \( E_1 = 0.00 \) V, \( t_1 = 250 \) ms
- \( E_2 \) = variable, \( t_2 \) = variable
- \( E_3 = 1.05 \) V, \( t_3 = 20 \) ms
$E_2 (V \text{ vs. SCE})$:  
- $+ 1.10$
- $\bullet 1.20$
- $\triangle 1.30$
- $\times 1.60$

Graph showing $I$ vs. $t_2$ (msec) with different symbol representations for different $E_2$ values.
C. Flow Injection Detection

Constant potential amperometry is applicable for the detection of numerous electroactive species; however, the loss of electrode activity at noble metal electrodes frequently is observed. The loss of electrode activity can be attributed to 1) the formation of a passivating oxide or 2) fouling of the electrode surface by residual products which remain strongly adsorbed on the electrode surface. In either case, continued oxidation of the analyte is inhibited and the analytical signal rapidly diminishes. Amperometric detection utilizing a stepped potential waveform has been developed which leads to greater stability of the electrochemical response. Results obtained by application of a double-step potential waveform have been reported (164-167), noting the observed increase in stability of the electrochemical response. However, recently, triple-step amperometric detection has received much attention (168-173) particularly for the anodic detection of organic compounds, e.g., alcohols (168), carbohydrates (169-172), amino acids (171, 173), and sulfur-containing organic compounds (173). Triple-step amperometry utilizes a potential waveform which incorporates voltammetric cleaning and reactivation of the electrode surface together with the amperometric measurement. Reproducible electrode activity is achieved during each cycle of the potential waveform, therefore, the value of current measured for a given concentration of analyte is constant.

Amperometric detection of compounds, whose oxidation is catalyzed by anodic formation of PtOH, is greatly enhanced through the application
of triple-step amperometry. The electrocatalyzed response is short-lived due to the transient lifetime of PtOH. Therefore, by application of a triple-step potential waveform, the surface is reproducibly regenerated and current is measured when the electrocatalyzed response is near its maximum value. The amperometric detection of $I^-\text{ was examined utilizing single (dc) and multi-step potential waveforms to illustrate the enhanced sensitivity of the measured signal in the potential region where the electrocatalyzed oxidation of } I^-\text{ to } IO_3^- \text{ occurs.}

The response of electrode current to a step change in potential will be considered in general terms so that the choice of the multi-step potential waveform and the observed analytical signal for specific reactions are more easily understood. In all instances, the contribution of double-layer charging current is ignored for simplicity.

The Cottrell equation, $I = nFAD^{1/2}C/(\pi t)^{1/2}$, describes the response of current as a function of time following a step in potential under the condition of no convection. The observed electrode current approaches zero as time approaches infinity (Figure VI-8-A). If the potential is stepped to a region where a mass-transport limited reaction occurs, the Cottrell equation is valid at short $t$, regardless of the geometric shape of the electrode or the existence and nature of convection. However, for long $t$, current deviates from the Cottrell equation and approaches a steady state value which is a function of the geometry of the electrode and the rate of convection (Figure VI-8-B). At a rotating disk electrode, the magnitude of the steady-state current is described
by the Levich equation and is independent of time.

When the potential is stepped to a region where surface oxide formation is the only faradaic reaction occurring, current \( I_{OX} \) decays according to the equation
\[
I_{OX} = cn/t
\]
where \( n \) is the applied overpotential, \( t \) is time, and \( c \) is a constant (174, 175) (Figure VI-9-A). In the presence of an irreversibly adsorbed, electroinactive species, \( I_{OX} \) is decreased at all values of \( t \) (Figure VI-9-B).

If a change in applied potential results in the desorption of an electroinactive species concomitantly with formation of oxide, the value of \( I_{OX} \) is decreased significantly at small \( t \). However, at longer \( t \),
It is larger than the value of $I_{ox}$ observed in the absence of an adsorbed species, since the total charge passed for oxide formation over an extended period of time must be virtually the same regardless of the initial coverage by an electroinactive species. The I-t response for this case is shown in Figure VI-10.

Oxidative desorption of an electroactive adsorbate by a process electrocatalyzed by the formation of surface oxide produces a I-t curve shown in Figure VI-11. Current is inhibited at short $t$ for $\theta > 0$ but enhancement of the current is observed at longer $t$. The total
charge passed upon electro-oxidative desorption over a long time period will exceed the charge passed for the formation of oxide because of the faradaic reaction of the analyte.

The magnitude of the current and the direction of deflection of the signal in relation to the baseline for pulsed amperometric detection is dependent upon the processes occurring at the sampling potential and the value of \( t \) selected for measurement of \( I \). Analytical application utilizing any of the responses is feasible provided that the electrode surface is reproducibly regenerated during each cycle of the applied
Figure VI-11: Expected anodic response following a positive potential step into a region where oxide formation occurs. [A-oxide formation in the absence of analyte, $\theta_A = 0$. B-oxide formation and concurrent oxidative desorption of the analyte, $\theta_A = 0.5$.]

waveform. Tailing of peaks is observed if the adsorbate is not completely removed from the electrode surface during the cleaning steps in the waveform.

The amperometric detection of I$^-$ at a Pt electrode was investigated taking advantage of the following characteristics of the electrochemical response of I$^-$: 1) I$^-$ is oxidized to I$_2$ by a mass-transport limited reaction in the region 0.55 V < E < 0.95 V; 2) I$^-$ is strongly adsorbed on a reduced Pt surface, consequently, anodic formation of surface oxide is suppressed in the region 0.55 V < E < 1.0 V; and 3) adsorbed I
is oxidatively desorbed at $E > 1.0$ V through an electrocatalytic reaction producing $\text{IO}_3^-$. The multi-step potential waveforms applied for flow injection detection are listed in Table VI-1. The resultant flow injection peaks for single (dc) and multi-step amperometry are illustrated in Figure VI-12. Each case will be discussed briefly.

Table VI-1. Multi-step potential waveforms utilized for the amperometric detection of $I^-$ at a Pt electrode

<table>
<thead>
<tr>
<th>Waveform</th>
<th>$E_1$ (mV); $t_1$ (ms)</th>
<th>$E_2$ (mV); $t_2$ (ms)</th>
<th>$E_3$ (mV); $t_3$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>700; 100</td>
<td>1300; 200</td>
<td>200; 150</td>
</tr>
<tr>
<td>B</td>
<td>600; 100</td>
<td>1300; 200</td>
<td>200; 150</td>
</tr>
<tr>
<td>C</td>
<td>1150; 100</td>
<td>200; 150</td>
<td>none</td>
</tr>
<tr>
<td>D</td>
<td>1150; 100</td>
<td>1300; 200</td>
<td>200; 150</td>
</tr>
</tbody>
</table>

Constant potential amperometry can be employed for the detection of $I^-$ by observing the mass-transport limited signal produced by the reaction $I^- \rightarrow \frac{1}{2}I_2 + e^-$ in the region $0.55$ V $< E < 0.95$ V without interference from surface oxide (Figure VI-12a). The electrode is pretreated by injecting a highly concentrated plug of $I^-$ which establishes the maximum equilibrium coverage by $I$ on the electrode surface. The equilibrium condition persists even for the absence of $I^-$ in the electrolytic solution provided the potential does not exceed 1.0 V. Hence, reproducible anodic peaks were obtained upon subsequent injection of $I^-$ into the $I^-$-free carrier stream. If the maximum
Figure VI-12: Flow injection peaks for 100 μM I⁻ in 0.5 M H₂SO₄ at a Pt wire electrode

Flow rate: 1.1 ml/min
Sample volume: 50 μl

Constant potential amperometry
  a. E = 700 mV

Triple-step potential amperometry
  b. waveform A
  c. waveform C
  d. waveform D
equilibrium coverage does not exist on the surface, \( I^- \) will preferentially adsorb on the electrode surface resulting in irreproducible anodic peaks.

Because adsorbed ions suppress the formation of surface oxide on Pt, \( I^- \) can be detected indirectly on the basis of the suppressed oxide current utilizing waveforms A and B. This mode of detection is employed successfully for flow injection detection if all adsorbed I from one detection cycle is removed prior to the next detection cycle. The following processes occur sequentially during a single application of the waveform: 1) \( I^- \) is oxidatively desorbed \( (E_2 = 1300 \text{ mV}) \) and surface oxide is formed; 2) the resulting surface oxide is cathodically reduced at \( E_3 = 200 \text{ mV} \) and \( I^- \) is adsorbed from the solution; and 3) the current sampled at \( E_1 = 600 \text{ mV} \) or 700 mV is less than the background signal for the absence of \( I^- \) in solution since adsorbed I suppresses the formation of surface oxide. Although the background signal for \( E_1 = 600 \text{ mV} \) (waveform B) was slightly lower than for \( E_1 = 700 \text{ mV} \) (waveform A), the height of the detection peak observed upon application of waveform A was approximately 3 times larger than the height of the detection peak observed upon application of waveform B. Hence, waveform A was preferred (Figure VI-12b).

Direct anodic detection of \( I^- \) can be accomplished by measuring the current produced as a result of the oxidative desorption of I (waveforms C and D). Although a limiting current value was not attained for the production of \( IO_3^- \), substantially increased sensitivity was observed. Application of a double-step potential waveform (C) resulted in
broadening of the detection peaks due to carry-over of adsorbed I from the previous detection cycle. Addition of a potential step for oxidative cleaning minimized peak broadening; however, sensitivity decreased. A larger quantity of oxide is formed during anodic cleaning which requires a larger cathodic current to reduce the surface oxide, thus, a longer time is required for the potentiostat to overcome the uncompensated value of \( R_{cell} \). As a result, a shorter effective time period in which the adsorption of \( I^- \) occurs and a decrease in sensitivity was observed. As the adsorption time for both waveforms (C and D) were increased, the analytical response became equivalent for the two waveforms (Figures VI-12c and VI-12d).

Examination of the relationship between the time spent at the adsorption potential and the height of the detection peak should provide information about the adsorption isotherm. Increased peak height should be observed with increasing adsorption time \( t_{ads} \), where \( t_{ads} = t_3 \) for waveforms A and D and \( t_{ads} = t_2 \) for waveform C) until equilibrium coverage is attained. Plots of peak height vs. \( t_{ads} \), for waveforms A, C, and D, are shown in Figure VI-13. Equilibrium coverage by I was not attained for \( t_{ads} \leq 500 \text{ ms} \). An estimate of exposure time \( (\mathcal{t}) \) required for maximum coverage to occur, assuming transport-limited adsorption for \( t < \mathcal{t} \), was calculated in the following manner: 1) Flux \( (F_x) \) is defined as \( F_x = \frac{I_{lim}}{nF} = A(D/\delta)c^b \). In this case, \( A = 0.050 \text{ cm}^2 \), \( D = 6.95 \times 10^{-5} \text{ cm}^2/\text{s} \), \( \delta = 3.8 \times 10^{-3} \text{ cm} \), and \( c^b = 1.0 \times 10^{-7} \text{ mol/cm}^3 \); therefore, \( F_x = 9.1 \times 10^{-11} \text{ mol/s} \). 2) The value of \( \tau_{max} \) for \( I^- \) on Pt is \( 1 \times 10^{-9} \text{ mol/cm}^2 \) (16). 3) The exposure time \( (\mathcal{t}) \) is given by
Figure VI-13: Peak height vs. $t_{ads}$ for triple-step amperometric detection of 100 $\mu$M I$^-$ in 0.5 M H$_2$SO$_4$ at a Pt wire electrode

Flow rate: 1.1 ml/min
Sample volume: 50 $\mu$l

a. waveform A
b. waveform C
c. waveform D
\[ \tau = \frac{\Gamma_{\text{max}}}{F_x}; \text{ hence, } \tau = 0.7 \text{ s}. \]

Additional data was collected to test this prediction; however, the observed value of \( t_{\text{ads}} \) was on the order of 10 s before maximum peak height was attained. Since these experiments were completed, it has been determined that all Pt oxide is not reduced under the conditions of these experiments \((E_{\text{ads}} = 200 \text{ mV}, t_{\text{ads}} \leq 500 \text{ ms})\). Therefore, these results are not valid for the determination of adsorption isotherm parameters. Nevertheless, the data are useful in predicting conditions for maximum sensitivity vs. efficiency for the pulsed detection technique. Experiments which utilize a four-step potential waveform are currently in progress.\(^1\) The processes occurring during the sequence of potential steps are as follows: 1) adsorbed I is oxidatively desorbed at \( E = 1300 \text{ mV} \); 2) the potential is stepped into the region of \( H_2 \) evolution \((E < -0.2 \text{ V})\) which facilitates reduction of the surface oxide and no \( I^- \) is adsorbed; 3) \( I^- \) is adsorbed at \( E = 200 \text{ mV} \) for various lengths of time (50-500 ms); and 4) current is sampled at \( E = 600 \text{ mV} \). A four-step potential waveform increases the sensitivity of the measured signal since more \( I^- \) adsorbs on the surface for shorter adsorption times and increases the reliability of adsorption isotherm data.

\(^1\) Polta, J. A., unpublished results, Iowa State University, 1984.
VII. THE REDUCTION OF IODATE

A. Introduction

Based on the results obtained for the oxidation of I⁻ to IO₃⁻ at a Pt electrode, it was concluded that the formation of IO₃⁻ is catalyzed by the initial stage of Pt oxide formation (i.e., PtOH) but is inhibited by the more stable form of Pt oxide (PtO). Numerous reactions, e.g., the evolution of O₂ (54) and the reduction of Ce⁴⁺ (176, 177) at Pt electrodes, are inhibited by PtO. In sharp contrast, the reduction of O₂ (178), V⁵⁺ (178), H₂O₂ (75), and IO₃⁻ (179, 180) occur more readily at an oxidized Pt electrode than at a reduced Pt electrode. Therefore, the cathodic behavior of IO₃⁻ at a Pt electrode was investigated by application of CV and QHMV to evaluate further the effect that Pt oxide exhibits on the reduction of IO₃⁻.

The electroreduction of IO₃⁻ has been studied by chronopotentiometric and voltammetric techniques (179, 180). Anson (179) observed that the reduction of IO₃⁻ at an oxidized Pt surface occurred at potentials from 200-600 mV more positive than the potential at which the reduction of IO₃⁻ occurred at a reduced Pt electrode. The decrease in η was attributed to catalysis of the cathodic reduction of IO₃⁻ when accompanied by the reduction of the oxide layer. A decrease in cathodic current owing to the reduction of IO₃⁻ was observed as the "catalyzing" oxide layer was removed from the electrode surface by reduction. Once the removal of the oxide layer was complete, no cathodic current was observed for IO₃⁻ until η was sufficiently large to cause the reduction
of IO$_3^-$ to occur at the reduced Pt electrode. The rate of current decay increased as the potential was maintained at successively more negative values. In contrast, no decrease in current with time was observed for reactions such as Fe$^{3+}$ or I$_2$ reduction which are not influenced by the oxide. Anson also observed that the peak for IO$_3^-$ reduction shifted with changes in pH in accordance with that observed for the reduction of Pt oxide. Based on these observations, Anson concluded that the oxide layer is essential for the reduction of IO$_3^-$ to proceed at $n < 750$ mV. Davis (180) also concluded that the reduction of IO$_3^-$ is facilitated by the simultaneous reduction of Pt oxide. Current densities, measured at 0.45 V vs. SCE, increased as $E_a$ became more positive. Davis also observed an abrupt change in the term $n\alpha$ ($n$ is the number of electrons and $\alpha$ is the transfer coefficient which is a measure of the symmetry of the reaction energy barrier) when the electrode had been reduced at $E < 0.25$ V. Therefore, he concluded that the reduction of IO$_3^-$ occurs via a different mechanism on a reduced Pt surface than on an oxidized Pt surface.

The anodic formation and cathodic dissolution of Pt oxide, in the absence of electroactive species, has been investigated (50, 52, 178). The results of those studies will be summarized briefly. The early stage of oxide formation, i.e., the formation of PtOH with minimal place exchange ($\theta_{OH} < 0.15$), is electrochemically reversible. However, as $E_a$ becomes more positive, the formation of a more stable oxide layer occurs as a result of place exchange between Pt and OH and, subsequently, further oxidation to PtO. Hence, the oxide formed at more positive
potentials is increasingly more irreversible and reduction occurs at more negative electrode potentials (Figure VII-1).

The mechanism of Pt oxide reduction is dependent upon the form of oxide. If the potential scan is reversed prior to the formation of PtO, the reductive process occurs according to the scheme (52)

\[
\begin{align*}
\text{OH}^+ & \rightarrow \text{PtOH} \\
\text{PtOH} + H^+ + e^- & \rightarrow \text{Pt} + H_2O
\end{align*}
\]

where place exchange is the rate determining step. The rate of the second step increases with increasingly negative values of potential. The reduction of PtO proceeds by the mechanism (52)

\[
\begin{align*}
\text{PtO} + H^+ + e^- & \rightarrow \text{PtOH} \\
\text{PtOH} + H^+ + e^- & \rightarrow \text{Pt} + H_2O
\end{align*}
\]

where the formation of PtOH is the rate determining step. In either case, the existence of PtOH during the reduction of Pt oxide is only transient. Hence, PtOH is, perhaps, responsible for catalyzing cathodic reactions, as well as catalyzing oxidative processes.

B. Cyclic Voltammetry

The I-E curve obtained for IO$_3^-$ at a Pt electrode is shown in Figure VII-2. A cathodic wave (A), for the reduction of IO$_3^-$ to I$^-$ at a reduced Pt surface, was observed in the region $-0.2 \ V < E < 0.3 \ V$ during the positive scan of potential. Iodide ions generated by this reduction reaction are adsorbed on the Pt surface and inhibit formation
Figure VII-1: I-E curves of Pt in 0.5 M H$_2$SO$_4$ as a function of $E_a$

Electrode rotation speed ($W$): 100 rpm

Potential scan rate ($\phi$): 4 V/min

--- 0.74 V
----- 0.83 V
------- 0.95 V
----- 1.10 V
--- 1.25 V
Figure VII-2: I-E curve of $4 \times 10^{-5}$ M $IO_3^-$ in 0.5 M $H_2SO_4$

at a Pt RDE

Electrode rotation speed ($W$): 1000 rpm

Potential scan rate ($\phi$): 6 V/min
of PtOH during the subsequent positive scan of potential; therefore, only double layer charging current is observed in the region $0.3 \, \text{V} < E < 0.95 \, \text{V}$. At $E > 0.95 \, \text{V}$, the anodic current increased rapidly and reached a maximum value at ca. $1.23 \, \text{V}$. Peak B is the combination of current produced as the result of oxidative desorption of I and the formation of the surface oxide. For the negative scan of potential, the cathodic wave C corresponds to the reduction of Pt oxide and some reduction of $\text{IO}_3^-$.

At $E < 0.3 \, \text{V}$, the cathodic wave A (already mentioned) was observed which corresponds to the reduction of $\text{IO}_3^-$ to I$^-$ on a reduced Pt surface with concurrent adsorption of I. Adsorption of H atoms is inhibited by the presence of adsorbed I therefore, the characteristic H adsorption and H desorption peaks are not observed.

Current-potential curves were recorded as a function of $\phi$ at a constant value of $\omega$. The reduction of $\text{IO}_3^-$ to I$^-$ (wave A) at a reduced Pt electrode was independent of $\phi$ which is characteristic of a mass-transport controlled reaction. The height of peak B, the simultaneous oxidation of adsorbed I and the Pt surface, varied with $\phi$ which is the typical behavior observed for surface-controlled reactions. The height of peak C also varied with $\phi$ due to the contribution to the total current from the reduction of Pt oxide, a surface-controlled reaction.

Current-potential curves were recorded also as a function of $\omega$ while holding $\phi$ constant. Current resulting from the reduction of $\text{IO}_3^-$ to I$^-$ at a reduced Pt electrode (wave A) increased linearly with $\omega^{0.5}$, i.e., the reduction of $\text{IO}_3^-$ is mass-transport limited at an overpotential of ca. $750 \, \text{mV}$. Peak B, the combination of current due to surface oxide...
formation and oxidative desorption of I, was independent of $\omega$ as expected for surface-controlled processes. The height of peak C increased non-linearly with $\omega^{1/2}$ indicating that a surface-controlled reaction, i.e., oxide reduction, is occurring simultaneously with the transport-coupled reduction of IO$_3^-$.

Current-potential curves recorded as a function of $E_a$ are shown in Figure VII-3. For $E_a \leq 1.0$ V, only the cathodic wave A was observed which corresponds to the reduction of IO$_3^-$ at the reduced Pt electrode. The formation of Pt oxide is inhibited by adsorbed I produced during reduction of IO$_3^-$ to I$^-$. Hence, no oxide formation occurs until $E > 1.0$ V. As $E_a$ was made more positive than 1.0 V the height of peak C, obtained only for $E_a > 1.0$ V, increased. The increase in current is attributed to the greater quantity of oxide which is formed at more positive values of $E_a$. No conclusion can be made from these data as to whether the amount of IO$_3^-$ reduction increased as $E_a$ was made more positive and the quantity of oxide available to catalyze the reaction increased. Therefore, the mass-transport coupled faradaic signal owing to the reduction of IO$_3^-$ was examined also as a function of $E_a$ by application of QHMV. These results will be discussed in the next section.

The reduction of IO$_3^-$ was investigated further utilizing a RRDE with a Pt disk and Pt ring. The processes occurring at the disk and the ring electrodes are considered here in general terms for a reversible reaction before discussing results specific to IO$_3^-$. Solution flows axially to the disk of a RRDE then flows radially across the ring.
Figure VII-3: I-E curves of $4 \times 10^{-5}$ M $IO_3^-$ in 0.5 M $H_2SO_4$ at a Pt RDE
Pt RDE as a function of $E_a$

Electrode rotation speed ($W$): 1000 rpm
Potential scan rate ($\psi$): 6 V/min

--- 1.0 V
--- 1.1 V
------ 1.2 V
------- 1.3 V
--- 1.4 V
electrode. Hence, the electrochemical production or consumption of an electroactive analyte at the disk can be monitored indirectly by observation of changes in the ring current. The ring electrode potential ($E_r$) usually is maintained at a constant value, while the potential of the disk electrode ($E_d$) is scanned between the anodic and cathodic limits. The current produced at the ring electrode ($I_r$) is recorded as a function of $E_d$.

The theoretical consideration of shielding and collection experiments has been described (1, 141, 142). The qualitative results will be discussed briefly. The so-called shielding experiment will be considered first. Suppose that the bulk solution contains an oxidized species (Ox), which can be reduced at $E < E^{0}_{\text{Ox/Red}}$, and the bulk concentration of the reduced species (Red) is zero. The potential of the ring electrode is maintained at $E_r = E_s$ where $E_s$ is on the limiting current plateau for the reaction $\text{Ox} + \text{n}e^- \rightarrow \text{Red}$, i.e., the concentration of Ox at the electrode surface is zero. At $E_d > E^{0}_{\text{Ox/Red}}$, no reaction occurs at the disk electrode and $I_r$ remains at a constant value corresponding to the transport-limited value for reduction of Ox at the ring electrode (Figure VII-4, region A); the ring is said to be "deshielded". However, when $E_d < E^{0}_{\text{Ox/Red}}$, the Ox species transported to the disk electrode are reduced; thus, the flux of Ox to the ring electrode decreases and the observed $I_r$ decreases (Figure VII-4, region B); the ring electrode is said to be "shielded" by the disk electrode.

For the so-called collection experiment, a value corresponding to the limiting current plateau for the reaction $\text{Red} \rightarrow \text{Ox} + \text{n}e^-$, i.e., the
Figure VII-4: Theoretical $I_d-E_d$ and $I_r-E_d$ behavior

Shielding experiment

$E_r = E_s$ where the concentration of Ox at the electrode surface is zero
surface concentration of Red is zero. At $E_d < E_{\text{Ox/Red}}$, no reaction occurs at the disk electrode and $I_r$ is zero (Figure VII-5, region A). However, at $E_d > E_{\text{Ox/Red}}$, Red species are generated at the disk electrode and transported radially over the ring electrode. Oxidation of Red occurs at the ring producing an anodic $I_r$ (Figure VII-5, region B).

The cathodic behavior of $\text{IO}_3^-$ was characterized at a RRDE with a Pt disk and Pt ring by application of a shielding experiment. Therefore, the reduction of $\text{IO}_3^-$ at the disk electrode was reflected by a decrease in the cathodic value of $I_r$. The ring electrode was potentiostated at $E_r = -0.1$ V, at which the mass-transport limited reduction of $\text{IO}_3^-$ occurs (see Figure VII-2). The resultant $I_r-E_d$ curve is shown in Figure VII-6. During the positive scan of $E_d$, $I_r$ increased steadily over the region $0.0 \text{ V} < E_d < 0.3 \text{ V}$ as current produced by $\text{IO}_3^-$ reduction at the reduced Pt surface decreased from the mass-transport limited value. The value of $I_r$ was constant in the region $0.3 \text{ V} < E_d < 1.03 \text{ V}$ indicating that $\text{IO}_3^-$ was not undergoing reaction at the disk electrode which was free of oxide at $E_d < 1.03 \text{ V}$ during the positive scan of potential. At $E_d > 1.03 \text{ V}$, the cathodic value of $I_r$ increased due to the oxidative desorption of I occurring at the disk electrode to produce additional $\text{IO}_3^-$ which was transported radially to the ring electrode. At $E_d > 1.25 \text{ V}$, $\text{IO}_3^-$ was no longer produced at the disk electrode; therefore, $I_r$ returned to the value observed in the region $0.3 \text{ V} < E_d < 1.03 \text{ V}$. During the negative scan of $E_d$, $I_r$ was constant over the region $1.3 \text{ V} > E_d > 0.85 \text{ V}$. However, at $E_d < 0.85 \text{ V}$, $I_r$
Figure VII-5: Theoretical $I_d - E_d$ and $I_r - E_d$ behavior

Collection experiment

\[ E_r = E_c \] where the concentration of Red at the electrode surface is zero
Figure VII-6: \( I_r - E_d \) curve of \( 4 \times 10^{-5} \text{ M IO}_3^- \) in 0.5 M H\(_2\)SO\(_4\) at a Pt/Pt RRDE

Electrode rotation speed (\( W \)): 1000 rpm
Potential scan rate (\( \phi \)): 6 V/min
\( E_r = -0.1 \text{ V} \)
decreased. This observed decrease in $I_r$ is attributed to the reduction of $\text{IO}_3^-$ at the disk electrode which causes a decrease in the amount of $\text{IO}_3^-$ transported to the ring electrode, i.e., the ring electrode is "shielded" by the disk electrode. The value of $I_r$ decreased to a minimum value at ca. $E_d = 0.43$ V, then increased as the reduction of $\text{IO}_3^-$ at the disk electrode diminished. The decrease in $\text{IO}_3^-$ consumption at the disk electrode was due to the depletion of the catalytically active oxide layer which was removed from the electrode surface by electro-reduction. The ring electrode was no longer shielded by the disk electrode. At $E_d < 0.1$ V, a decrease in $I_r$ was observed as $\text{IO}_3^-$ was reduced at the oxide free Pt surface.

The results obtained by potentiodynamic experiments just described are in support of the conclusion that catalysis of the reduction of $\text{IO}_3^-$ occurs at an oxidized Pt surface, presumably by PtOH, generated during reduction of the oxide. In review: 1) no cathodic peak is observed for the reduction of $\text{IO}_3^-$ at a reduced Pt electrode until $\eta > 750$ mV; and 2) the mass-transport coupled reduction of $\text{IO}_3^-$ is observed simultaneously with Pt oxide reduction in the region $0.85$ V > $E_d$ > 0.15 V (peak C).

C. Square-Wave Hydrodynamically Modulated Voltammetry

QHMV, utilizing the staircase potential waveform, was applied to isolate the mass-transport coupled component of current due to the reduction of $\text{IO}_3^-$ from the current produced simultaneously for reduction of Pt oxide. The $\Delta I$-E curve is shown in Figure VII-7. During the
Figure VII-7: ΔI-E curve of $4 \times 10^{-5}$ M $\text{IO}_3^-$ in $0.5 \text{ M H}_2\text{SO}_4$

at a Pt RDE

Lower rotation speed ($W_l$): 1000 rpm
Upper rotation speed ($W_u$): 4000 rpm
Potential step increment ($\Delta E$): 5 mV
Time delay ($t_d$): 150 ms
Number of data points ($N$): 10
positive scan of potential, a cathodic wave (A) was observed at $E < 0.2$ V resulting from the mass-transport limited reduction of $\text{IO}_3^-$ at a reduced Pt surface. No $\Delta I$ was observed throughout the remainder of the positive scan of potential. During the negative scan of potential, $\Delta I$ was zero until $E < 0.7$ V. Peak B is attributed to the mass-transport coupled reduction of $\text{IO}_3^-$ occurring simultaneously with the surface-controlled cathodic reduction of Pt oxide. The reduction of $\text{IO}_3^-$ ceased when Pt oxide reduction was complete ($E = \text{ca.} 0.3$ V). The mass-transport controlled reaction of $\text{IO}_3^-$ at a reduced Pt electrode was observed at $E < 0.2$ V (wave A). A series of $\Delta I$-$E$ curves was recorded as a function of $E_a$ (Figure VII-8) to determine if the quantity of oxide formed on the electrode surface exhibited any effect on the quantity of $\text{IO}_3^-$ that can be reduced in the region of peak B. The height of peak B decreased as the potential scan was reversed at successively less positive values of potential; hence, the quantity of oxide present does effect the amount of $\text{IO}_3^-$ that is reduced at an oxidized Pt electrode. The formation of Pt oxide is inhibited in the presence of adsorbed I therefore, no oxide formation occurs until $E_a > 1.0$ V. The $\Delta I$-$E$ curve recorded for $E_a = 1.0$ V contained no peak B which demonstrates that Pt oxide is essential for the reduction of $\text{IO}_3^-$ at $n < 750$ mV in the region of peak B. The transport-controlled reduction of $\text{IO}_3^-$ at a reduced Pt electrode (A) was not altered by changes in $E_a$. 
Figure VII-8: ΔI-E curves of $4 \times 10^{-5}$ M $\text{I}_3^-$ in 0.5 M $\text{H}_2\text{SO}_4$ at a Pt RDE as a function of $E_a$

Lower rotation speed ($W_1$): 1000 rpm
Upper rotation speed ($W_u$): 4000 rpm
Potential step increment (ΔE): 5 mV
Time delay ($t_d$): 150 ms
Number of data points (N): 10

--- 1.0 V
----- 1.2 V
-------- 1.4 V
--- 1.6 V
VIII. CONCLUSIONS

The purpose of this research was to develop the software necessary for modulated hydrodynamic voltammetric techniques and to evaluate their application to the study of surface-catalyzed reactions. QHMV permits extraction of the convective-coupled faradaic current from the total electrode current. Application of QHMV allows one to investigate the effect that the potential-dependent surface state has on reactions which are coupled to the mass-transport of the analyte from the bulk solution. Of major significance is the ability to observe mass-transport coupled reactions occurring at an electrode, covered by an inhibiting oxide layer, which are catalyzed by the anodic evolution of $O_2$.

A survey of anodic reactions utilizing CV and QHMV demonstrated the complementary nature of the two techniques and illustrated that QHMV is an invaluable technique for the study of mass-transport coupled reactions that are occurring simultaneously with surface oxidation and $O_2$ evolution. It was a general observation that many of the reactions studied were kinetically inhibited, i.e., electrochemically irreversible, at metal surfaces without the oxide layer; however, in the process of forming the oxide, the overall rate of the reaction increased significantly, i.e., electrocatalysis of the reaction occurred. It was also observed that those reactions which involve the uptake of an O-atom derived the most electrocatalytic benefit from the oxide layer and the evolution of $O_2$.

The oxidative reactions of $I^-$ in acidic media at a Pt electrode were examined in detail. The convective components of the total electrode current include: 1) the mass-transport limited formation of
I\textsubscript{2} at \(E > 0.45\) V; 2) the mass-transport coupled oxidation of \(I^-\) to \(IO_3^-\), which is catalyzed by the anodic formation of PtOH; and 3) the mass-transport limited production of \(IO_3^-\), which is concluded to be electrocatalyzed by OH, an intermediate product of \(O_2\) evolution. Observation of the latter two components was possible only upon application of QHMV. The catalytic reduction of \(IO_3^-\) at a Pt electrode was demonstrated also utilizing QHMV.

The anodic detection of \(I^-\) was investigated by constant and multi-step potential amperometry. Iodide was detected by measuring the current resulting from: 1) the mass-transport limited production of \(I_2\) from \(I^-\), 2) the suppression of the anodic formation of Pt oxide, and 3) the electrocatalyzed oxidation of \(I^-\) to \(IO_3^-\). Enhanced sensitivity of the measured signal was observed in the potential region where the electrocatalyzed oxidation of \(I^-\) to \(IO_3^-\) occurs.
IX. FUTURE RESEARCH

This research project has made possible the study of mass-transport coupled reactions occurring simultaneously with surface oxidation and \( \text{O}_2 \) evolution. Countless analyte/electrode combinations remain to be examined. Organic as well as inorganic reactants should be studied. Reactions occurring at metal electrodes with ad-atoms, \( \text{e.g.} \), Ru ad-atoms on Pt; metal-oxide electrodes, \( \text{e.g.} \), PbO\(_2\) and RuO\(_2\)/TiO\(_2\); and metal alloys should be investigated. By observing the behavior of the mass-transport coupled current, reactions and their mechanisms may be understood more completely. Also, properties of the electrode material and the oxide layers which form on the electrode surface may be elucidated further by the application of QHMV since the behavior of the mass-transport coupled current reflects changes occurring on the electrode surface, \( \text{e.g.} \), changes in the catalytic properties or changes in the conductance properties.

The development of computer-controlled QHMV should continue by investigating the possibility that the positive potential limit may be extended even further and could be limited, ultimately, only by dissolution of the electrode material. This can be accomplished by increasing the potential range of the A/D converter and reducing the noise, both of which are limiting factors in the present system.
X. BIBLIOGRAPHY


XI. ACKNOWLEDGEMENTS

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To Wayne, thanks for waiting patiently while I finished my graduate work so many miles away.
XII. APPENDIX

This appendix contains printouts of the computer programs for:
1) QHMV utilizing a staircase potential waveform, 2) QHMV utilizing a
triple-step potential waveform, and 3) the collection of data for
$\Delta I$ vs. $t_2$ plots to examine the time dependence for conversion of active
PtOH to the inactive OHPt and PtO.
10 REM SQUARE-WAVE MODULATION VOLTAMMETRY
15 REM **********SWHVMA.BAS**********  9/17/82
20 REM SET D/A CONVERTERS TO ZERO
30 HP=128:LP=0
40 POKE(HEX("C008")),LP:POKE(HEX("C009")),HP
50 POKE(HEX("C00A")),LP:POKE(HEX("C00B")),HP
60 POKE(HEX("C00C")),LP:POKE(HEX("C00D")),HP
70 POKE(HEX("C00E")),LP:POKE(HEX("C00F")),HP
75 REM DATA STORAGE MATRICES
80 DIM E(1150):DIM DI(1150)
90 REM PRINT CHANNEL ASSIGNMENTS
100 PRINT "D/A CHANNEL ASSIGNMENTS"
110 PRINT " A --- POTENTIAL OUTPUT TO ROTATOR"
120 PRINT " B --- POTENTIAL TO ESTAT OR ANALOG SCALING DEVICE"
130 PRINT " C --- CURRENT OUTPUT TO RECORDER"
140 PRINT " D --- POTENTIAL OUTPUT TO RECORDER"
150 PRINT:PRINT "A/D CHANNEL ASSIGNMENTS"
160 PRINT " O --- CURRENT INPUT FROM POTENTIOSTAT"
170 PRINT " 1 --- POTENTIAL FROM ESTAT OR ANALOG DEVICE"
180 PRINT:PRINT
200 REM EXPERIMENTAL CONDITIONS
210 INPUT "VOLTAGE FOR LOW AND HIGH ROTATION SPEEDS (1000 RPM/V)";WL,WH
220 INPUT "CATHERODIC AND ANODIC LIMITS (V)";EC,EA
230 INPUT "POTENTIAL INCREMENT";EI
240 INPUT "TIME DELAY (MSEC); NOT LESS THAN 100 MSEC";ID
250 INPUT "NUMBER OF DATA POINTS COLLECTED";N
255 REM COMPENSATION FOR ANALOG SCALING DEVICE
260 INPUT "ENTER 'Y' IF ANALOG SCALING DEVICE IS BEING USED";SD$'
270 IF SD$='Y' THEN 275 ELSE 300
275 INPUT "ENTER DEAMP VALUE";DV
280 EA=EA/DV:EC=EC/DV:EI=EI/DV
282 TD=ID-100
290 REM SET INITIAL CONDITIONS
300 Q=EC+1=1;Y=0
310 REM SET LOW ROTATION SPEED
320 W=(WL+10)*12.8:h=INT(W);L=(W-H)*256
330 POKE(HEX("C008")),L:POKE(HEX("C009")),H
340 IF U=1 THEN 470
400 REM AVERAGE HIGH CURRENT VALUES
410 IH=I/Y:IH=IH*1000;IH=INT(IH):IH=IH/1000
420 DI=IH-IL;DI=DI*1000;DI=INT(DI):DI(U-1)=DI/1000
425 PRINT U-1;X(U-1),IL,HI,DI(U-1)
430 REM CALCULATE AND TEST NEW POTENTIAL VALUE
440 Q=Q+EI
450 IF Q>EA THEN 770
460 IF Q<EC THEN 900
470 REM SET POTENTIAL
480 E=Q*10)*12.8:h=INT(E);L=(E-H)*256
189

485 PRINT Q,
490 POKE(HEX("CO0A")),L:POKE(HEX("CO0B")),H
500 REM CHECK AND STORE POTENTIAL VALUE
510 Z=9:POKE(HEX("CO09")),Z
520 H=PEEK(HEX("CO05")):L=PEEK(HEX("CO04"))
530 H=H-128:L=(INT(L/16))/16:E=(H*L)*320/4096
532 IF IV=0 THEN 538 ELSE 534
534 E=EMV
538 E(U)=E
540 REM TIME DELAY BEFORE MEASURING CURRENT
550 FOR T=1 TO 3:D=NEXT T
560 REM SAMPLE CURRENT
561 I=0
562 FOR C=1 TO N
563 Z=8:POKE(HEX("CO03")),Z
564 H=PEEK(HEX("CO05")):L=PEEK(HEX("CO04"))
565 H=H-128:L=(INT(L/16))/16:E=(H*L)*320/4096
566 I=I+1
570 NEXT C
580 REM CHECK VALUE OF ROTATION SPEED
590 IF Y=1 THEN U=U+1:Y=0:GOTO 310
600 REM SET HIGH ROTATION SPEED
610 W=(W+10)*12.8:H=INT(W):L=(W-H)*256
620 POKE(HEX("CO08")),L:POKE(HEX("CO09")),H
630 Z=1:N=I*1000:II=INT(I):II=II/1000
640 I=I+1
650 NXT IX
660 REM CHECK VALUE (FROM INITIAL
670 IF Y=1 THEN U=U+1:Y=0:GOTO 310
680 REM SET LOW ROTATION SPEED TO ZERO
690 H=128:L=0:POKE(HEX("CO08")),L:POKE(HEX("CO09")),H
700 X=0
710 NEXT U
720 REM PLOT DATA
730 INPUT "DATA COLLECTED, ENTER 'Y' TO PLOT DATA",DC$ 740 IF DC$="Y" THEN 860 ELSE INPUT "ARE YOU SURE",DC$
750 IF DC$="Y" THEN 2000 ELSE 830
760 FOR U=1 TO X
770 H=U:Z=(U-10)*12.8:H=INT(H):L=(H-H)*256
780 POKE(HEX("CO08")),L:POKE(HEX("CO09")),H
790 I=I+1:N=I*10:II=INT(I):II=II/1000
800 POKE(HEX("CO08")),L:POKE(HEX("CO09")),H
810 NEXT U
820 IF DC$="Y" THEN 860 ELSE 960
830 GOTO 2000
840 END
10 REM SQUARE WAVE TRIPLE PULSE
15 REM ************************************1/20/83
20 REM SET D/A CONVERTERS TO ZERO
30 H=128: L=0
40 POKE (HEX("0009")),L,POKE(HEX("CO09")),H
50 POKE(HEX("CO0A")),L,POKE(HEX("CO0B")),H
60 POKE(HEX("CO0C")),L,POKE(HEX("CO0D")),H
70 POKE(HEX("CO0E")),L,POKE(HEX("CO0F")),H
75 REM LIST CHANNEL ASSIGNMENTS
80 PRINT "D/A CHANNEL ASSIGNMENTS"
90 PRINT "B—POTENTIAL OUTPUT TO ROTATOR"
100 PRINT "C—CURRENT OUTPUT TO RECORDER"
110 PRINT "D—POTENTIAL OUTPUT TO RECORDER"
120 PRINT "A/D CHANNEL ASSIGNMENTS"
130 PRINT "A—CURRENT INPUT FROM ESTAT"
140 PRINT "B—POTENTIAL FROM ESTAT"
150 PRINT "C—CURRENT INPUT FROM ESTAT"
160 PRINT "D—POTENTIAL FROM ESTAT"
200 REM DEFINE DATA STORAGE MATRICES
210 DIM E(200);DIM I(200):DIM II(2)
300 REM DEFINE VARIABLE EXPERIMENTAL CONDITIONS
310 INPUT "LOW AND HIGH ROTATION SPEEDS (1000 RPM/ST "",LW,HW
315 PRINT "ENTER POTENTIAL VALUES IN VOLTS, TIME DELAYS IN MSEC"
320 INPUT "E(RED),E(OX)"",E1,E2
330 INPUT "E(SAMP, INITIAL),E(SAMP, FINAL),E(SAMP, STEP)"",E3,E4,E5
340 INPUT "TIME DELAYS AT EACH POTENTIAL RESPECTIVELY",TA,TB,TC
350 INPUT "NUMBER OF DATA POINTS COLLECTED AT EACH POTENTIAL",NN
360 X=0;Y=1;E1=E3
400 REM SET LOW ROTATION SPEED
410 W=(LW+10)*12.8:H=INT(W):L=(W-H)*256
420 POKE(HEX("CO08")),L,POKE(HEX("CO09")),H
425 X=X+1
430 REM SET REDUCING POTENTIAL
440 E=(E1+10)*12.8:H=INT(E):L=(E-H)*256
450 POKE(HEX("CO0A")),L,POKE(HEX("CO0B")),H
460 FOR T=1 TO TA:NEXT T
470 REM SET OXIDIZING POTENTIAL
480 E=(E2+10)*12.8:H=INT(E):L=(E-H)*256
490 POKE(HEX("CO0C")),L,POKE(HEX("CO0D")),H
500 FOR T=1 TO TB:NEXT T
510 REM SET SAMPLING POTENTIAL
520 E=(E3+10)*12.8:H=INT(E):L=(E-H)*256
530 POKE(HEX("CO0A")),L,POKE(HEX("CO0B")),H
540 FOR T=1 TO TC:NEXT T
630 REM SAMPLE CURRENT
640 Z=0
650 FOR XX=1 TO NN
660 Z=8:POKE(HEX("CO03")),Z
670 H=PEEK(HEX("C005")):L=PEEK(HEX("C004"))
680 H=H-128:L=(INT(L/16))/16:II=(H+L)*320/4096
690 I=I+II
700 NEXT XX
710 I=I+N:R=I*1000:I=INT(I):I=I/1000
720 LI(Y)=I
730 NEXT YY
740 IF H<1 THEN 10
750 Z=POKE(HEX("C003")),Z
760 H=PEEK(HEX("C005")):L=PEEK(HEX("C004"))
770 H=H-128:L=(INT(L/16))/16:E=H+L)*320/4096
780 EE=E+EE:NEXT HH
790 E(X)=EE/10
800 PRINT E(X)
810 REM TEST ROTATION SPEED
820 IF Y=1 THEN 770
830 IF Y=2 THEN 790
840 Y=2:W=(H*10)*12.8:H=INT(W):L=(W-H)*256
850 POKE(HEX("C005")),L:POKE(HEX("C004")),H
860 QUIT 430
790 REM CALCULATE DIFFERENCE CURRENT AND STORE IN MATRIX
792 I(X)=I(2)-I(1)
794 Y=1
800 REM CALCULATE NEW POTENTIAL VALUE
810 EA=EA+ES
820 IF EA>EA THEN 900 ELSE 800
900 REM SET ROTATION SPEED AND POTENTIAL TO ZERO
910 H=128:L=0
920 POKE(HEX("C005"),L:POKE(HEX("C004")),H
930 POKE(HEX("C00A")),L:POKE(HEX("C009")),H
1000 INPUT "PLOT DATA",PS$,
1010 IF PS$="Y" THEN 1020 ELSE 900
1011 PRINT "DATA IS PLOTTED POINT BY POINT"
1012 PRINT "ELECTRIC PENLIFT IS NOT CONTROLLED IN THIS PLOTING ROUTINE"
1015 REM SET RECORDER TO INITIAL POTENTIAL, ZERO CURRENT
1020 PRINT "SET RECORDER TO INITIAL POTENTIAL, ZERO CURRENT"
1020 H=E3:Z=Z-(H+10)*12.8:II=INT(Z)/II=(Z-H)*256
1040 POKE(HEX("C00F")),L:POKE(HEX("C00E")),H
1045 H=128:L=0
1050 POKE(HEX("C005"),L:POKE(HEX("C004")),H
1060 INPUT "DATA TO RECORDER",DR$,
1070 IF DR$="Y" THEN 1100 ELSE 900
1100 FOR H=1 TO X
1110 E=E(Y):E=(E+10)*12.8:II=INT(E)/II=(E-H)*256
1120 POKE(HEX("C005"),L:POKE(HEX("C004")),H
1130 I=I+1:II=(I+10)*12.8:II=INT(I)/II=(I-H)*256
1140 POKE(HEX("C005"),L:POKE(HEX("C004")),H
1150 FOR SS=1 TO 500: NEXT SS
1200 FOR CC=1 TO 400: NEXT CC
1210 NEXT M
1300 INPUT "RECHECK DATA",RD$
1310 IF RD$="Y" THEN 1020 ELSE 1800
1800 INPUT "REPEAT EXPERIMENT WITH SAME CONDITIONS",SC$
1810 IF SC$="Y" THEN 360 ELSE 1820
1820 INPUT "REPEAT EXPERIMENT WITH DIFFERENT CONDITIONS",DC$
1830 IF DC$="Y" THEN 310 ELSE 2000
1980 INPUT "ARE YOU SURE",RS
1985 IF RS="N" THEN 1000 ELSE 1800
2000 END
10 REM **************************IPUST.BAS******************************1/20/83
20 REM SET D/A CONVERTERS TO ZERO
30 H=128:L=0
40 POKE(HEX("C00B")),L:POKE(HEX("C009")),H
50 POKE(HEX("C00A")),L:POKE(HEX("C00B")),H
60 POKE(HEX("C00C")),L:POKE(HEX("C00D")),H
70 POKE(HEX("C00E")),L:POKE(HEX("C00F")),H
80 PRINT "D/A CHANNEL ASSIGNMENTS"
90 PRINT "A———CURRENT OUTPUT TO ROTATOR"
90 PRINT "B———POTENTIAL OUTPUT TO ROTATOR"
100 PRINT "C———CURRENT OUTPUT TO RECORDER"
110 PRINT "D———POTENTIAL OUTPUT TO RECORDER"
120 PRINT "A/D CHANNEL ASSIGNMENTS"
130 PRINT "A———CURRENT INPUT FROM ESTAT"
140 PRINT "B———POTENTIAL FROM ESTAT"
150 PRINT "C———POTENTIAL FROM ESTAT"
200 REM DEFINE MATRIX
210 DIM E(200);DIM I(200):DIM M(2)
300 REM DEFINE VARIABLE EXPERIMENTAL CONDITIONS
310 INPUT "LOW AND HIGH ROTATION SPEEDS (1000 RPM/V)";LW,HW
315 PRINT "ENTER CURRENT VALUES AS MILLIAMPS, TIME DELAYS AS MSEC"
320 INPUT "E(RED),E(OK),E(SAMPLING)";E1,E3,E2
330 INPUT "TIME DELAY AT REDUCING POTENTIAL",TA
340 INPUT "INITIAL AND FINAL TIME DELAYS AND STEP",TI,T2,TS
345 INPUT "TIME DELAY BEFORE SAMPLING CURRENT",TT
350 INPUT "NUMBER OF DATA POINTS COLLECTED AT EACH POTENTIAL",NN
360 X=0:Y=1:TO=TI
400 REM SET LOW ROTATION SPEED
410 W=(LW+1)*12.8:H=INT(W):L=(L-W)*256
420 POKE(HEX("C00B")),L:POKE(HEX("C009")),H
425 X=X+1
430 REM SET REDUCING POTENTIAL
440 E=(E1+1)*12.8:H=INT(E):L=(E-H)*256
450 POKE(HEX("C00A")),L:POKE(HEX("C00B")),H
460 FOR T=1 TO TA:NEXT T
470 REM SET OXIDIZING POTENTIAL
480 E=(E3+1)*12.8:H=INT(E):L=(E-H)*256
490 POKE(HEX("C00A")),L:POKE(HEX("C00B")),H
500 FOR T=1 TO TC:NEXT T
510 REM SET SAMPLING POTENTIAL
520 E=(E2+1)*12.8:H=INT(E):L=(E-H)*256
530 POKE(HEX("C00A")),L:POKE(HEX("C00B")),H
540 FOR T=1 TO TT:NEXT T
630 REM SAMPLE CURRENT
640 I=0
650 FOR XX=1 TO NN
660 Z=8:POKE(HEX("C003")),Z
670 H=PEEK(HEX("C005")):L=PEEK(HEX("C004"))
194

680 H=H-128: I=(INT(I/16))/16: II=(H+L)*320/4096
690 I=I+1
700 NEXT XX
710 I=I/NN: I=I+1000: I=INT(I): I=I/1000
720 II(Y)=I
730 PRINT II(Y),
732 REM CHECK POTENTIAL VALUE AND STORE
733 EE=0
734 FOR HH=1 TO 10
735 Z=6: POKHEX("C003"), 2
736 H=PEEK(HEX("C005")): L=PEEK(HEX("C004"))
737 H=H-128: I=(INT(I/16))/16: E=(H+L)*320/4096
738 EE=EE+1: NEXT HH
739 EX=EE/10
740 PRINT EX(X)
750 REM TEST ROTATION SPEED
760 IF Y=1 THEN 770
762 IF Y=2 THEN 790
770 Y=2: W=(H+I)*12.8: H=INT(W): L=(W-H)*256
772 POKHEX("C008"), L: POKHEX("C009"), H
773 QUIT 430
790 REM CALCULATE DIFFERENCE CURRENT AND STORE IN MATRIX
792 I(X)=II(2)-II(1)
794 Y=1
800 REM CALCULATE NEW TIME DELAY
810 TC=TC+1S
820 IF TC>T2 THEN 900 ELSE 400
900 REM SET ROTATION SPEED AND POTENTIAL TO ZERO
910 H=128: L=0
920 POKHEX("C005"), L: POKHEX("C004"), H
930 POKHEX("C004"), L: POKHEX("C005"), H
932 INPUT "PLOT DATA", PDS
935 IF PDS="Y" THEN 1020 ELSE 890
1020 PRINT "SET RECORDER TO ZERO"
1030 H=128: L=0
1040 POKHEX("C005"), L: POKHEX("C004"), H
1045 H=128: L=0
1050 POKHEX("C004"), L: POKHEX("C005"), H
1055 INPUT "DATA TO RECORDER", DRS
1070 IF DRS="Y" THEN 1100 ELSE 890
1100 FOR M=1 TO X
1110 E=15*/P0.004: E=(E+10)*12.8: H=INT(E): L=(E-H)*256
1120 POKHEX("C005"), L: POKHEX("C004"), H
1130 I=I(Y): I=(I+10)*12.8: H=INT(I): L=(I-H)*256
1140 POKHEX("C008"), L: POKHEX("C009"), H
1150 FOR SS=1 TO 500: NEXT SS
1160 REM LOWER PEN
1180 REM LIFT PEN
1200 FOR CC=1 TO 400: NEXT CC
1210 NEXT M
1300 INPUT "RECHECK DATA", RD$
1310 IF RD$="Y" THEN 1020 ELSE 1800
1800 INPUT "REPEAT EXPERIMENT WITH SAME CONDITIONS", SC$
1810 IF SC$="Y" THEN 360 ELSE 1820
1820 INPUT "REPEAT EXPERIMENT WITH DIFFERENT CONDITIONS", DC$
1830 IF DC$="Y" THEN 310 ELSE 2000
1980 INPUT "ARE YOU SURE", RS
1985 IF RS=="N" THEN 1000 ELSE 1800
2000 END