FINAL TECHNICAL REPORT

The Fundamental Role of Nano-Scale Oxide Films in the Oxidation of Hydrogen and the Reduction of Oxygen on Noble Metal Electrocatalysts

Grant No. DE-FG02-01ER15238

Submitted by

Digby D. Macdonald (Principal Investigator), Kamrun Nahar (Post Doctoral Scholar), Adan Sun (Graduate Assistant), Jianer Bao (Graduate Assistant), Bum-Wook Roh (Graduate Assistant), and LaSalle Swenson (Graduate Assistant).

Center for Electrochemical Science and Technology
Department of Materials Science and Engineering
Pennsylvania State University
201 Steidle Building
University Park, PA 16802

Tel: (814) 863-7772, Fax: (814) 863-4718, Email: ddm2@psu.edu

Submitted to

Paul H. Maupin
Program Manager
Chemical Energy and Chemical Engineering Program
Molecular Processes and Geosciences
Division of Chemical Sciences, Geosciences, and Biosciences
Office of Basic Energy Sciences
Office of Science, U.S. Department of Energy
301-903-4355 - 301-903-4110 (fax)

March 28, 2005

TABLE OF CONTENTS

	<u>Page</u>
List of Figures	iv
List of Tables	viii
Executive Summary	1
I. Introduction	3
II. Background	5
II-1 Charge Transfer on Passivated Platinum	5
II-2 Surface Oxide Films.....	8
II-3 Anodic Oxide Film Formation on Platinum.....	13
II-4 Electron Transfer Theory	13
References	15
III. Research Progress	17
III-1. Task 1: Continued Development of the Theory of Passivity	17
III-1.1 Introduction.....	17
III-1.2 Background of Resonant Tunnel Diodes	19
Global Coherent Resonant Tunneling	19
Sequential Tunneling.....	21
Effects of Impurity Scattering in RTDs	23
III-1.3 Electron Tunneling through Barrier Oxide Layer	23
Electron Transfer Theory for the Passive Oxide Film and the 23	
Relevance to the Resonant Tunnel Diodes	23
Potential Distribution in the Barrier Oxide Layer	24
III-1.4 Summary and Conclusions.....	29
List of Symbols	30
Greek Symbols	31
References	31
III-2. Task 2: Experimental Characterization of Passive Films on Noble	
Metals and Noble Metal Alloys	35
III-2.1 Anodic Oxide Film.....	36
III-2.2 Steady State Growth of Pt Oxide Film.....	40
III-2.3 Electronic Properties	45
III-2.4 Compositions of Oxide Film.....	52
III-2.5 Growth Mechanism of Pt Oxide Film.....	54
References.....	63
III-3 Task 3 and 4: Kinetic Study of Oxygen Reduction and Hydrogen Oxidation	
on Platinum Electrode.....	64
III-3.1 Cyclic Voltammogram of Platinum	64
III-3.2 Hydrogen Oxidation on Oxidized Platinum.....	68

	<u>Page</u>
III-3.3 Measurement of Film Thickness via Tunneling Spectroscopy	73
III-3.4 Oxygen reduction on Passive Platinum.....	74
Possible Role of Surface Defects in the Oxygen Electrode Reaction	78
References	81
III-5 Task 5: The Evidence of the Involvement of Oxygen Vacancies in Oxygen Electrode Reaction	82
III-5.1 Titanium Oxide Formation and Semiconductive Properties	83
III-5.2. Anodic Processes in Deoxygenated Solution (Oxygen Evolution Reaction)	86
III-5.3 Cathodic Processes in Oxygen Saturated Solutions (Oxygen Reduction Reaction).....	88
References	89
III-6 Task 6: Experimental Investigation of the Role of Substitutional Defects in the Oxidation of Hydrogen on Defective Tungsten Carbide.....	90
III-6.1 Initial results concerning subtask 1: Systematic synthesis of defective tungsten carbide (WC_xO_{1-x}).....	91
References	92
III-7 Task 7: Mechanistic Analysis and the Prediction of Electrocatalytic Activity	93
IV Status Summary of Personnel	94
V. Publications and Presentations	95
Appendix I: Rate Constants for the PDM	96
Appendix II: Potential Dynamic Current Behavior on Passive Platinum	99
A. Growth of the Platinum Oxide Film During Hydrogen Oxidation.....	99
B. Current Density for Hydrogen Oxidation on Oxidized Film.....	103
C. Calculation of Cyclic Voltamogram for Platinum.....	106

LIST OF FIGURES

Figure II-1.1. Anodic polarization curves for oxidation of H_2 on platinized nickel in 0.1 m NaOH solution at 150°C and 6.9MPa. The broken line is a fit of Equation (II-3), yielding a tunneling constant of $\beta = 2 \times 10^8 \text{ cm}^{-1}$, and indicating that direct quantum mechanical tunneling occurs through the passive oxide film. “RPM” refers to the rotation rate of the flow-activating impeller.

Figure II-1.2. Current-voltage curves for the reduction of oxygen on platinum in 0.01 m LiOH solution at 275°C as a function of the voltage sweep rate. The two curves for $v = 5.2 \text{ mV/min}$ were measured in opposite directions, with the lower curve being measured in the positive to negative voltage direction and the upper curve in the reverse direction.

Figure II-2.1. Interfacial defect generation/annihilation reactions that occur in the growth of anodic barrier oxide films according to the Point Defect Model [22,23]. m = metal atom, $V_M^{\times'}$ = cation vacancy on the metal sublattice of the barrier layer, $M_i^{\times+}$ = interstitial cation, M_M = metal cation on the metal sublattice of the barrier layer, V_O = oxygen vacancy on the oxygen sublattice of the barrier layer, O_O = oxygen anion on the oxygen sublattice of the barrier layer, $M^{\delta+}$ = metal cation in solution. Note that cation vacancies are generated at the film/solution interface and are annihilated at the metal/film interface whereas cation interstitials and oxygen vacancies are generated at the metal/film interface and are annihilated at the film/solution interface.

Figure II-2.2. Dimensionless concentration of oxygen vacancies vs. dimensionless distance within the passive film formed on tungsten in phosphate buffer solution (pH = 2.1) at a voltage of 6 V_{SCE} .

Figure III-1.1. Point Defect Model. Pt $\equiv$ platinum atom; v_{Pt} $\equiv$ platinum vacancy at metal site; platinum cation in a cation position; $V_{Pt}^{\times'}$ $\equiv$ platinum cation vacancy; $Pt_s^{\delta+}$ $\equiv$ platinum cation in the solution phase; $V_o^{\bullet\bullet}$ $\equiv$

Figure III-1.2. Energy band diagram for the transfer Hamiltonian model.

Figure III-1.3. Energy band diagram of sequential tunneling model

Figure III-1.4. Defect Concentration Profile and Potential Distribution through Platinum Oxide Film using Point Defect Model (PDM) plus Boltzmann Distribution

Figure III-1.5. Potential distribution through the oxide film on platinum as calculated using the linearized defect concentration plus Boltzmann's distribution.

Figure III-2.1. Cyclic voltammograms for platinum in 0.5M H_2SO_4 measured at a voltage sweep rate of 50mV/s ($T = 20^\circ\text{C}$). Working electrode surface area = 0.32 cm^2 .

Figure III-2.2. Cyclic voltammograms for platinum in 0.5M H_2SO_4 measured at a voltage sweep rate of 50mV/s ($T=60^\circ\text{C}$). Working electrode surface area = 0.32 cm^2 .

Figure III-2.3. Cyclic voltammograms for platinum in 0.5M H_2SO_4 measured at a voltage sweep rate of 50mV/s ($T=80^\circ\text{C}$). Working electrode surface area = 0.32 cm^2 .

Figure III-2.4. Cyclic voltammograms for platinum in 0.5M H₂SO₄ measured at a voltage sweep rate of 50mV/s at three different temperatures. Working electrode surface area = 0.32 cm².

Figure III-2.5. Cyclic voltammograms for platinum in 0.5M H₂SO₄ measured at a voltage sweep rate of 50mV/s (T=60°C) with different upper limits of the potential.

Figure III-2.6. Cyclic voltammograms for platinum in 0.5M H₂SO₄ measured at a voltage sweep rate of 50mV/s (T=80°C) with different upper limit of sweep potential.

Figure III-2.7. Steady state current density as a function of formation potential at different temperatures.

Figure III-2.8. Nyquist plots for oxidized platinum at different oxide formation potentials. T = 20°C.

Figure III-2.9. Nyquist plots for oxidized platinum at different oxide formation potentials. T = 60°C.

Figure III-2.10. Nyquist plots for oxidized platinum at different oxide formation potentials. T = 80°C.

Figure III-2.11. Nyquist plot and Bode plot of oxidized platinum at 1.24V_{SHE}. T= 20°C.

Figure III-2.12. K-K transform of EIS data of oxidized platinum at 1.19V_{SHE} at T=20°C.

Figure III-2.13. Mott-Schottky plot oxidized platinum at the oxide formation potential of 1.39V_{SHE} in 0.5M H₂SO₄ solution after polarization for 24 hrs at T=20°C. Sinusoidal perturbation frequency = 10⁴ Hz. Sinusoidal amplitude =10mV (peak-to peak). Voltage scan rate = 100 mV/s.

Figure III-2.14. Mott-Schottky plot of oxidized platinum at different formation potentials in 0.5 MH₂SO₄ solution for 24 hrs at T=20°C. Sinusoidal perturbation frequency = 10⁴ Hz. Sinusoidal amplitude =10mV (peak-to peak). Voltage scan rate = 100 mV/s.

Figure III-2.15. Mott-Schottky plot of oxidized platinum at different formation potentials in 0.5 MH₂SO₄ solution for 24 hrs at T=60°C. Sinusoidal perturbation frequency = 10⁴ Hz. Sinusoidal amplitude =10mV (peak-to peak). Voltage scan rate = 100 mV/s.

Figure III-2.16. Mott-Schottky plot of oxidized platinum at different formation potentials in 0.5 MH₂SO₄ solution for 24 hrs at T=80°C. Sinusoidal perturbation frequency = 10⁴ Hz. Sinusoidal amplitude =10mV (peak-to peak). Voltage scan rate = 100mV/s

Figure III-2.17. Mott-Schottky plot of oxidized platinum constructed from the capacitance data at 1194 Hz in 0.5 MH₂SO₄ solution at T=20°C. Sinusoidal amplitude =10mV (peak-to peak).

Figure III-2.18. Mott-Schottky plot for oxidized platinum at 1.39 V_{SHE} in 0.5 MH₂SO₄ solution for 24 hrs as a function of scan rates at T=20°C. Sinusoidal perturbation frequency = 10⁴ Hz. Sinusoidal amplitude =10mV (peak-to peak).

Figure III-2.19. Mott-Schottky plot for oxidized platinum at 1.39 V_{SHE} in 0.5M H₂SO₄ solution for 24 hrs as a function of frequencies at T=20°C. Sinusoidal amplitude =10mV (peak-to peak). Voltage scan rate = 100 mV/s.

Figure III-2.20. Mott-Schottky plot for oxidized platinum at 1.24 V_{SHE} in 0.5 MH₂SO₄ solution for 24 hrs as a function of temperatures. Sinusoidal perturbation frequency = 10⁴ Hz. Sinusoidal amplitude =10mV (peak-to peak). Voltage scan rate = 100 mV/s.

Figure III-2.21 Donor density calculated in terms of Mott-Schottky methods as a function of formation potential at three temperatures.

Figure III-2.22. XPS spectra of the Pt4f regions recorded at two different takeoff angles for Pt surfaces passivated in 0.5M H₂SO₄ for 24 hrs at different potentials at T=20°C.

Figure III-2.23. Schematic of physicochemical processes that are envisioned to occur within the barrier oxide (PtO_{□□}) layer on passive platinum, according to the truncated Point Defect Model. Pt ≡ platinum atom; Pt_i^{z+} ≡ interstitial platinum cation; v_{Pt} ≡ platinum vacancy in the Pt; Pt_{Pt} ≡ platinum cation in a normal cation position; Pt^{+□} ≡ platinum cation in the solution phase; V_O^{••} ≡ oxygen vacancy; O_O ≡ oxygen ion in an anion site.

Figure III-2.24. Nyquist plot of experimental and simulated impedance data for oxidized platinum in 0.5M H₂SO₄ at different formation voltage at T=20°C.

Figure III-2.25 Concentration of Oxygen vacancies vs.the distance within the passive film formed on platinum in 0.5M H₂SO₄ solution at a voltage of 1.14V_{SHE}.

Figure III-3.1. Cyclic voltammogram of platinum in 0.1M KOH at 20°C with progressively more positive reversing potentials. Sweep rate = 30mV/s, rotation speed = 900rpm.

Figure III-3.2. Cyclic voltammograms for the oxidation and reduction of a platinum electrode in 0.1M KOH at 20°C as a function of voltage sweep rate. Rotation speed = 900rpm. Initial voltage sweep direction: negative to positive.

Figure III-3.3. Oxidation and reduction of platinum in 0.1M KOH. Sweep rate: 100mV/s. Sweep direction: positive. Rotation speed: 900rpm.

Figure III-3.4. Hydrogen oxidation behavior on platinum in 0.1M KOH. (a) sweep rate: 5mV/s. (b) 50mV/s. Rotating speed: 900rpm. Initial potential sweep direction: negative to positive.

Figure II-1. Anodic polarization curves for oxidation of H₂ on platinized nickel in 0.1 m NaOH solution at 150°C and 6.9 MPa. The broken line is a fit of Equation (II-3), yielding a tunneling constant of $\beta = 0.75 \times 10^8 \text{ cm}^{-1}$, and indicating that direct quantum mechanical tunneling occurs through the passive oxide film. “RPM” refers to the rotation rate of the flow-activating impeller.

Figure III-3.5. Calculated potential dependence of film thickness. Data are based on the results obtained with potential sweep rate of 5mV/s and reversal potential of 0.5V_{SCE}.

Figure III-3.6 Linear potential sweep voltammograms for the cathodic reduction of oxygen on platinum as a function of voltage sweep rate. Rotation speed: 900rpm, sweep direction: negative. Ring potential was held at 0.3V (vs. SCE) to oxidize any peroxide produced.

Figure III-3.7 Tafel plots for oxygen reduction on platinum in 0.1M KOH at 20oC. The voltage sweep rates are: (a) 100mV/s, (b) 30mV/s, (c) 0.1mV/s. The equilibrium potential for the oxygen electrode reaction is shown by the dotted line in each figure and the apparent exchange current densities are indicated. Note the pseudo Tafel region at low overpotentials.

Figure III-3.8. Tafel plot for the potentiostatic reduction of oxygen. The current values in green for $E > E_{corr}$ are positive (anodic oxidation); all other current values are negative (cathodic reduction).

Figure III-3.9. Proposed mechanisms for the oxygen electrode reaction on passive metals involving surface oxygen vacancies.

Figure III-3.10. Multi-step reaction schemes on platinum oxide film surface involving oxygen vacancies.

Figure III-5.1. Phase diagram of the titanium-oxygen system, showing stoichiometry of the titanium oxides against the log of conductivity of oxide phases [3].

Figure III-5.2. Electrochemical impedance spectrum of the titanium oxide film formed at 10mA/cm² on pure titanium, recorded at a potential 1.0V_{sce} with an AC amplitude of 10mV. (○) Z', (■) Z''

Figure III-5.3. Variation of anodic oxide film thickness on titanium with formation current density, with the final stage of growth being carried out potentiostatically at 20V_{sce}.

Figure III-5.4. Mott-Schottky plots obtained from the titanium oxide films formed with various film formation current densities at a frequency of 1000Hz; film formation current density (◆)25mA/cm², (●)20mA/cm², (▼)15mA/cm², and (▲)10mA/cm².

Figure III-5.5. Variation of the donor density in anodic oxide film formed on titanium in 0.5M sulfuric acid solution with formation current rate

Figure III-5.6. Potentiodynamic curves(i-E) recorded from 0 to 5 V_{sce} in nitrogen purged 0.5M hydrosulfuric acid solution with the anodic oxide films formed on titanium, scan rate 5 mV/s

Figure III-5.7. Variation of the peak current density at the upper vertex potential, 5.0 V_{sce}, with donor density of the oxide film, as determined by potentiodynamic polarization, for the oxygen evolution reaction in nitrogen purged, 0.5M sulfuric acid solution at 20°C.

Figure III-5.8. Variation of the peak current density at the lower vertex potential, -0.7V_{sce} with donor density of the oxide film, as determined by the potentiodynamic polarization, for the oxygen reduction reaction on passivated titanium of constant passive film thickness, in oxygen saturated, 0.5M sulfuric acid solution.

Figure III-6.1. Tungstic acid precipitation trials: “26”-peak location vs. saturation fraction.

Figure III-6.2. 850°C carburization of Trial 1 tungstic acid

Figure AI-1. Interfacial defect generation/annihilation reactions that occur in the growth of anodic barrier oxide films according to the Point Defect Model [3]. m = metal atom, $V_M^{Z'}$ = cation vacancy on the metal sublattice of the barrier layer, M_i^{Z+} = interstitial cation, M_M = metal cation on the metal sublattice of the barrier layer, V_O = oxygen vacancy on the oxygen sublattice of the barrier layer, O_O = oxygen anion on the oxygen sublattice of the barrier layer, M^{F+} = metal cation in solution.

Figure AII-1. Point Defect Model for the anodic oxide film on platinum.

LIST OF TABLES

Table III-1.1. Parameters used in modeling the electronic structure of the oxide film on platinum.

Table III-2.1. Atomic concentration of the Pt4f regions recorded at two different takeoff angles for Pt surfaces passivated in 0.5M H₂SO₄ for 24 hrs at three different potentials.

Table III-2.2. Extracted kinetic parameters from optimization of PDM for n-type platinum oxide formed at potential 1.29V_{SHE} on EIS data at three different temperatures.

Table III-4.1. Rate constants $k_i = k_i^0 e^{a_i V} e^{b_i L} e^{c_i pH}$ for the interfacial defect generation and annihilation reactions employed in the Point Defect Model. $K = \frac{\overline{\varepsilon F}}{RT}$, $\gamma = \frac{F}{RT}$

Table III-4.2. Definition of the standard rate constants for the interfacial defect generation and annihilation reactions employed in the Point Defect Model. Note that the base rate constant for the i^{th} reaction is designated k_i^{00} .

Table AI-1. Rate constants $k_i = k_i^0 e^{a_i V} e^{b_i L} e^{c_i pH}$ for the interfacial defect generation and annihilation reactions employed in the Point Defect Model. $K = \frac{\overline{\varepsilon F}}{RT}$, $\gamma = \frac{F}{RT}$

Table AI-2. Definition of the standard rate constants for the interfacial defect generation and annihilation reactions employed in the Point Defect Model. Note that the base rate constant for the i^{th} reaction is designated k_i^{00} .

EXECUTIVE SUMMARY

The derivation of successful fuel cell technologies requires the development of more effective, cheaper, and poison-resistant electrocatalysts for both the anode (H_2 oxidation in the presence of small amounts of CO from the reforming of carbonaceous fuels) and the cathode (reduction of oxygen in the presence of carried-over fuel). The proposed work is tightly focused on one specific aspect of electrocatalysis; the fundamental role(s) played by nanoscale (1-2 nm thick) oxide (“passive”) films that form on the electrocatalyst surfaces above substrate-dependent, critical potentials, on charge transfer reactions, particularly at elevated temperatures ($25^\circ\text{C} < T < 200^\circ\text{C}$). Once the role(s) of these films is (are) adequately understood, we will then use this information to specify, at the molecular level, optimal properties of the passive layer for the efficient electrocatalysis of the oxygen reduction reaction. The work, which involves both theory and experiment, is being carried out in seven tightly coupled tasks, as follows:

- Potential profiles across the nanoscale oxide films have been calculated by solving Poisson’s equation, together with the Boltzmann and Nernst-Planck equations within the framework of the Point Defect Model (PDM) for the defect structure of the film. Although Esaki band-to-band tunneling has yet to be incorporated into the theory, because of the significant mathematical difficulties involved, the current work indicates that the electric field strength is not a strong function of distance through the film. The residual nonlinearity in the potential versus distance will likely disappear once Esaki (band-to-band) tunneling of electrons in the barrier layer is incorporated into the model. Most importantly, Esaki tunneling is expected to provide an analytical explanation of the buffering of the electric field strength at a value that is significantly below the dielectric strength of the oxide.
- The steady state growth of the oxide film on platinum in the oxygen reduction region shows that the steady state current density is independent of the oxide formation potential, which is consistent with the diagnostic criteria obtained from the PDM for an n-type oxide film. The capacitance of thin oxide films formed anodically on Pt as a function of formation potential, as determined by Mott-Schottky analysis, demonstrates unequivocally, and for the first time, the n-type electronic character of the film, indicating that the defects in the film are either platinum interstitials or oxygen vacancies. Angle resolved XPS analysis of platinum oxide films formed anodically at ambient temperature shows that at formation potential above $1.4V_{\text{SHE}}$ the inner layer of the film contains Pt^{2+} and the outer layer contains Pt^{4+} .
- Optimization of the PDM on the impedance data for the passive state on platinum has yielded a set of parameter values that can be used for predicting steady state and transient film formation kinetic processes. To our knowledge, this is the first time that values for these kinetic parameters, including rate constants and transfer coefficients for film formation and dissolution and the generation and annihilation of cation interstitials at the film boundaries for platinum, have ever been determined.
- Kinetic studies of oxygen reduction and hydrogen oxidation on platinum have been carried out in the oxide formation region and theoretical expressions have been developed within the framework of the Point Defect Model to account for the data, particularly those obtained under cyclic voltammetric conditions. Kinetic parameters (exchange current densities) extracted from Tafel plots for oxygen reduction on oxidized and bare platinum under potentiodynamic conditions have been obtained. On bare platinum, the (negative) current corresponds to oxygen reduction, but on the oxide covered surface the (positive) current is dominated by the anodic oxidation of platinum, resulting in a positive polarization current at potentials more positive than the open circuit value. The current in the oxide region is found to be independent of potential, as predicted by the Point Defect Model for an n-type passive film, in which the current is carried by platinum cation interstitials or by oxygen vacancies or by both. Any oxygen reduction that occurs within

the oxide region is obscured by the platinum oxidation current. Accordingly, the electrochemical behavior of platinum in the oxide formation region corresponds to a conventional mixed potential corrosion system, and the negative displacement of the open circuit potential from the OER equilibrium potential is attributed to the existence of a significant anodic passive current, due to the oxidation of platinum, and to the poor kinetics for the reduction of oxygen on the oxidized surface.

- A new method has been developed for measuring the thickness of very thin oxide films that form anodically on metal substrates, such as platinum. The method utilizes the current density for the direct quantum mechanical tunneling of charge carriers across the oxide film from the metal to a reaction center contained within a redox species, in this case the oxidation of hydrogen at the oxide-covered surface under mass transfer control. The thickness of the film is proportional to the natural logarithm of the ratio of the current observed on the film free surface to that obtained by direct tunneling across the film. The proportionality constant is the inverse of the tunneling constant, which may be calculated from quantum mechanics or may be measured, if some other method is available for determining the film thickness under well defined conditions. This new method is only applicable to very thin films (0.1 – 1.0 nm), such as those that form on platinum in the high oxygen reduction region, but it overcomes the difficulties encountered by more traditional techniques, such as capacitance methods and ellipsometry.
- The oxygen electrode reaction has been studied on passive titanium by cyclic voltammetry, electrochemical impedance spectroscopy (EIS), and ellipsometry, in order to understand the role of oxygen vacancies in the reaction mechanism. The passive films were formed by initial galvanostatic polarization at different film formation current densities, followed by potentiostatic polarization, resulting in oxide films of almost constant thickness ($\sim 44.7 \pm 2$ nm), but with significantly different oxygen vacancy concentrations. We found that the donor density decreases with increasing film formation current density, and that the oxygen electrode reaction rate (oxygen evolution and oxygen reduction) is promoted by oxygen vacancies in the oxide film. However, we have yet to distinguish between the role of oxygen vacancies in promoting electron transfer through the oxide film (via vacancy-to-vacancy tunneling) and the possible role of surface oxygen vacancies as catalytic reaction centers for the oxygen reduction reaction. The mathematical basis for distinguishing these cases is currently under development. Titanium was chosen for this study, because the oxide is exclusively an oxygen vacant material and because the oxygen vacancy concentration can be readily changed by electrochemical and/or chemical means over a wide range.
- Defective tungsten carbide ($\text{WC}_{1-x}\text{O}_x$) has been investigated sporadically as a PEM fuel cell electro-oxidation catalyst since the 1960s, and shows a relationship between defect concentration and catalytic activity for the oxidation of hydrogen. We are currently developing a procedure to produce defective tungsten carbide in a systematic manner, in order that we may study its defect-concentration-catalytic activity relationship in detail greater detail than has been achieved in the past. Significant progress has been made towards developing synthetic procedures for producing materials with known defect structures. Again, we are developing methods for distinguishing between the role of vacancies in promoting electron transfer through the oxide film (via vacancy-to-vacancy tunneling) and the possible role of surface vacancies as catalytic reaction centers for the hydrogen (and methanol) oxidation reaction.

A major, current thrust is completing the development of an apparatus that may be used to accurately measure kinetic parameters for the oxidation of hydrogen and methanol and the reduction of oxygen on electrocatalysts at temperatures up to 200°C. The impetus for this work is the expectation that Proton Exchange Membrane (PEM) fuel cells will eventually operate at temperatures significantly in excess of 100°C, in order to reduce catalyst loading and to mitigate CO poisoning. Currently, little information exists in the literature on the activity of electrocatalysts at temperatures above about 60°C.

I. INTRODUCTION

The derivation of successful fuel cell technologies requires the development of more effective, cheaper, and poison-resistant electrocatalysts for both the anode (H_2 oxidation in the presence of small amounts of CO from the reforming of carbonaceous fuels) and the cathode (reduction of oxygen in the presence of carried-over fuel). The rate of reduction of oxygen at the (air) cathode is frequently the performance-limiting factor, so that advances are required in electrocatalysis science and technology for this reaction, in particular. One strategy for overcoming the limitations of current catalysts is to operate the cell at elevated temperatures. Operating temperatures as high as 200°C are now contemplated for certain PEM fuel cells, most notably direct methanol fuel cells (DMFCs). Extensive literature exists on electrocatalysis of the hydrogen oxidation and oxygen reduction reactions, and no attempt is made here to review the previous work in any detail. It is sufficient to note that very little work has been reported for temperatures in excess of 60°C .

The present project is tightly focused on one specific aspect of electrocatalysis; the fundamental role(s) played by nanoscale oxide (“passive”) films that form on the electrocatalyst surfaces above substrate-dependent, critical potentials, on charge transfer reactions, particularly at elevated temperatures ($25^\circ\text{C} < T < 200^\circ\text{C}$). The need to explore this issue at elevated temperatures is dictated by the fact that high efficiency, high power fuel cells of the future (particularly MeOH/O_2) will operate at considerably higher temperatures than do current systems. Higher temperatures increase reaction rates and hence decrease the required catalyst loading, which translates into lower cost. However, higher temperature also gives rise to several deleterious phenomena, including higher fuel cross over rates and membrane dehydration. These issues are being addressed in numerous programs elsewhere, and hence will not be considered further here.

As noted above, the present project focuses on the *fundamental* role(s) played by nanoscale oxide films (1 to 5 nm thick) that form on metal surfaces under anodic polarization conditions, on the kinetics of the hydrogen oxidation and oxygen reduction reactions. That the oxide films play critical roles in determining the rates of redox reactions at metal surfaces has been known for many decades. In particular, the pioneering work of Gurney [1,2], Vetter et. al. [3,4] and others [5-21] on resonant quantum mechanical tunneling provides a theoretical basis for further development. However, it is the development of a mechanistic description of the growth and properties of passive films that form on metal surfaces, in the form of the Point Defect Model (PDM) [22,23], that provides the current opportunity to advance the field. Of particular importance is the fact that the PDM provides analytical relationships between the barrier oxide layer thickness (L) and the concentration (C) profiles for crystallographic defects (cation vacancies, oxygen vacancies, and cation interstitials) within the layer and the applied voltage (V). The $L(V)$ relationship is important, because it determines the tunneling distance for the transfer of charge across the film, while the $C(V)$ relationship determines the concentration of resonant states within the layer, in the case of resonant tunneling. The latter also provides a theoretical basis for calculating the concentration of oxygen vacancies at the barrier layer/solution interface.

It is postulated in the present work that oxygen vacancies are intimately involved in the OER and may represent the “missing link” in the theory of the electrocatalysis of the reduction of oxygen. In any event, the tunneling probability has a significant impact on the exchange current density for a redox reaction and hence upon the catalytic activity of the surface.

In this program, we are:

- Further developing the Point Defect Model (PDM) for describing nano scale oxide films on metal surfaces as a function of formation conditions, with particular emphasis on describing the crystallographic and electronic defect structures.
- Combining the theory of resonant tunneling with the PDM, in order to develop a comprehensive theory for electrocatalysis at oxide-covered surfaces.

- Using steady-state current/voltage techniques and electrochemical impedance spectroscopy (EIS) to measure charge transfer kinetic data (exchange current densities, transfer coefficients, and reaction orders) for the reduction of oxygen (O_2) on oxidized platinum and for H_2 oxidation on bare Pt. The kinetic parameters are being extracted from the current/voltage data by fitting the data to the generalized Butler-Volmer.
- Comparing the measured kinetic data with parameter values calculated from the comprehensive tunneling theory, where appropriate.
- Deducing mechanisms of the reactions (HER and OER) occurring on oxidized platinum by using kinetic data that have been corrected for the presence of the film (this correction is necessary, because only part of the applied voltage occurs across the film/solution interface).
- Identifying the most important factors controlling the kinetics of the charge transfer reactions of interest on noble metal surfaces.

This report presents the progress achieved as of January 31, 2005 in our current, three-year project.

II. BACKGROUND

II-1. Charge Transfer on Passivated Platinum

The impact of oxide films on metal surfaces on the kinetics of charge transfer (redox) reactions is well illustrated by the experimental data shown in Figures II-1.1 and II-1.2. In Figure II-1.1 are shown data obtained by the author and his colleagues for the oxidation of hydrogen on platinized nickel in 0.1 m NaOH at 150°C, while corresponding data for the reduction of oxygen on platinum in 0.01 m LiOH at 275 °C are presented in Figure II-1.2. The broad features that are evident in Figure II-1.1 for hydrogen oxidation were observed at temperatures extending from 50 °C to 300 °C.

Figure II-1.1. Anodic polarization curves for oxidation of H_2 on platinized nickel in 0.1 m NaOH solution at 150°C and 6.9 MPa. The broken line is a fit of Equation (II-3), yielding a tunneling constant of $\beta = 2 \times 10^8 \text{ cm}^{-1}$, and indicating that direct quantum mechanical tunneling occurs through the passive oxide film. “RPM” refers to the rotation rate of the flow-activating impeller.

Figure II-1.2. Current-voltage curves for the reduction of oxygen on platinum in 0.01 m LiOH solution at 275°C as a function of the voltage sweep rate. The two curves for $v = 5.2 \text{ mV/min}$ were measured in opposite directions, with the lower curve being measured in the positive to negative voltage direction and the upper curve in the reverse direction.

For the hydrogen oxidation case, one sees that, upon increasing the voltage in the positive direction from the open circuit value (equilibrium potential for H_2/OH^-), the current at first increases and then reaches a plateau corresponding to rate control by the mass transfer of H_2 to the surface. Upon increasing the potential still further, however, a point is reached where the logarithm of the current density decreases linearly with increasing voltage (as indicated by the line with a negative slope). At still

higher voltages, the current density again increases with increasing voltage, corresponding to oxygen evolution.

The onset of the linear decrease in $\ln(i)$ with V is attributed to the formation of an oxide film on the platinum surface. This postulate is advanced, because the voltage at which the decrease first occurs corresponds to the equilibrium voltage for the PtO/Pt reaction, as calculated from thermodynamics. Accordingly, following Gurney [1,2], Vetter et.al. [3,4], Moffat and coworkers [24], and many others, we write the current due to the tunneling of charge carriers across the oxide film as

$$i = \hat{i}_0 e^{-\beta L} \quad (\text{II-1})$$

where β is the tunneling constant, L is the film thickness, and $\hat{i}_0$ is a constant (the “film-free” current density). According to the PDM [22,23], the thickness of the barrier layer, in the case for which no change in oxidation state occurs upon dissolution, can be written as

$$L = \left(\frac{1-\alpha}{\varepsilon} \right) (V - V_o) \quad (\text{II-2})$$

where α is the polarizability of the film/solution interface ($0 < \alpha < 1$), ε is the electric field strength within the oxide, V is the applied voltage, and V_o is a constant that depends upon the pH.

A more general expression for $L(V)$, which recognizes oxidative or reductive dissolution of the oxide, is given later in this proposal. Substitution of Equation (II-2) into Equation (II-1) therefore yields

$$\ln(i) = \ln(i_o) - \beta \left(\frac{1-\alpha}{\varepsilon} \right) (V - V_o) \quad (\text{II-3})$$

This equation does indeed predict that $\ln(i)$ decreases linearly with V , as observed in Figure II-1. By using $\alpha \sim 0.5$, $\varepsilon \sim 2 \times 10^6$ V/cm, and the gradient of Equation (II-3) determined from Figure II-1, we obtain a “back-of-the-envelope” estimate of $\beta \sim 2 \times 10^8$ cm⁻¹. Values for β determined at temperatures from 100°C to 300°C ranged from 0.2×10^8 to 2×10^8 cm⁻¹, which is in satisfactory agreement with the values obtained by others for completely different systems under ambient conditions [see Ref. 24, and references therein]. Thus, in the case of the oxidation of hydrogen on platinum in the voltage region where an oxide film forms on the surface, the current appears to be controlled by the direct quantum mechanical tunneling of charge carriers across the film. However, the success of Equation (II-4) does not exclude non-resonant tunneling (tunneling via non-isoenergetic, inter band-gap states in the film). Finally, it is evident that the formation of the oxide film strongly inhibits the hydrogen electrode reaction (HER) on platinum, *but it is stressed that this is of no consequence to fuel cell operation, because the anode operates at a potential that is more than 700 mV more negative than that at which the oxide first forms. The sole purpose of displaying the data in Figure II-1 is to demonstrate the utility of using the hydrogen electrode reaction as a probe for detecting the formation of the oxide on the metal.*

The situation with respect to the reduction of oxygen on platinum in high temperature alkaline solution (Figure II-1.2) is of particular interest, because an oxide presumably exists on the surfaces of Pt crystallites under normal operating conditions of an air cathode. Thus, on sweeping the potential in the negative direction from the open circuit value, the current increases (in the negative direction) and eventually reaches a plateau. Provided that the sweep rate is sufficiently high (1200 mV/min), the current remains constant as the voltage is swept in the negative direction until it again increases (to more negative values) due to hydrogen evolution. However, if the voltage sweep rate is lower than 1200 mV/min, the current decreases to a value that depends upon the sweep rate in a rather sensitive fashion. At more negative voltages, the current again increases because of hydrogen evolution. To our knowledge, the data

plotted in Figure II-1.2 are the only data that are currently available for the reduction of oxygen on platinum at temperatures that are significantly greater than 100°C.

Noting that the platinum surface under open circuit conditions is (presumably) covered with PtO, the initial plateau in the current might indicate that oxygen reduction on the oxidized surface is fast and hence that the overall rate is controlled by mass transfer of oxygen to the interface. As the PtO is reduced, due to sweeping the potential to more negative values, particularly at low voltage sweep rates, the current decreases, which implies that, on the bare metal, the charge transfer reaction is slow compared with the same reaction on the oxide covered surface. This behavior is *completely opposite to that observed for hydrogen oxidation*, as shown in Figure II-1.1. In the oxygen reduction case, it may well be that the most important factor controlling the rate is the interaction of the dioxygen molecule with the surface and that the tunneling of charge carriers is of secondary importance (i.e., is fast). In this regard, it is also important to note that the features in the polarization curve for oxygen reduction discussed above *generally are not observed at ambient temperature*. This is probably because the kinetics of film reduction are sufficiently slow that the impact of film removal in the case of O₂ reduction is not observed in many, if not most, experiments. However, these effects are observed at highly elevated temperatures (275°C), and work currently underway is exploring this issue at technologically important temperatures (60°C – 200°C). We note, however, that an alternative explanation of the data exists; that the cathodic peak observed on sweeping the current in the negative potential direction is due to the reduction of the oxide on the surface, rather than due to the reduction of oxygen. These two possibilities can be delineated by studying the potentiostatic polarization behavior under variable mass transfer rate conditions, work that is now under way.

Although the oxygen electrode reaction (OER) is one of the most studied reactions in electrochemistry, controversy remains with respect to mechanistic detail. Of particular importance for the present work is the almost complete lack of experimental information for this reaction at elevated temperatures (T > 60°C) and the lack of emphasis in current models and mechanisms of the properties of the passive oxide film on the substrate, for those cases where the reaction occurs on a passivated surface. When the oxide is considered, attention is usually focused only on tunneling of charge carriers from the metal to the reaction center at the outer surface and on the interfacial properties, as they affect adsorption. Little attention has been paid to the crystallographic and electronic defect structures. This issue is best illustrated by reference to a specific example. Thus, in an excellent, recent study of O₂ reduction on oxide-covered (“passive”) ruthenium in alkaline solution, cyclic voltammetry (CV) and rotating ring-disk electrode (RRDE) techniques were used to ascertain the role of the oxide in the reduction process [25]. The results were interpreted in terms of the classical Wroblowa et.al. [26] mechanism. The authors concluded that the reaction proceeds primarily via the four-electron pathway with minimal production of peroxide *and that the reaction is very different on the two substrates* (Ru and RuO_x). However, the analysis did not recognize the fact that the oxide film that forms on ruthenium under the experimental conditions is three dimensional in nature and hence will exert an influence on the kinetics of the reaction that is not captured by considering the oxide/solution interface alone.

A tentative, but extremely important conclusion from the present work is that oxygen vacancies are most likely the active sites on the surface of the oxide film that covers platinum (and other noble metals) in the OER potential region. Thus, while many other mechanisms have been proposed for the OER [27-30], most of which involve the initial, homolytic dissociation of O₂, i.e.

followed by charge transfer, e.g.

etc., none have invoked oxygen vacancies as being intimately involved in the OER. Thus, these mechanisms generally fail to distinguish between bare metal and oxide-covered surfaces, but it is clear from the data given above and later in this report that the distinction must be made. As a working hypothesis, we suggest the following possible mechanism for the OER on oxide-covered surfaces

or

One theoretical concept that has received considerable attention in recent years concerns the relationship between catalytic activity for O_2 reduction and the number of unpaired d electrons in the catalyst. For example, Bockris and Reddy [27], citing the work of Rao, argue that the linear dependence of the maximum coverage of adsorbed oxygen on the composition of the Pt-Rh alloy system reflects an underlying change in the density of the bonding d electrons (note that the electron configurations of Pt and Rh are $5d^96s^1$ and $4d^85s^1$, respectively). They further note that the oxygen coverage on gold, which has no unpaired d electrons, is very low and displays a Tafel constant for oxygen reduction of $-2RT/F$. On the other hand, Pd ($4d^{10}$), which has intermediate maximum oxygen coverage, yields a Tafel constant of $-RT/F$ and a change in the rate-determining step for the reaction. As the composition of the alloy of these two metals changes, the Tafel constant changes abruptly from one value to the other, with the change occurring at a sufficient palladium content to create d orbital vacancies. While the d -electron theory often provides an attractive rationalization for the electrocatalytic activity of noble metal alloys, it, too, ignores the impact that the three-dimensional oxide film surely has on the kinetics of charge transfer at high potentials. However, the d electron concept may still be useful within the context of a theory that postulates quantum mechanical transmission of charge carriers through an oxide film, because of the impact that the density of states in the metal, from which the tunneling charge carriers originate, has on the rate constant.

II-2. Surface Oxide Films

The importance of defining the properties of the oxide (“passive”) film that forms anodically on the metal surface arises from the following factors:

- The thickness of the film, through which charge carriers must pass, is a linear function of voltage (Figure II-1.1 and see below), with the thickness depending upon the rate of dissolution at the film/solution interface and the rate of generation of oxygen vacancies at the metal/film interface.
- The defects within the film (cation vacancies, cation interstitials, and oxygen vacancies) may act as inter bandgap states for resonant tunneling, thereby greatly increasing the thickness of the layer over which tunneling can occur.

- Surface defects (e.g., oxygen vacancies) may act as reaction sites, as postulated in Reactions R4 to R8, and as has been firmly established in gas phase reactions and for oxygen evolution on oxide substrates.
- The potential distribution through the passive film has a major impact on the value of the tunneling probability, as calculated using Gamow's equation.

To date, the linear dependence of film thickness on voltage has been recognized in electron transfer theory (e.g., by Schultze and Stimming [6]), but only in an *ad hoc* fashion (i.e., the dependence did not follow from some mechanistic treatment of the growth of passive films). However, the dependence of film thickness on other important system variables, such as pH, which determines the dissolution rate, has not been correctly captured in any of those previous publications. Similarly, previous theories have assumed that the concentration of inter bandgap states is constant throughout the thickness of the film. Noting that passive films on pure metals are defect semiconductors, and that the defects act as the inter bandgap states, the uniform concentration assumption is clearly incorrect. This is because defects are generated and annihilated at interfaces that are separated by a few nano meters, and hence the concentration gradients are predicted to be quite large.

Furthermore, the current theories assume a single type of inter bandgap state, whereas real passive films frequently have two or more different types of defect (e.g., cation vacancies, oxygen vacancies, and cation interstitials, as in the case of the passive film on iron [31]) that are separated significantly in energy and whose concentrations exhibit quite different dependencies on distance through the film and voltage. For example, the passive film on copper is known to change from n-type to p-type as the voltage is increased across the passive range, clearly demonstrating a change in the dominant defect type. Finally, the potential within the film is commonly assumed to vary linearly with distance, with a gradient (electric field) that depends upon the applied voltage. Neither of these assumptions is correct, particularly the second assumption. Thus, overwhelmingly, the experimental evidence now indicates that the electric field is buffered by internal, band-to-band ("Esaki") tunneling, which renders the field insensitive to the applied voltage. Introduction of a constant electric field is expected to have a major impact on the value of the tunneling probability and hence upon the calculated exchange current density for the reaction, when compared to existing theories.

Figure II-2.1. Interfacial defect generation/annihilation reactions that occur in the growth of anodic barrier oxide films according to the Point Defect Model [22,23]. m = metal atom, $V_M^{\chi'}$ = cation vacancy on the metal sublattice of the barrier layer, $M_i^{\chi+}$ = interstitial cation, M_M = metal cation on the metal sublattice of the barrier layer, $V_O^{\cdot\cdot}$ = oxygen vacancy on the oxygen sublattice of the barrier layer, O_O = oxygen anion on the oxygen sublattice of the barrier layer, $M^{\delta+}$ = metal cation in solution. Note that cation vacancies are generated at the film/solution interface and are annihilated at the metal/film interface whereas cation interstitials and oxygen vacancies are generated at the metal/film interface and are annihilated at the film/solution interface.

Although a number of models for passive films exist, all but one are properly classified as being “local” models that have been developed to account for passivity in specific systems [23]. Thus, the Cabrera-Mott high field model (HFM) [32] assumes interstitial cation transport only, that rate control resides at the metal/film interface via cation injection from the metal into the film, and that no dissolution of the film occurs at the film/solution interface. Accordingly, the model cannot account for the existence of steady states in the film thickness or current and hence is at odds with experimental results. The assumption that the film grows at the film/solution interface by reaction of transmitted cations with the solvent is generally invalid, because it is now known that barrier layers grow by the generation of oxygen vacancies at the metal/film interface and hence grow into the metal (only the porous outer layer grows by cation transmission through the film). The HFM also assumes that the electric field strength decreases as the film thickness increases. The invalid nature of the postulates upon which the HFM is based has been recently demonstrated in studies of transient film growth [33]. Likewise, the place exchange mechanism, which is used frequently to account for oxide formation on noble metals, is based upon the unlikely occurrence of cooperative rotation of MO dipoles over macroscopic dimensions. While such a process might be viable for the formation of oxide films that are no more than two oxygen monolayers thick over microscopic lateral dimensions, it is deemed to be highly unlikely for the formation of three dimensional oxide films on entropy grounds. In this context, it is interesting to note that the place exchange mechanism was once favored for explaining the formation of the passive film on iron. Subsequent work has shown that this mechanism is not viable, although differentiating between the place exchange mechanism and other film growth mechanisms has proven to be difficult.

A general theory for the passive state has been developed in the form of the Point Defect Model (PDM) [22,23]. This model is based on the following postulates: (i) Passive films are bilayer structures comprising a defective oxide inner layer that grows into the metal and an outer layer that grows from cations that are ejected from the barrier layer, (ii) the defects that are responsible for the properties of the barrier layer are cation vacancies, oxygen vacancies, and cation interstitials, (iii) the electric field strength is independent of distance through the barrier layer, (iv) the electric field is independent of the applied voltage (thus is actually predicted as a consequence of Esaki tunneling within the barrier layer [22,23]), and (v) dissolution occurs at the barrier layer/solution interface. Reaction analysis shows that the barrier layer grows by the generation of oxygen vacancies while the transmission of cations, either via cation vacancies or cation interstitials, results in the formation of the outer layer by hydrolysis and precipitation. The outer layer is normally porous and does not account for the phenomenon of passivity, except in the case of the “valve” metals, such as Al, Ti, Zr, Nb, and W. In these cases, the outer layer can be made to be “dense” by various sealing procedures (e.g., boiling anodized aluminum in water).

The reactions envisioned to occur at the interfaces in the PDM are shown in Figure II-2.1. Reactions 1 and 2 and Reactions 4, 5, and 6 are “lattice conservative” processes, in that their occurrence does not result in the movement of a boundary, which requires the creation or destruction of the lattice [as $M_M + (\chi/2)V_o^{\bullet\bullet} + xe'$, i.e., as $MO_{\chi/2}$]. On the other hand, Reaction 3 results in the formation of the barrier layer lattice at the metal/film interface while Reaction 7 results in the destruction of the lattice at the barrier layer/solution interface. It is important to note that passive films achieve steady states in thickness and current via equality in the rates of Reactions 3 and 7. This equality results in the steady-state thickness of the barrier layer being [c.f. Equation (II-2)]

$$L_{ss} = \frac{1}{\varepsilon} \left[1 - \alpha - \frac{\alpha\alpha_7}{\alpha_3} \left(\frac{\delta}{\chi} - 1 \right) \right] V + \frac{1}{\varepsilon} \left\{ \frac{2.303n}{\alpha_3\chi\gamma} - \beta \left[\frac{\alpha_7}{\alpha_3} \left(\frac{\delta}{\chi} - 1 \right) + 1 \right] \right\} pH + \frac{1}{\alpha_3\chi K} \ln \left(\frac{k_3^0}{k_7^0} \right) \quad (\text{II-4})$$

where, as before, α and ε are the polarizability of the film/solution interface and the electric field strength, respectively, $K = eF/RT$, and χ and δ are the oxidation states of the cation in the film (stoichiometry of $MO_{\chi/2}$) and in the solution, β is the dependence of the voltage drop across the film/solution interface on

pH, k_3^o and α_3 are the standard rate constant and the transfer coefficient, respectively, for the film generation reaction (Reaction 3, Figure II-2.1), and k_7^o and α_7 are the corresponding quantities for film dissolution (Reaction 7). In many cases, $\chi = \delta$ (e.g. for NiO on Ni in a Ni^{2+} solution), in which case Equation (II-4) reduces to the simpler of Equation (II-2). In any event, a linear dependence of passive film thickness on applied voltage is a ubiquitous observation.

The steady state current is given by

$$I_{ss} = \delta F [k_3^o e^{a_1 V} + k_2^o e^{a_2 V} e^{-b_2 L_{ss}} + k_7^o e^{a_7 (\delta - \chi) V} (C_{H^+} / C_{H^+}^o)^n] \quad (\text{II-5})$$

which predicts that the current contains contributions from the movement of cation vacancies (first term), metal interstitials (second term), and oxygen vacancies (third term, written in terms of film dissolution). Note that, in this expression, k_i^o and α_i represent the standard rate constant and transfer coefficient for the i^{th} interfacial reaction shown in Figure II-2.1, and that the steady state thickness is given by Equation (II-4).

An important feature of Equations (4) and (5), as far as the present work is concerned, is that they yield diagnostic criteria for identifying the dominant defect in the film [22,23]. This is important, because the identity of the defect determines the electronic nature of the barrier layer, the knowledge of which is essential for developing an accurate model for electron transfer and hence for the electrocatalysis of charge transfer reactions of interest in fuel cell technology (H_2 and MeOH oxidation and O_2 reduction). Thus, cation vacancies impart p-type character to the film whereas oxygen vacancies and cation interstitials impart n-type character, in keeping with the films being defect semiconductors. For example, the passive films on Ni, Zn, and W have been found to be p-type, n-type, and n-type, respectively, corresponding to the dominant defects being cation vacancies, cation interstitials, and oxygen vacancies. The defect identity in PtO on Pt is currently unknown, as is the electronic character.

The PDM has been extensively developed to describe the barrier oxide layers on a wide variety of metals, as noted above, but considerably less work has been carried out on describing the outer layer. In the case of the passive films on Ni and Zn, the outer layer is highly porous hydroxide and hence does not significantly contribute to the phenomenon of passivity. This is also expected to be the case for PtO on Pt and hence the outer layer of $\text{Pt}(\text{OH})_2$ is not expected to represent a significant mass transfer barrier. Nevertheless, extension of the PDM to incorporate the outer layer needs to be accomplished, as has been done for the passive film on lithium [34], so that the model is complete.

As noted earlier in this report, an accurate description of the electronic structure, including the potential distribution, is vital for the development of charge transfer theory and hence electrocatalysis on passivated substrates. Previous models have taken the electronic structures of abrupt junction, low dopant level (10^{15} - 10^{16} cm^{-3}) semiconductor models to describe passive films. However, these models are inappropriate, as noted previously [22,23], primarily because the dopant levels (donors and acceptors) in passive films are known to be of the order of 10^{20} - 10^{21} cm^{-3} and because the linearity of L_{ss} with V [c.f., Equations (2) and (4)], which is a ubiquitous observation, requires that the electric field strength be independent of the applied voltage (note that no evidence exists for a voltage dependence for α). The extraordinarily high dopant level has led one of the authors to describe barrier oxide layers on metals as metal/ n^+ -i- p^+ /solution junctions. Indeed, it appears that the closest classical analog for the electronic structure of passive films is a tunnel diode, in which the n^+ (excess of oxygen vacancies and/or cation interstitials) and p^+ (excess of cation vacancies) regions at the metal/film and film/solution interfaces, respectively, are degenerate (i.e., the Fermi levels lie above the conduction band edge in the n^+ region and below the valence band edge in the p^+ region) and hence are “semi-metals.” These regions cannot support high local electric fields, so that the potential is essentially independent of distance. Contrariwise, in the depletion (-i-) region, the field strength is constant, independent of the bias voltage, and the voltage that is imposed across the junction is accommodated by changes in the thickness of the depletion region and as

changes in voltage across the interfaces. In the case of passive films, this is augmented by a change in the thickness of the barrier layer; a feature that is seldom, if ever, taken into account in the “classical” models.

The independence of the field strength on applied voltage, which is consistent with the linear dependence of L_{ss} on V , has been explained in terms of Esaki tunneling [22,23]. This process corresponds to the quantum mechanical tunneling of electrons (or holes in the reverse direction) from the valence band edge (or close to it) to empty states close to the conduction band edge. This “internal” current is exponentially dependent on the local field, such that as the field increases the current also increases to establish a counter field. Thus, the field strength is “buffered” and hence is insensitive to the applied voltage, V . This model for the electronic structure of a barrier layer has received strong support in the photo inhibition of passivity breakdown [22,23].

With respect to the distribution in the concentration of inter band gap states in a passive film, the normalized concentration of oxygen vacancies in the passive film formed on tungsten, as calculated from the Point Defect Model, is shown in Figure II-2.2. The total thickness of the passive film formed under the conditions indicated in the caption is about 15 nm, assuming an anodizing constant of 2.5 nm/V. It is evident from Figure II-2.2 that a region of ca 3-4 nm exists over which the concentration of oxygen vacancies (“inter band gap states”) is not constant, and hence it is this region that is at odds with the constant concentration assumption in previous models. While we do not have any experimental confirmation that the oxygen vacancy profile is actually as described in Figure II-2.2, SIMS and XPS work reported by Shibata, et. al. [35] for the oxide film on zirconium shows that the oxygen vacancy concentration does indeed vary as predicted. Note that the oxide films on both metals (W and Zr) are oxygen ion (vacancy) conductors.

Figure II-2.2. Dimensionless concentration of oxygen vacancies vs. dimensionless distance within the passive film formed on tungsten in phosphate buffer solution (pH = 2.1) at a voltage of 6 V_{SCE} .

A highly relevant question arises as to whether the PDM can be applied to the anodic oxide films on noble metals. While there is nothing in the theory that excludes the model, and while the success of Equation (II-3) in accounting for the data in Figure II-1.1 is impressive, anodic oxide films on noble metals have always been treated differently than those on active metals, such as iron and nickel. The origin of this difference can be traced to the fact that the oxide films on some noble metals, *when formed under specific conditions*, are very thin, amounting to only a few monolayers in thickness. However, thick films do form, and this is expected to be the case at elevated temperatures. Indeed, the comparison between theory and experiment shown in Figure II-1.1 argues strongly that the thickness of the oxide film is such that the assumptions underlying the PDM are valid. Nevertheless, we do not have an independent measure of the film thickness, so that this question must be resolved by future experiment.

II-3. Anodic Oxide Film Formation on Platinum

Exclusive literature exists on the formation of anodic oxide films on noble metals, particularly films on platinum and iridium. Much of this work stems from Conway's group at the University of Ottawa [36-40], from Damjanovic's laboratory at the Allied Chemical Corporation [41,42], and from many other groups interested in the electrocatalysis field [43,44]. For example, Conway, et. al. [38] found that the oxide formed on Pt comprises a bilayer of a "monolayer" inner film and a thick(er) outer layer, with the latter forming at high anodic potentials. This bilayer structure is an integral part of the PDM, which proposes that the inner layer forms directly from the metal via the generation and annihilation of point defects and that the outer layer forms by dissolution/precipitation or from restructuring of the inner layer [38]. These workers concluded that the inner ("2-D") layer could be reduced independently of the outer layer; a finding that was contrary to the earlier work of Shibata [45], who proposed that reduction occurred at the outer surface of the thick, outer layer.

In a later study, Conway and Jerkiewicz [40] explored anodic oxide growth on Pt single crystal surfaces (100 and 111) and on polycrystalline platinum in 0.5 M H₂SO₄ at 25 °C. Film charge densities in excess of 1000 $\mu\text{C}/\text{cm}^2$ were reported, corresponding to nominal thickness in excess of 0.75 nm (assuming a density for PtO of 14.1 g/cm³). This film thickness is comparable to that formed on nickel at lower voltages and is well within the envelope of validity of the PDM, particularly when it is noted that the oxide film had not attained a steady state thickness. Furthermore, Conway and Jerkiewicz [40] found that the film thickness varies linearly with the applied voltage, as predicted by Equation (II-4). The film thickness (charge density) was found to increase logarithmically with time, a relationship that is predicted by a variety of mechanisms, including the place exchange model [37,46], the high field model [42,48], and the PDM [22,23]. Conway and Jerkiewicz's studies [40] also showed that the rate of growth of the oxide on Pt(100) is significantly faster than on Pt(111); a finding that was rationalized in terms of the place exchange model by noting that each Pt atom in a (111) surface has nine nearest neighbors (6 in the surface plane and 3 immediately below), and hence should be more tightly bound than an atom in a (100) surface, which has only eight nearest neighbors (4 in the surface plane and 4 beneath). Thus, place exchange with oxygen was postulated to be more difficult (and hence slower) in the former than in the latter. However, these same results are readily accounted for by the PDM through Equation (II-4), by noting that the film thickness depends upon the standard rate constant for oxygen vacancy generation at the metal/film interface, which also depend on the state of bonding of Pt atoms at the metal/film interface. Because oxygen vacancy generation requires the local expansion of the Pt lattice at the metal/film interface, the energy required to form an oxygen vacancy in the Pt(111) case should be larger than that required for the Pt(100) interface. Accordingly, it is reasonable to expect that the standard rate constant for Reaction (3), Figure II-2.1, will be greater for Pt(100) than it is for Pt(111). In summary, the data currently available for the growth of anodic oxide films on Pt are not unequivocally in support of any mechanism. Thus, *a principal, long-term goal of the work is to distinguish between various growth mechanisms, including the place exchange mechanism, the high field mechanism, and the PDM in accounting for anodic oxide film growth kinetics and properties over a wide range in temperature.*

II-4. Electron Transfer Theory

As noted in the Introduction, the theory of electron transfer via quantum mechanical tunneling is extensively developed, starting with the work of Gurney [1,2] in the early 1930s and furthered by the studies of Marcus [12], Levich [49], Dogadnadze [50], Kuznetsov [18], Schmidt [51], Schmickler [7,8], and others, in the 1960s and 1970s, to name but a few of the many contributors to the field. Extensive reviews [18-21] have been published on this subject, including a recent review by Kuznetsov and Ulstrup [18] that summarizes the more recent advances. Space does not permit a detailed review of the literature to be made here; instead only a brief, *simplified* account is given of the salient features that impact on the present proposal.

According to classical electron transport theory, the current density for a redox reaction in which QMT is occurring is given by [20]

$$i \propto \iint n(E, V) N(E, x) P_T(E, x) dE dx \quad (\text{II-6})$$

where $n(E, V)$ is the density of electrons having energy E in the metal at the applied voltage V , $N(E, x)$ is the number of acceptor species having energy E at a distance x from the metal surface, and $P_T(E, x)$ is the probability of tunneling of an electron from the metal to the acceptor. The quantity $n(E, V)$ is given in more fundamental terms in terms of the product of the density of states, $\rho(E)$ in the metal and the Fermi distribution function, $F(E, V)$, as follows [20]:

$$n(E, V) = \rho(E) F(E, V) = B(E + \rho_o V)^{1/2} / [1 + \exp\{(E + e_o V - E_f) / kT\}] \quad (\text{II-7})$$

where E_f is the Fermi energy, e_o is the electronic charge, and ρ_o is a constant. Considerable attention has been focused on the distribution of the acceptors, $N(E, V)$, because of the importance of coupling between various energy modes in determining the probability of electron transfer to the reactant in the solution phase. In the present work, emphasis is being placed on assessing the tunneling probability, $P_T(E, x)$, as it relates to charge transfer across passive films.

Within the WKB (Wentzel-Kramer-Brillouin) approximation [20,21], the tunneling probability is given as

$$P_T = \exp \left(-2 \int_a^b \left\{ \frac{8\pi^2 m}{h^2} [U(x) - E] \right\}^{1/2} dx \right) \quad (\text{II-8})$$

where $U(x)$ is the potential energy of the electron in the barrier and E is the total energy. Equation (II-8) is readily evaluated for “ideal” barriers, such as parabolic, rectangular, and Eckart potential barriers [20]. On the other hand, Vetter and Schultze [3,4] and later Schultze and Stimming [6] and Schmickler and Ulstrup [10] extended these ideas to film-covered electrodes (e.g., passive iron), but the potential function chosen for $U(x)$ does not conform with our present knowledge of the electronic structures of passive films. Note that the crucial requirement is the derivation of a realistic function for $U(x)$ from passivity theory followed by evaluation of P_T using Equation (II-8) via numerical integration, if necessary. This approach contrasts previous efforts that have utilized ideal barriers, which render Equation (II-8) amenable to analytical solution, rather than choosing a barrier function that conforms to the known properties of the system. Thus, with the respect to the classical electron transfer theory at passive metals, as developed by Gerisher et. al. [52,53] and Schmickler and coworkers [7,8], it is assumed (explicitly or implicitly) that: (i) The electric field within the film varies linearly with the applied voltage or the potential distribution corresponds to that of a classical semiconductor/solution in which the doping level is of the order of 10^{16} cm^{-3} ; (ii) the defect (and hence inter band-gap state) concentration is constant (abrupt junction model); (iii) the passive film consists of a single, homogeneous oxide film; and (iv) the thickness of the layer is constant and hence is independent of the applied voltage. It is now known that all of these assumptions are invalid, with the consequence that the current theory for electron transfer at passive metals must be significantly modified.

The above formalism applies strictly to direct tunneling, in which charge carriers are transferred in a single step across the film. Accordingly, the theory is valid for films that are a few tenths of a nanometer thick at most. However, the barrier oxide layers (“inner layer” of the passive film) on most metals are of the order of a few nanometers thick, which is generally regarded as being too great a distance for direct tunneling to be significant. Accordingly, a more appropriate theory must consider “long range electron tunneling” (LRET), in which charge transfer occurs via inter band-gap states

(resonant tunneling). If a single resonant state exists within the bandgap, then the tunneling probability can be written as

$$P_T(\text{resonance}) = P_1(E_r)P_2(E_r) / [P_1(E_r) + P_2(E_r)] \quad (\text{II-9})$$

where E_r is the resonant state energy and $P_1(E_r)$ and $P_2(E_r)$ are the tunneling probabilities from the metal to the resonant state and from the resonant state to the redox species at the film/solution interface, respectively, as given by Equation (II-8). Clearly, Equation (II-9) can be generalized to cover a spectrum of resonant states, whose energies are determined by the local electrostatic potential within the film and whose concentration varies with distance through the film.

It is a postulate of the present work that, for pure metals at least, the inter band-gap states in the passive film are crystallographic defects (cation vacancies, cation interstitials, and oxygen vacancies). Thus, a major goal of the present work was to combine ET and passivity theory, as indicated above, to provide a comprehensive model for the LRET through passive films, recognizing the fact that passive films that exceed a few tenths of a nanometer in thickness (which include most, if not all passive films) are already too thick to transfer charge carriers by direct tunneling.

Finally, as noted recently by Nazmutdinov, et.al. [18], a full, “first principles” prediction of reaction rate using charge transfer theory still eludes electrochemists and this limitation is expected to hold in this work as well. The difficulty lies in describing, in microscopic detail, the geometry and electronic structure of the reactant, the equilibrium and non-equilibrium structure of the solvent (and hence in calculating the reorganization energy), and the structure and composition of the electrical double layer. Furthermore, considerable difficulty currently exists in describing the states of chemisorbed species. The goal of the present work was much less ambitious; it was to explore ET theory together with passivity theory to estimate the *relative* rates of reactions (H_2 oxidation and O_2 reduction) on bare and passive platinum. On reviewing ET theory, it appears that our goal was best approached by using the atom superposition electron delocalization molecular orbital (ASED-MO) technique that has been applied with considerable success to modeling the rate-determining step in the reduction of oxygen on bare platinum in acidic solutions [20]. In using this technique, the potential energy hyper-surfaces for the reactants transitioning to the products in the rate determining step might be calculated while avoiding some of the difficulties associated with calculating solvent reorganization energies via the Marcus continuum model. However, this approach proved to be impractical with the current state-of-knowledge and could only result in qualitative estimates.

References:

1. R. W. Gurney and E. U. Condon, *Phys. Rev.*, **33**, 127 (1929).
2. R. W. Gurney, *Proc. Roy. Soc.*, **A134**, 137 (1931).
3. J. W. Schultze and V. K. J. Vetter, *Electrochim. Acta*, **18**, 889 (1973).
4. V.K.J. Vetter and J.W. Schultze, *Ber. Bunsen. Phys. Chem.*, **77**, 945 (1973).
5. P. Kohl and J.W. Schultze, *Ber. Bunsen. Phys. Chem.*, **77**, 953 (1973).
6. J.W. Schultze and U. Stimming, *Z. Phys. Chem. N.F.*, **98**, 285 (1975).
7. W. Schmickler, *J. Electroanal. Chem.*, **82**, 65 (1977).
8. W. Schmickler, *J. Electroanal. Chem.*, **134**, 167 (1982).
9. S.U.M. Khan and W. Schmickler, *J. Electroanal. Chem.*, **134**, 167 (1982).
10. W. Schmickler and J. Ulstrup, *Chem. Phys.*, **19**, 217 (1977).
11. W. Schmickler, *J. Electroanal. Chem.*, **113**, 159 (1980).
12. R.A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).
13. J. Ulstrup and J. Jortner, *J. Phys. Chem.*, **63**, 4358 (1975).
14. W. Schmickler, *J. Electroanal. Chem.*, **204**, 31 (1986).
15. K.L. Sebastian, *J. chem. Phys.*, **90**, 5056 (1989).

16. B.B. Smith and J.T. Hynes, *J. Chem. Phys.*, **99**, 6517 (1993).
17. W. Schmickler and D. Henderson, *Progr. Surf. Sci.*, **22**, 323 (1986).
18. A.M. Kuznetsov and J. Ulstrup, *Electrochim. Acta*, **45**, 2339 (2000); R. R. Nazmutdinov, et. al., *Electrochim. Acta*, **45**, 3521 (2000).
19. W. Schmickler, *Interfacial Electrochemistry*, Oxford University Press, Oxford, UK, 1996.
20. J. O'M. Bockris and S.U.M. Khan, *Surface Electrochemistry*, Plenum Press, N.Y., 1993; J. O'M. Bockris and S.U.M. Khan, *Quantum Electrochemistry*, Plenum Press, N.Y., 1979; J. O'M. Bockris and R. Abdu, *J. Electroanal. Chem.*, **448**, 189 (1998).
21. M. J. Weaver, *Compr. Chem. Kinetics*, **27**, 1 (1987); W. R. Fawcett and M. Opallo, *Angew. Chem. Int. Edit.*, **33**, 2131 (1994).
22. D.D. Macdonald, *J. Electrochem. Soc.*, **139**, 3434 (1992).
23. D.D. Macdonald, *Pure Appl. Chem.*, **71**, 951 (1999).
24. T.O. Moffat, H. Yang, F-R. F. Fan, and A.J. Bard, *J. Electrochem. Soc.*, **139**, 3158 (1992).
25. J. Prakash and H. Joachin, *Electrochim. Acta*, **45**, 2289 (2000).
26. H.S. Wroblowa, Y.D. Pan, and G. Razumney, *J. Electroanal. Chem.*, **60**, 195 (1976).
27. J. O'M. Bockris and A.K.N. Reddy, *Modern Electrochemistry*, Vol. 2, Plenum Press, 1973.
28. M.R. Tarasevich, A. Sadkowski, and E. Yeager, in *Compreh. Treat. Electrochem.* (Ed. B.E. Conway, J. O'M. Bockris, E. Yeager, S.U.M. Khan, and R.E. White), Plenum Press, 1983.
29. R. Adzic, in *Mod. Asp. Electrochem.* (Ed. R.E. White, J.O'M. Bockris, and B.E. Conway), **21**, 163 (1990) (Plenum Press).
30. T. Mallouk, Penn State University, private communication (2000).
31. A.J. Davenport, L. J. Oblonsky, M. P. Ryan, and M. F. Toney, *J. Electrochem. Soc.*, **147**, 2162 (2000).
32. N. Cabrera and N.F. Mott, *Rep. Progr. Phys.*, **12**, 163 (1948).
33. L. Zhang, E. Sikora, J. Sikora, and D.D. Macdonald, *J. Electrochem. Soc.*, **145**, 898 (1998).
34. O. Pensado-Rodriguez, J. Flores, M. Urquidi-Macdonald, and D.D. Macdonald, *J. Electrochem. Soc.*, **146**, 1326 (1999).
35. T. Shibata, Univ. Osaka, private communication (1994).
36. D. Gilroy and B. E. Conway, *J. Phys. Chem.*, **46**, 875 (1968).
37. H. Angerstein-Kozłowska, B. E. Conway, and W. B. A. Sharp, *J. Electroanal. Chem.*, **43**, 9 (1973).
38. B. E. Conway, G. Tremiliosi-Filho, and G. Jerkiewicz, *J. Electroanal. Chem.*, **297**, 435 (1991).
39. B. E. Conway and G. Jerkiewicz, *J. Electroanal. Chem.*, **339**, 123 (1991).
40. G. Tremiliosi-Filho, G. Jerkiewicz, and B. E. Conway, *Langmuir*, **8**, 658 (1992).
41. A. Damjanovic and V. I. Birss, *J. Electrochem. Soc.*, **130**, 1688 (1983); **138**, 2549 (1991).
42. A. Damjanovic, L. S. R. Yeh, and J. F. Wolf, *J. Electrochem. Soc.*, **127**, 874 (1980); *Electrochim. Acta*, **26**, 825 (1981), *J. Electrochem. Soc.*, **129**, 55 (1982).
43. N. M. Markovic and P. N. Ross, *Electrochim. Acta*, **45**, 4101 (2000).
44. S. Gottesfeld, G. Maia, J. B. Floriano, G. Tremiliosi-Filho, E. A. Ticianelli, and E. R. Gonzalez, *J. Electrochem. Soc.*, **138**, 3219 (1991).
45. S. Shibata, *J. Electroanal. Chem.*, **89**, 37 (1978).
46. N. Sato and M. Cohen, *J. Electrochem. Soc.*, **111**, 512 (1964).
47. D. A. Harrington, *J. Electroanal. Chem.*, **420**, 101 (1997).
48. L. Young, *Anodic Oxide Films*, Academic Press, NY, 1963.
49. V.G. Levich, *Adv. Electrochem. Electrochem. Eng.*, **4**, 249 (1966).
50. R.R. Dogonadze, in *Reactions of Molecules at Electrodes*, (Ed. N.S. Hush), Wiley-Interscience, N.Y., Chapter 3, 1973.
51. P. Schmidt, *Chem. Soc. Specialist Periodical Repts.*, Vol. 5, 1975 (Roy. Soc. Chem., London).
52. H. Gerischer, *Z. Phys. Chem. N.F.*, **26**, 223 (1960).
53. H. Gerischer, *Z. Phys. Chem. N.F.*, **27**, 48 (1961).

III. RESEARCH PROGRESS

III-1. Task 1: Continued Development of the Theory of Passivity (Researcher: Dr. Kamrun Nahar)

In this initial task, we have further developed the theory of the growth of the thin oxide film on noble metal electrocatalysts in the oxygen reduction region within the framework of the Point Defect Model. In particular, we have extended the PDM by:

1. Incorporating outer layer formation.
2. Modeling the electronic structure by assuming that the film is a defect semiconductor and by incorporating non-uniform doping.

The outer layer forms via the precipitation as hydroxides, oxyhydroxides, or oxides of cations that are ejected from the barrier layer, via the restructuring of the outer surface of the barrier layer, or via both processes occurring simultaneously. Since charge transfer takes place at the barrier layer/outer layer interface, where electron transfer is facilitated, the electrochemical kinetic properties of the outer layer can be described in terms of a diffusional (Warburg) impedance of finite thickness within the framework of porous electrode theory.

Task Status:

III-1.1 Introduction

The theory of electron tunneling at metal/solution interfaces started with Gurney's work on the hydrogen electrode reaction (HER) soon after the development of quantum mechanics in the late 1920s and early 1930s [1,2]. Gurney's work was soon recognized as being a triumph for quantum mechanics, the other being α -particle emission from radioactive nuclei [3]. Subsequently, numerous studies have been reported on the subject [3-9], culminating in the award of a Nobel Prize to Marcus [73,74]. Not surprisingly, the subject is well-developed, at least for metal/solution interfaces, in the absence of surface oxide films. In the presence of an oxide film, the treatments have tended to be somewhat simplistic. The current density for a redox reaction in which quantum mechanical tunneling occurs is written as

$$i \propto \iint n(E,V)N(E,x)P_T(E,x)dEdx \quad (\text{III-1.1})$$

where $n(E,V)$ is the density of electrons, having energy E in the metal at the applied voltage V , $N(E,x)$ is the number of acceptor species having energy E at a distance x from the metal surface, and $P_T(E,x)$ is the probability of tunneling of an electron from the metal to the acceptor. The density of electrons in the metal, $n(E,V)$ can be written in terms of the product of density of states $\rho(E)$ and the Fermi distribution function $F(E,V)$ as

$$n(E,V) = \rho(E)F(E,V) = B(E + \rho_o V)^{1/2} / [1 + \exp\{(E + e_o V - E_f)/kT\}] \quad (\text{III -1.2})$$

where E_f is the Fermi energy, e_o is the electronic charge, and ρ_o is a constant. Using the WKB (Wentzel-Kramer-Brillouin) approximation, the tunneling probability $P_T(E,x)$ is written as

$$P_T = \exp \left(-2 \int_a^b \left\{ \frac{8\pi^2 m}{h^2} [V(x) - E] \right\}^{1/2} dx \right) \quad (\text{III -1.3})$$

where $V(x)$ is the potential energy of the electron in the barrier and E is the total energy. It is crucial to derive a realistic function for $V(x)$ for the oxide covered film to determine the tunneling probability and in turn, a realistic expression for the current density by solving Equation (III-1.1). Researchers previously developed electron transfer (ET) theory at passive metals using ideal barrier assumptions and low doping concentrations. Schultze and Vetter [10,11] and Schmickler and Ulstrup [12,13,14,15], for example, derived different ET theories for film covered electrodes. These theories can be applied for direct tunneling through passive oxide films that are a few tenths of a nanometer thick, but the potential functions chosen in the previous research do not conform to our present knowledge of the electronic structure of the barrier oxide layers whose thickness is of the order of a few a nanometers and have been determined to have the characteristics of highly doped defect semiconductors. The Point Defect Model (PDM) developed by Macdonald and co-researchers [16-23] describes passive film growth on noble-metal electrodes from a perspective that is proven to be more realistic and different from the other existing theories in this field.

Figure III-1.1. Point Defect Model. $Pt \equiv$ platinum atom; $v_{Pt} \equiv$ platinum vacancy at metal site; $Pt_{Pt} \equiv$ platinum cation in a cation position; $V_{Pt}^{\chi'} \equiv$ platinum cation vacancy; $Pt_s^{\delta+} \equiv$ platinum cation in the solution phase; $V_O^{..} \equiv$ oxygen vacancy; $O_O \equiv$ oxygen ion in a normal site on the oxygen sub-lattice.

A more appropriate electron transfer theory for the barrier oxide layers can be described in terms of long range electron tunneling (LRET). “Tunnel diodes” appear to provide the closest classical analogs for the electronic structures of the passive films. In tunnel diodes, the internal electric field is buffered by Esaki tunneling and charge transfer occurs via band-to-band resonant states. The goal of our research is to combine appropriate electron transfer theory with passivity theory in terms of the Point Defect Model (PDM, Figure III-1.1), in order to develop a comprehensive model for the electron transfer theory through passive films that exceed a few tenths of a nanometer in thickness. We focus on developing a more realistic expression for the potential distribution function through the barrier oxide layer and on determining the tunneling probability by using the tunnel diode theory. In this report, a potential distribution function is developed by considering the oxide film as graded (both nonlinear and linear) p-n junctions, rather than an abrupt p-n junction, to determine whether the idea of Esaki or band-to-band tunneling through the passive film is a valid one. Defect concentrations through the film are calculated using the PDM and Nernst-Planck equations.

In the following sections, we describe the tunnel diode theory and different methods to calculate the transmission probability for resonant tunneling diodes, the appropriateness of the use plus the application of these theories to passive oxide films, solution of the Poisson’s equation along with the PDM plus the Boltzmann statistics to obtain defect concentrations and the potential distribution through the barrier oxide layer.

III-1.2 Background of Resonant Tunnel Diodes

Tsu and Esaki [24] introduced the idea of resonant tunneling diode (RTD) in finite semiconductor superlattices. The RTD utilizes electron-wave resonance in multi-barrier heterostructures. The physics and applications of RTDs have been studied extensively in the last couple of decades (e.g. [25,8,5,4]). Frensley [26,27] developed numerical methods to evaluate the resonant states in semiconductor superlattices. Gergel et al. [28] obtained current-voltage characteristics of resonant tunneling structures using the transfer matrix method and determined charge density in the quantum well using transfer Hamiltonian approach. Jogai et al. [29] solved the time-independent Schrödinger equation and Poisson’s equation simultaneously under high applied bias and showed that strongly localized states occur in the quantum well and accumulation regions. These localized states trap charges that change the shape of the band edge and need to be included in resonant tunneling and the Coulomb interaction must be accounted for. More recently, Gelmont et al.[30] studied the electron transport in RTDs with staggered-bandgap structure and demonstrated that the conduction band electron transport is extremely dependant on the coupling between the conduction and valence bands and that an accurate estimate of current density requires the application of a multi-band model.

Global Coherent Resonant Tunneling

A resonant tunneling diode (RTD) typically consists of an undoped quantum well layer sandwiched between undoped barrier layers and heavily doped emitter and collector regions. Quasi-bound states (resonant states) are formed in the quantum wells, which accommodate electrons for a time, that is characteristics of the barrier structure. The expression for the current density in a finite structure is given by [24]

$$J = J_{\rightarrow} - J_{\leftarrow} \quad (\text{III -1.4})$$

In global coherent tunneling, no phase-coherence breaking of an electron occurs in the structure. The transfer matrix method, self-consistent scheme and transfer Hamiltonian approach are three different

methods typically used to calculate the transmission probability within the global coherent tunneling process.

- Transfer Matrix Method

In the transfer matrix method, first given by Tsu and Esaki [24], the 1D Schrödinger equation is solved numerically and the transfer matrices for the heterostructures are calculated. The 1D, time-independent, effective mass Schrödinger equation is written as

$$H\Psi(x) = \frac{\hbar^2}{2} \nabla \left(\frac{1}{m^*(x)} \nabla \right) \Psi(x) + V(x) \Psi(x) = E_x \Psi(x) \quad (\text{III -1.5})$$

where m^* is the x -dependent conduction band effective mass and the potential energy $V(x)$ consists of the electron affinity and the self-consistent Hartree potential, which is defined in the next subsection. In the transfer matrix method, the potential distribution of a resonant tunneling structure is approximated by a series of small steps. The wave function in the i th section can be expressed as

$$\Psi_{k_x^{(i)}}^{(i)}(x) = A_{k_x^{(i)}}^{(i)} \exp(ik_x^{(i)}x) + B_{k_x^{(i)}}^{(i)} \exp(-ik_x^{(i)}x) \quad (\text{III -1.6})$$

where $k_x^{(i)}$ is a complex wave number. The coefficients, $A_{k_x^{(i)}}^{(i)}$, $B_{k_x^{(i)}}^{(i)}$, in the adjacent sections are then related to each other as follows:

$$\begin{pmatrix} A_{k_x^{(i+1)}}^{(i+1)} \\ B_{k_x^{(i+1)}}^{(i+1)} \end{pmatrix} = T^{(i)} \begin{pmatrix} A_{k_x^{(i)}}^{(i)} \\ B_{k_x^{(i)}}^{(i)} \end{pmatrix} \quad (\text{III -1.7})$$

where the matrix $T^{(i)}$ is defined as

$$T^{(i)} = \begin{pmatrix} \alpha_+^{(i)} P & \alpha_-^{(i)} / Q \\ \alpha_-^{(i)} Q & \alpha_+^{(i)} / P \end{pmatrix} \quad (\text{III -1.8})$$

$$\alpha_+^{(i)} = \frac{1}{2} \left\{ 1 \pm \left(m^{*(i+1)} / m^{*(i)} \right) \left(k_x^{(i)} / k_x^{(i+1)} \right) \right\} \quad (\text{III -1.9})$$

$$P = \exp \left\{ i \left(k_x^{(i)} - k_x^{(i+1)} x_{i+1} \right) \right\} \quad (\text{III -1.10})$$

$$Q = \exp \left\{ -i \left(k_x^{(i)} - k_x^{(i+1)} x_{i+1} \right) \right\} \quad (\text{III -1.11})$$

The coefficients at the emitter and collector edges are connected by the transfer matrix T as

$$\begin{pmatrix} A_{E_x}^L \\ B_{E_x}^L \end{pmatrix} = T \begin{pmatrix} A_{E_x}^R \\ B_{E_x}^R \end{pmatrix} \quad (\text{III -1.12})$$

$$T = T^{(N)} T^{(N-1)} T^{(N-2)} \dots T^{(2)} T^{(1)} \quad (\text{III -1.13})$$

The transmission probability $T(E_x)$ through the RTD is then given as

$$T(E_x) = \frac{m^{*L} k^R |A_{E_x}^R|^2}{m^{*R} k^L |A_{E_x}^L|^2} \quad (\text{III -1.14})$$

- Self-consistent Method

In the self-consistent scheme, space-charge build-up, which gives rise to non-uniform potential profiles, and leads to a non-equilibrium electron distribution in the quantum well, is considered. The self-consistent Hartree potential, $V_{sc}(x)$ is calculated by solving Poisson's equation, which is written as

$$\frac{d}{dx} \left(\varepsilon(x) \frac{dV_{sc}(x)}{dx} \right) = -e_0 \{N_D^+(x) - n(x)\} \quad (\text{III -1.15})$$

where $\varepsilon(x)$ is the electric field strength, N_D^+ is the donor density, $n(x)$ is the electron density, and e_0 represents the charge of an electron.

The electron density $n(x)$ in the RTDs is expressed in terms of the electron wavefunction, $\Psi(x)$, as given in Equation (2.27) of Reference [4]. Equation (III -1.15), Schrödinger's equation, and the equation for the electron density are simultaneously solved numerically to obtain $V_{sc}(x)$ and $\Psi(x)$.

- Transfer Hamiltonian Method

In the transfer Hamiltonian approach, the resonant tunneling structure is divided into three regions: emitter, well, and collector for a double barrier system and the electron transfer between these regions is described using a tunneling Hamiltonian for a single barrier (Figure III-2.1.2). The total Hamiltonian of the system, H^{total} is then expressed as

$$H^{total} = H_e^0 + H_c^0 + H_w \quad (\text{III -1.16})$$

and

$$H_w = H_w^0 + H_{ew} + H_{cw} + H_{other} \quad (\text{III -1.17})$$

Sequential Tunneling

During the resonant tunneling process, the electrons stay in the quantum wells for a dwell time that varies with the parameters of the system and are likely to experience scattering that may cause the breaking of phase-coherence. Due to scattering with phonons and ionized impurities, the electrons may lose momentum and energy and relax to local, quasi-equilibrium states. This characteristic is modeled in sequential tunneling theory that describes resonant tunneling as two continuous tunneling processes, i.e. tunneling from the emitter to the quantum well and from the quantum well to the collector, in the case of a double-barrier system. Between of these two processes, momentum and/or energy relaxation of the electrons occur, leading to phase-coherence breaking and hence give rise to the new, quasi-equilibrium states of the electrons (Figure III-1.3).

Figure III-1.2. Energy band diagram for the transfer Hamiltonian model.

where H_e^0 , H_c^0 , and H_w are the Hamiltonian functions for free electrons in the emitter, collector, and quantum well, respectively. H_w is the total Hamiltonian of the well, which includes tunneling Hamiltonians between the emitter and quantum well (H_{ew}) and between the collector and quantum well (H_{cw}). H_{other} represents other interactions that the electrons may experience in the quantum well. The transmission probability is then calculated using the Green's function of the electrons in the well.

Figure III-1.3. Energy band diagram of sequential tunneling model

Luryi [31,32] proposed the sequential tunneling model and Weil and Vinter [33] demonstrated that this model, in the limit of no scattering in the well, reduces to the global coherent tunneling model. Two important physical aspects of the sequential tunneling are: (1) the effects of scattering on the transmission probability, and (2) the non-equilibrium distribution of electrons.

Effects of Impurity Scattering in RTDs

RTDs typically consist of undoped quantum wells and barriers, impurity scattering is not supposed to have any effect on the transmission probability. However, in reality, ionized donors may diffuse into the quantum wells giving rise to elastic Coulomb scattering centers. As the perpendicular motion of the electrons in a resonant tunneling structure is quantized into resonant states, the selection rule for the possible final states of electrons after impurity scattering is different from that for the free electrons. The transmission probability, $T(E_x)$, is then a function of both the total electron energy and the lateral momentum. Details of the impurity scattering in RTDs can be found in [4].

III-1.3 Electron Tunneling through Barrier Oxide Layer

The current-voltage characteristics of resonant tunnel diodes show negative resistance, which can be accounted for by interband resonant tunneling [34,35]. The energy band diagrams shown in [24,34,35] under different bias conditions clearly show the tunneling conditions in tunnel diodes. Esaki [34] demonstrated that negative resistance, which is characteristic of tunnel diodes, can be observed in a metal-oxide-semiconductor junction. Schmickler [12,36] developed a theory of resonant tunneling at film-covered electrodes that was based on the Franck-Condon approximation and second order perturbation theory, with respect to the electronic matrix element. It was shown that localized electronic states in the band gap of an oxide film deposited on a metal electrode can serve as intermediate states in electrochemical redox reactions. Depending upon the barrier parameters and the position of the intermediate states, resonance tunneling was estimated to be up to 10^2 times more effective than direct tunneling. Schmickler and Ulstrup [13] presented a theory of elastic coherent tunneling through metal oxide film based on linear response theory and transfer Hamiltonian mechanism and the potential barrier in the film was assumed to be trapezoidal. Schmickler [14] studied two electron transfer mechanisms through a space charge barrier and, based upon the experimentally observed current-potential characteristics, concluded that both direct elastic tunneling and resonance tunneling occur in real systems. Schultze and Macagno [11] studied ET reactions on passive electrodes for various film thicknesses and found that the influence of film thickness was less than expected from theoretical models. More recent studies on electrochemical electron transfer processes were performed by Schmickler [15], Bockris and Abdu [37], Kuznetsov and Ulstrup [9], Schmickler and Mohr [38], and Kuznetsov et al. [39].

Because of its thickness ($>$ a few nanometers) and high carrier concentrations, we propose that the barrier oxide layer have similar electronic properties to tunnel diodes, which were first discovered by Esaki [40]. Due to the large carrier density, the carrier distribution becomes degenerate i.e. the Fermi level on the p-side lies below the top of the valence band and that on the n-side lies above the bottom of the conduction band.

Electron Transfer Theory for the Passive Oxide Film and the Relevance to the Resonant Tunnel Diodes

As explained above, the electronic structure of the barrier oxide layer has close relevance to the electronic structure of tunnel diodes. The platinum oxide film has been characterized [41] as n-type semiconductor. The momentum/energy relaxation time through this n-type film will be calculated and

compared with the electron dwell time of the semiconducting oxide film. In the quantum mechanical picture, the electron dwell time is defined as the tunneling delay time to the incident electron wave as follows [4]

$$\tau_d(E_x) = \hbar \frac{\Gamma}{(E_x - E_x^0)^2 + \Gamma^2} \quad (\text{III -1.18})$$

which, at resonance, leads to

$$\tau_d(E_x) = \frac{\hbar}{\Gamma} \quad (\text{III -1.19})$$

where Γ is the tunneling width. If the mean free time of electrons in the barrier oxide film is found to be shorter than the electron dwell time, then the sequential tunneling model, which recognizes scattering and electron relaxation in the quantum wells, will be adopted to calculate the transmission probability and in turn, the current density through the passive oxide film. Otherwise, the transfer Hamiltonian model will be used to calculate the transmission probability through the oxide film. The reason for selecting the transfer Hamiltonian model over the transfer matrix theory, which is a more general model, is that the former is more analytical than the latter and many researchers have used it to analyze the effects of electron-phonon or electron-electron interactions on resonant tunneling, because its extension to the incoherent tunneling regime is quite straightforward [4].

Potential Distribution in the Barrier Oxide Layer

Modeling of the electronic structure of passive films follows the techniques that have been used in the past to model highly (degenerately) doped junctions with modifications to incorporate boundary conditions and dopant profiles. The modeling activities involve solving Poisson's equation

$$\nabla^2 \phi = -\rho_x / \varepsilon_f \hat{\varepsilon} \quad (\text{III -1.20})$$

for graded p - n junctions, where ϕ is the electric potential, ε_f is the permittivity of free space, $\hat{\varepsilon}$ is the dielectric constant, and ρ_x is the charge density at any point given by

$$\rho_x = \sum_i z_i c_i \quad (\text{III -1.21})$$

The parameter z_i is the charge on the species i , which includes electrons, holes, various defects (oxygen vacancies, cation vacancies, cation interstitials) and dopants (alloy components). The electrons and electron holes are modeled in terms of the Boltzmann or Fermi-Dirac statistics, whereas the concentration profiles for the defects are obtained by solving appropriate Nernst-Planck equations.

- Exponentially Graded p - n Junction Model
The Boltzmann distribution is written as

$$n = n_i \exp[-q(\phi - E_f^n)/kT] \quad (\text{III -1.22})$$

$$p = n_i \exp[q(\phi - E_f^p)/kT] \quad (\text{III -1.23})$$

where n and p represent densities of electrons and holes respectively, $n_i(\#/cm^3)$ is the electron/hole concentration in intrinsic semiconductors, q is electron charge, k is Boltzmann constant, T is the Kelvin temperature, and E_f^p and E_f^n represent the Fermi energies at the p and n side of the junctions, respectively. Let us consider oxygen vacancies as the donor and cation vacancies as the acceptor. According to the PDM, oxygen vacancies, which are generated at the metal/film interface and annihilated at the film/solution interface, act as donors, whereas cation vacancies, which are generated at the film/solution interface and annihilated at the metal/film interface, act as acceptors. The fluxes of the point

defects in the barrier layer may be written as $J_O = -D_O \frac{\partial C_O}{\partial x} - 2D_O KC_O$ and

$J_M = -D_M \frac{\partial C_M}{\partial x} - \chi D_M KC_M$ for oxygen vacancies and cation vacancies, respectively, where D (cm^2/s) and C (mol/cm^3) are the diffusivity and concentration, χ is the metal oxidation state, and subscripts O and M stand for oxygen vacancies and cation vacancies. Additionally, $K = \frac{\varepsilon F}{RT}$, R is the gas constant,

T is the absolute temperature, and ε is electric field strength. The continuity equation $\frac{\partial C_i}{\partial t} = -\nabla J$ leads to the Nernst-Planck equation

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + z_i D_i K \frac{\partial C_i}{\partial x} \quad (\text{III -1.24})$$

The second order, steady-state (i.e. $\frac{\partial C_i}{\partial t} = 0$) Nernst-Planck equation can be solved analytically using the following boundary conditions.
At $x = 0$,

$$J_{V_o}(0) = -k_4 C_O(0) \quad (\text{III -1.25})$$

$$J_M(0) = -k_3 \quad (\text{III -1.26})$$

where J_i represents the flux of species i , C_O and C_M are the concentrations of oxygen vacancies and cation vacancies, respectively, and k_i is the i th reaction rate constant.

At $x = L$,

$$J_O(L) = -k_2 \quad (\text{III -1.27})$$

$$J_M(L) = k_1 C_M(L) \quad (\text{III-1.28})$$

The steady-state solution of the Nernst-Planck equation is then written as

$$\frac{C_o(x)}{C_o(L)} = \chi k_2 \left[\left(\frac{1}{k_4} - \frac{1}{2KD_o} \right) e^{-2Kx} + \frac{1}{2KD_o} \right] / 2$$

$$\frac{C_M(x)}{C_M(0)} = k_3 \left[\left(\frac{1}{k_l} - \frac{1}{\chi KD_M} \right) e^{\chi K(x-L)} + \frac{1}{\chi KD_M} \right]$$

After summing up the charges due to the point defects and electrons/holes, the Poisson's equation in (III-1.20) becomes

$$-\frac{d^2\phi}{dx^2} = Ae^{-2Kx} + Be^{\chi Kx} + C + C_1 \left[e^{\beta_1(\phi - E_f^p)} - e^{-\beta_1(\phi - E_f^n)} \right] \quad (\text{III -1.29})$$

where

$$\beta_l = \frac{q}{kT}$$

$$A = \frac{F}{\varepsilon_f \hat{\varepsilon}} \chi C_o^L k_2 \left[\frac{1}{k_4} - \frac{1}{2KD_o} \right]$$

$$B = -\frac{F}{\varepsilon_f \hat{\varepsilon}} \chi C_M^L k_3 \left[\frac{1}{k_l} - \frac{1}{\chi KD_M} \right] e^{-\chi KL}$$

$$C = \frac{F}{\varepsilon_f \hat{\varepsilon}} \left[\frac{\chi C_o^L k_2}{2KD_o} - \frac{C_M^L k_3}{KD_M} \right]$$

$$C_1 = \frac{qn_i}{\varepsilon_f \hat{\varepsilon}}$$

After some algebraic calculations, Poisson's equation can be written as

$$-\frac{d^2U}{dx^2} = \beta_1 Ae^{-2Kx} + \beta_1 Be^{\chi Kx} + \beta_1 C + \frac{1}{L_d^2} e^{\frac{\beta_1 V}{2}} \sinh U \quad (\text{III -1.30})$$

where

$$U = \beta_1 \left\{ \phi - \frac{1}{2} (E_f^n + E_f^p) \right\}$$

$$2C_1\beta_1 = \frac{1}{L_d^2}$$

$$V = E_f^n - E_f^p$$

The first three parts in Equation (III -1.30) represent exponentially graded p - n junctions in which the net impurity concentration is given by $N_D - N_A = \beta_1 Ae^{-2Kx} + \beta_1 Be^{\chi Kx} + \beta_1 C$ with N_D and N_A being the density of donors (oxygen vacancies) and acceptors (cation vacancies), respectively. Equation (III -1.30) cannot be solved analytically. However, using numerical techniques, this equation can be solved to obtain the potential distribution through the passive oxide film. Note that in formulating

Poisson's equation, no electroneutrality condition was assumed. Under forward bias conditions, the current flow across the transition region gives rise to very small gradients in the quasi-Fermi levels, which can be neglected for the derivation of the potential distribution. The use of this pseudo-equilibrium model is particularly important in the derivation of the capacitance.

The finite difference method was used to discretize the second order differential equation (III-1.30), which was then solved using the following boundary conditions.

$$\text{At } x = 0, \phi = \phi_2 = \phi_{fs} + E_f^p \quad (\text{III -1.31})$$

$$\text{i.e. At } z = 0, U = \beta_1 \left(\beta_{fs} - \frac{V}{2} \right) \quad (\text{III -1.32})$$

and

$$\text{at } x = L, \frac{d\phi}{dx} = \varepsilon \quad (\text{III -1.33})$$

$$\text{i.e. at } z = \frac{L}{L_D} e^{\frac{\beta_1 V}{4}}, \frac{dU}{dz} = \varepsilon \beta_1 L_D e^{-\frac{\beta_1 V}{4}} \quad (\text{III -1.34})$$

The solutions of the steady-state Nernst-Planck and the Poisson's equations are shown in Figure III -1.4. The semi-nonlinearity in the potential profile is unlike that assumed in conventional theories of electron transfer through oxide films. It is suspected that this nonlinearity in potential energy will be compensated by Esaki (band-to-band tunneling) when this feature is added to the model, particularly when the donor and acceptor densities are approximately constant with distance through the film (the uniform doping approximation). For a strongly exponentially doped junction and even for a linearly graded junction, the potential profile through the film is expected to deviate significantly from linearity, because the internal band-to-band tunneling current is expected to be highly position dependent within the film. Exploration of this feature is currently underway.

- Linearly Graded p-n Junction

By further linearization of the exponential terms in Equation (III -1.30) and keeping first two terms, the Poisson's equation can be written as

$$-\frac{d^2 U}{dx^2} = \bar{A} + \bar{B}z + \sinh U \quad (\text{III -1.35})$$

where

$$z = \frac{x}{L_D} e^{\frac{\beta_1 V}{4}}$$

$$\bar{A} = \beta_1 L_D^2 (A + B + C) e^{-\frac{\beta_1 V}{2}}$$

$$\bar{B} = \beta_1 L_D^3 e^{-\frac{3}{4}\beta_1 V}$$

This model is similar to the one developed by Shockley [42], and Morgan and Smits [43] for linearly graded p-n junctions. Numerical solution of this model is required to calculate the potential distribution through the passive oxide film. The finite difference approach was used to discretize the second order

Figure III-1.4. Defect Concentration Profile and Potential Distribution through Platinum Oxide Film using Point Defect Model (PDM) plus Boltzmann Distribution

differential Equation (III -1.35) and was solved using Newton iteration method and the same boundary conditions as in (III -1.31) and (III -1.33).

The potential distribution found from the solution of the linearly graded junction is plotted in Figure III-2.1.5. Due to the linearization of the defect concentration, this potential distribution is observed to be slightly different from that shown in Figure III-2.1.4. The distribution is clearly non-linear, but the deviations are quite small. Further, the potential distribution, in this case, is closer to the linear distribution assumed in common theories for passive films than is that for the exponentially graded junction. In the conventional theory of electron transfer through passive films, it is often assumed that the film thickness remains constant as a function of applied potential, which is contradictory to the PDM. Also, in conventional theories, the dopant concentrations are taken to be constant throughout the passive oxide film which is also in contradiction to the PDM and is confirmed in the simulation results in Figures III -1.4(a) and III -1.4(b).

There are several parameters (rate constants, diffusivities etc.) that are important in affecting calculations of barrier layer properties using the PDM. Values for these parameters may be obtained using electrochemical impedance spectroscopy (EIS), as described later in this report. Thus, the parameter values are obtained by optimizing the PDM on the experimental impedance data. Values for other parameters must be assumed at the present time. The combined effect of these parameters on the PDM is very critical, and the stability of the numerical methods depend highly on the reliability of the parameter values. Parameter values used in the simulations are listed in Table III-1.1.

Figure III-1.5. Potential distribution through the oxide film on platinum as calculated using the linearized defect concentration plus Boltzmann's distribution.

Table III-1.1. Parameters used in modeling the electronic structure of the oxide film on platinum.

Parameters	Value
D_1	8.41×10^{-17} , cm ² /s
D_2	1.19×10^{-17} , cm ² /s
k_{100}	9.79×10^{-10} , cm/s
k_{200}	3.33×10^{-11} , mol/cm/s
k_{300}	1.4×10^{-11} , mol/cm/s
k_{400}	4.4751×10^{-17} , cm/s
k_{500}	1.03×10^{-10} mol ⁽¹⁻ⁿ⁾ /cm/s
Dielectric Constant, ϵ	30.4
α	0.68
α_1	0.5
α_2	0.4
α_3	0.32
α_4	0.1
V	0.8, Volt
β	-0.0025
pH	3
n	0.6
ϕ_0	0.02, Volt
L	5.5 Å

III-1.4 Summary and Conclusions

Resonant tunnel diodes have been proposed to be the closest analog to the barrier oxide layers on metals, including platinum. Potential profiles, calculated by solving Poisson's equation in conjunction with Boltzmann's and Nernst-Planck's equations, along with the Point Defect Model (PDM), are found to be non-linear, although the deviations from linearity appear to be small, particularly when the film is

assumed to be linearly graded. Exponential grading appears to yield a more non-linear potential profile through the film, but in both cases (linear and exponential grading) Esaki (band-to-band) tunneling, which has been proposed to buffer the electric field has not been incorporated into the model. Additionally, the PDM predicts that the thickness of the barrier layer varies linearly with applied voltage, whereas the conventional models for the electronic structures of passive films often tacitly assume that the thickness of the barrier layer is constant. While significant progress has been made in defining the electronic structure of the barrier oxide layer on a metal, the mathematical difficulties inherent in incorporating Esaki tunneling and degeneracy, simultaneously, necessarily means that the model is incomplete and hence that our conclusions with regard to the potential distribution are highly tentative.

List of Symbols

C_i	Concentration of species i, mol/cm ³
D_i	Diffusion coefficient of species i, cm ² /s
E	Energy, J
E_f	Fermi energy, J
e_0, q	Electronic charge, C
E_f^n	Fermi energy at the n-side of a p-n junction, J
E_f^p	Fermi energy at the p-side of a p-n junction, J
F	Farady's constant, C/mol
$F(E)$	Fermi distribution function
h	Planck's constant, J.s
H	Hamiltonian
i	Current density, amp/cm ²
J	Current density, amp/cm ²
$J_{\rightarrow}$	Anodic current density, amp/cm ²
$J_{\leftarrow}$	Cathodic current density, amp/cm ²
J_i	Flux of species i, mol/cm ² /s
k	Boltzmann constant, J/K
k_i	Reaction rate constant of species i
$k_x^{(i)}$	Complex wave number
L	Film thickness, cm
m	Electron mass, kg
m^*	Effective electron mass, kg
n	Density of electrons, #/cm ³
n_i	Electron/hole concentration in intrinsic semiconductors, #/cm ³
N	Number of acceptor species, #/cm ³
N_D	Donor density, #/cm ³
N_A	Acceptor density, #/cm ³
p	Density of holes, #/cm ³
P_T	Transmission probability
T	Absolute temperature, K
U	Potential (dimensionless)
V	Potential, volt
V_{sc}	Self-consistent Hartree potential, volt
x	Space variable, cm
z	Dimensionless space variable

Greek symbols

α	Polarizability
β	Dependence of the potential drop at barrier layer/solution interface
ε	Electric field strength, V/cm
ε_f	permittivity of free space, Farad/cm
$\hat{\varepsilon}$	dielectric constant
ρ	Density of states, $\text{cm}^{-3}\text{eV}^{-1}$
ρ_0	Constant
τ_d	Electron dwell time, s
Γ	Tunneling width, cm
χ	Metal oxidation state

References:

1. R.W. Gurney and E.U. Condon. Quantum Mechanics and Radioactive Disintegration. *Physical Review*, **33**, 127 (1929).
2. R.W. Gurney. The Quantum Mechanics of Electrolysis. *Proceedings of the Royal Society of London, Series A*, **134**, 137 (1931).
3. J.O'M. Bockris and A.K.N. Reddy. *Modern Electrochemistry*, volume 1. Plenum Press, New York, 1970.
4. H. Mizuto and T. Tanoue. *The Physics and Applications of Resonant Tunnelling Diodes*. Cambridge University Press, 1995.
5. R.J.D. Miller, G.L. Melendon, A.J. Nozik, W. Schmickler, and F. Willig. *Surface Electron Transfer Processes*. VCH Publishers, Inc., New York, 1995.
6. E. Burstein and S. Lundqvist, editors. *Tunneling Phenomena in Solids*. Plenum Press, New York, 1969.
7. L.I. Trakhtenberg V.I. Gol'danskii and V.N. Fleurov, editors. *Tunneling Phenomena in Chemical Physics*. Gordon and Breach Science Publishers, 1989.
8. L.L. Chang, E.E. Mendez, and C. Tejedor, editors. *Resonant Tunneling in Semiconductors. Physics and Applications*, volume 277 of *NATO ASI Series, Series B: Physics*. Plenum Press, New York, 1991.
9. A.M. Kuznetsov and J. Ulstrup. Theory of electron transfer at electrified surfaces. *Electrochimica Acta*, **45**, 2339 (2000).
10. J.W. Schultze and K.J. Vetter. The Influence of the Tunnel Probability on the Anodic Oxygen Evolution and the Other Redox Reactions at Oxide Covered Platinum Electrodes. *Electrochimica Acta*, **18**, 889 (1973).
11. J.W. Schultze and V.A. Macagno. Electron Transfer Reactions on Passive Tantalum Electrodes. *Electrochimica Acta*, **31**, 355 (1986).
12. W. Schmickler. A theory of resonance tunnelling at film covered metal electrodes. *J. Electroanal. Chem.*, **82**, 65 (1977).
13. W. Schmickler and J. Ulstrup. A theory of electron transfer reactions at film-covered metal electrodes. *Chemical Physics*, **19**, 217 (1977).
14. W. Schmickler. Electron Transfer Reactions at Oxide Electrodes Involving Tunnelling through a Space Charge Barrier. *Ber. Bunsenges. phys. Chem.*, **82**, 477 (1978).
15. W. Schmickler. Electron Ion Transfer Reactions on Metal Electrodes. *Electrochimica Acta*, **41**, 2329 (1996).

16. D.D. Macdonald. The Point Defect Model for the Passive State. *J. Electrochem. soc.*, **139**, 3434 (1992).
17. D.D. Macdonald. Passivity-the key to our metal-based civilization. *Pure Appl. Chem.*, **71**, 951 (1999).
18. D.D. Macdonald and M. Urquidi-Macdonald. Theory of Steady-state Passive Films. *J. Electrochem. Soc.*, **137**, 2395 (1990).
19. L. Zhang and D.D. Macdonald. On the transport of point defects in passive films. *Electrochimica Acta*, **43**, 679 (1998).
20. O. Pensado-Rodriguez, J. R. Flores, M. Urquidi-Macdonald, and D.D. Macdonald. Electrochemical Behavior of Lithium in Alkaline Aqueous Electrolytes: Ii. Point Defect Model. *J. Electrochem. Soc.*, **146**, 1326 (1999).
21. D.D. Macdonald, S.R. Biaggio, and H. Song. Steady-state Passive Films. *J. Electrochem. Soc.*, **139**, 170 (1992).
22. L. Zhang, D.D. Macdonald, E. Sikora, and J. Sikora. On the Kinetics of Growth of Anodic Oxide Films. *J. Electrochem. Soc.*, **145**, 898 (1998).
23. G.R. Engelhardt, D.D. Macdonald, and M. Urquidi-Macdonald. Development of fast algorithms for estimating stress corrosion crack growth rate. *Corrosion Science*, **41**, 2267 (1999).
24. R. Tsu and L. Esaki. Tunneling in a finite superlattice. *Appl. Phys. Lett.*, **22**, 562, (1973).
25. W.R. Frensley. Effect of inelastic processes on the self-consistent potential in the resonant-tunneling diode. *Solid State Electronics*, **32**, 1235 (1989).
26. W.R. Frensley. Numerical evaluation of resonant states. *Superlattices and Microstructures*, **11**, 347 (1992).
27. C.L. Fernando and W.R. Frensley. An efficient method for the numerical evaluation of resonant states. *Journal of Applied Physics*, **76**, 2881 (1994).
28. V. Gergel, I. Lapushkin, and A. Zakharova. Self-consistent calculation of current-voltage characteristics of resonant tunnelling structures with type ii heterojunctions, *Solid-State Electronics: An International Journal*, **39**, 1445 (1996).
29. B. Jogai, C.I. Huang, and C.A. Bozada. Electron density in quantum well diodes. *Journal of Applied Physics*, **66**, 3126 (1989).
30. B. Gelmont, D. Woolard, W. Zhang, and T. Globus. Electron transport within resonant tunneling diodes with staggered-bandgap heterostructures. *Solid State Electronics*, **46**, 1513 (2002).
31. S. Luryi. Frequency limit of double-barrier resonant-tunneling oscillators. *Applied Physics Letters*, **47**, 490 (1985).
32. S. Luryi. Coherent versus incoherent resonant tunneling and implications for fast devices. *Superlattices and Microstructures*, **5**, 375 (1989).
33. T. Weil and B. Vinter. Equivalence between resonant tunneling and sequential tunneling in double-barrier diodes. *Applied Physics Letters*, **50**, 1281 (1987).
34. L. Esaki. Long Journey into Tunneling. *Proceedings of the IEEE*, **62**, 825 (1974).
35. L. Esaki. Discovery of Tunnel diode. *IEEE Transactions on Electronic Devices*, **ED-23(7)**, 644 (1976). W. Schmickler. Resonance tunnelling through oxide layers on passive iron electrodes. *J. Electroanal. Chem.*, **83**, 387 (1977).
36. J.O'M. Bockris and R. Abdu. A theoretical study of the electrochemical reduction of oxygen. *Journal of Electroanalytical Chemistry*, **448**, 189 (1998).
37. W. Schmickler and J. Mohr. The rate of electrochemical electron transfer reactions. *Journal of Chemical Physics*, **117**, 2867 (2002).
38. A.M. Kuznetsov, R.R. Nazmutdinov, and W. Schmickler. Monte Carlo simulation of electrochemical electron transfer processes. *Journal of Electroanalytical Chemistry*, **532**, 171 (2002).
39. L. Esaki. New phenomenon in narrow germanium p-n junctions. *Phys. Rev.*, **109**, 603 (1958).

40. A. Sun and D. D. Macdonald. Study of growth and properties of thin anodic oxide films on platinum. Presented at the 204th Meeting of The Electrochemical Society, Orlando, Florida, USA, October 2003.
41. W. Shockley. Theory of p-n junctions in semiconductors and p-n junction transistors. *The Bell System Technical Journal*, **28**, 435 (1949).
42. S.P. Morgan and F.M. Smits. Potential distribution and capacitance of a graded p-n junction. *The Bell System Technical Journal*, 1573 (1960).
43. J.S. Newman. *Electrochemical Systems*. Physical and chemical engineering sciences. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1973.
44. P.N. Brown, A.C. Hindmarsh, and L.R. Petzold. *SIAM J. Sci. Comput.*, **15**, 1467 (1994).
45. R.L. Stepelman and M. Carver, editors. North Holland Publishing Company, Amsterdam, 1983.
46. W. Hackbusch and U. Trottenberg, editors. *Multigrid Methods III*, volume 98 of *International series of Numerical Mathematics*. Birkhäuser Verlag, 1991.
47. W. Briggs. *A Multigrid Tutorial*. SIAM, Philadelphia, Pennsylvania, 1987.
48. J. Wu, V. Srinivasan, J. Xu, and C.Y. Wang. Newton-Krylov-multigrid algorithms for battery simulation. *J. Electrochem. Soc.*, **149**, A1342 (2002).
49. C. Kittel. *Introduction to Solid State Physics*. John Wiley and Sons, Inc., New York, 4th edition, 1971.
50. D.J. Griffiths. *Introduction to Quantum Mechanics*. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 4th edition, 1995.
51. E.E. Mendez and K.V. Klitzing, editors. *Physics and Applications of Quantum Wells and Superlattices*. NATO ASI Series, Series B: Physics. Plenum Press, New York, 1987.
52. M.E. Davis. *Numerical Methods and Modeling for Chemical Engineers*. John Wiley and Sons, Inc., New York, 1984.
53. S.C. Chapra and R.C. Canale. *Numerical Methods for Engineers*. McGraw Hill, 1998.
54. G. Arfken. *Mathematical Methods for Physicists*. Academic Press, New York, 5th edition, 1968.
55. V.M. Volgin, O.V. Volgina, and A.D. Davydov. Finite difference method of simulation of non-steady-state ion transfer in electrochemical systems with allowance for migration. *Computational Biology and Chemistry*, **27**, 185 (2003).
56. V.M. Volgin, O.V. Volgina, and A.D. Davydov. Numerical simulation of electrochemical diffusion-migration model with reaction at electrodes. *Computer Methods in Applied Mechanics and Engineering*, **132**, 305 (1996). A. Greenbaum, editor. *Iterative Methods for Solving Linear Systems, Frontiers in Applied Mathematics*. SIAM, Philadelphia, Pennsylvania, 1997.
57. J. Ulstrup. Solid-electrolyte Tunneling. *Surface Science*, **101**, 564 (1980).
58. W. Schmickler. Resonance Tunneling through Oxide Layers on Passive Iron Electrodes. *Journal of Electroanalytical Chemistry*, **83**, 387 (1977).
59. B. Pettinger, H.R. Schöppel, T. Yokoyama, and H. Grischer. Tunneling Processes at Highly Doped ZnO-Electrodes in Aqueous Electrolytes. Part ii: Electron Exchange with the Valence Band. *Ber. Bunsenges. physik. Chem.*, **78**, 1024 (1974).
60. Y. Zhang and R. Lake. Self-consistent transit time model for a resonant tunnel diode. *IEEE Transactions on Electron Devices*, **51**, 535 (2004).
61. N.G. Tarr, D.L. Pulfrey, and D.S. Camporese. An analytical model for the MIS tunnel junction. *IEEE Transactions on Electronic Devices*, **ED-30**, 1760 (1983).
62. J.O'M. Bockris and A.K.N. Reddy. *Modern Electrochemistry*, volume 2. Plenum Press, New York, 1970.
63. J.O'M. Bockris and S.U.M. Khan. *Quantum Electrochemistry*, volume 1. Plenum Press, New York and London, 1979.
64. A. Gibson, R. Haydock, and J.P. LaFemina. The electronic structure of neutral and charged surface vacancy defects in periclase. *Applied Surface Science*, **72**, 285 (1993).
65. S. Kimura, J. Yamauchi, and M. Tsukada. First principles study on electronic structure of the (001) surface of SrTiO_3 . *Physical Review*, **51**, 11049 (1995).

66. A. Stashans, F. Erazo, J. Ortiz, and P. Valverde. Oxygen vacancy defects on the sr₂tiO₃ (001) surface: a quantum-chemical study. *Philosophical Magazine B*, **81**, 1977 (2001).
67. G. Bastard and J.A. Brum. Electronic states in semiconductor heterostructures. *IEEE Journal of Quantum Electronics*, **QE-22**, 1625 (1986).
68. C.B. Duke and M.E. Alferieff. Field Emission through Atoms Adsorbed on a Metal Surface. *Journal of Chemical Physics*, **46**, 923 (1967).
69. J.W. Gadzuk and E.W. Plummer. Field Emission Energy Distribution (feed). *Reviews of Modern Physics*, **45**, 487 (1973).
70. J.J. Kelly and R. Memming. The influence of surface recombination and trapping on the cathodic photocurrent at p-type iii-iv electrodes. *J. Electrochem. Soc.*, **129**, 730.
71. R.A. Marcus. On the Theory of Oxygen-Reduction Reactions Involving Electron Transfer. i. *Journal of Chemical Physics*, **24**, 966 (1956).
72. R.A. Marcus. On the Theory of Electron-Transfer Reactions. vi. Unified Treatment for Homogeneous and Electrode Reactions. *Journal of Chemical Physics*, **43**, 679 (1965).
73. H. Lawrence and R.M. Warner. Diffused junction depletion layer calculations. *The Bell System Technical Journal*, 389 (1960).
74. B.R. Chawla and H.K. Gummel. Transition region capacitance of diffused p-n junctions. *IEEE Transactions on Electronic Devices*, **ED-18**, 178 (1971).
75. J. Prakash and H. Joachin. Electrocatalytic activity of ruthenium for oxygen reduction in alkaline solution on transfer processes. *Electrochimica Acta*, **45**, 2289 (2000).
76. S. Sze. *The Physics of Semiconductor Devices*. Wiley and Sons, New York, 2nd edition, 1981.

Issues/Concerns: None.

III-2. Task 2: Experimental Characterization of Passive Films on Noble Metals and Noble Metal Alloys (Researcher: Adan Sun)

Characterization of the passive film formed on platinum is being carried out to determine:

1. Identity of the principal defect(s) and hence the electronic type (n- vs. p-type semiconductor).
2. The structure of the passive film (single layer versus bilayer).
3. The thickness of the barrier layer as a function of voltage.
4. The importance of dissolution processes in controlling the properties of the film.
5. The growth model for the film from an analysis of potentiostatic current and film thickness transients, with the latter being determined by fast recording, spectroscopic ellipsometry.
6. Transport data for the defects in the film and kinetic data for defect generation and annihilation at the interfaces (c.f., previous work on Ni and W) by electrochemical impedance spectroscopy (EIS).

Data from all of these studies are required to accurately characterize the electronic structures of passive films and hence to develop viable models for electron transfer and electrocatalysis.

The identity of the principal defect in the barrier oxide film on platinum has been determined by Mott-Schottky (M-S) analysis [1]. In M-S analysis, the capacitance of the passive film is measured at a suitably high frequency as a function of voltage. According to Mott-Schottky theory [2], the space charge capacitance of an n-type semiconductor is given by

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon\epsilon_0 N_D A^2} \left(V - V_{fb} - \frac{kT}{e} \right) \quad (\text{III-2.1})$$

where A is the area, N_D is the donor concentration, ϵ_0 is the vacuum permittivity, ϵ is the dielectric constant of the oxide, V is the applied potential, V_{fb} is the flat band potential, e is the electron charge, and kT/e has a value of about 25 mV at room temperature. A similar expression exists for p-type material, except that the slope of $1/C^2$ vs V is of the opposite sign. In addition to confirming the electronic nature of the film, M-S analysis yields the dopant concentration (donor or acceptor) in the film as a function of voltage; information that is vital for modeling purposes.

One way to measure the thickness of the passive films is the application of ellipsometry. The method is particularly attractive for probing the properties of passive films, because it is non-destructive and can be carried out *in situ*, is extremely sensitive to minute interfacial effects, and can be used to measure film thickness ranging from monoatomic to micron dimensions. Ellipsometry [3] involves measurement of the change in the state of polarization of light upon reflection from the sample surface. The state of polarization is defined by the phase and amplitude relationships between the two component plane waves (p wave and s wave) into which the electric field is resolved. In general, reflection causes a change in relative phases of the p and s waves and a change in the ratio of their amplitudes, because the two components travel different path lengths (the p-wave tends to be reflected at the film/solution interface, whereas the s-wave tends to reflect from the metal/film interface). The change in phase is characterized by the angle Δ , while the amplitude ratio change is characterized by $\tan[\psi]$. Accordingly, an ellipsometric measurement essentially involves the determination of Δ and $\tan[\psi]$. The thickness and the dielectric properties (complex refractive index) of the film are then deduced by an analysis of the ellipsometry parameters. If the film is electrochemically active, a potential difference applied across the film may change the film parameters (e.g., thickness and refractive index) and hence alter the polarization of the reflected light. Monitoring the polarization of the reflected light while changing the applied voltage can be done *in situ*, as noted above, thereby attesting to the enormous power of electrochemical

ellipsometry. In the present program, we are using *in situ* electrochemical ellipsometry to measure the thickness of passive films on platinum under steady state and transient conditions.

An ultimate characterization of the passive films on noble metals and alloys is being performed using electrochemical impedance spectroscopy (EIS). Rather than deriving “equivalent electrical circuits,” which are analogs and not models, EIS is being employed to distinguish between different mechanisms and to determine kinetic parameters, as has been previously done for the passive films on Ni [4]. The power of EIS lies in the fact that each frequency yields a separate experimental observation, so that it is possible, by measuring the impedance at many frequencies, to resolve the kinetic parameters (rate constants and transfer coefficients) for multistep reaction mechanisms. All impedance data employed in the analysis are being verified as conforming to the constraints of linear system theory (LST) by using the Kramers-Kronig transforms [5].

Task Status:

III-2.1 Anodic Oxide Film

The kinetics of oxide film growth on Pt was first studied by using cyclic voltammetry. Figure III-2.1 shows a typical cyclic voltammogram measured by cycling the potential between 0.05 and 1.4V_{SHE} at ambient temperature (20°C) in 0.5M H₂SO₄ solution.

The reduction peak centered at 0.63V_{SHE} reflects the reduction of the α -oxide film, which is consistent with data reported in the literature [6-10]. The two anodic peaks at lower potentials correspond to the oxidation of adsorbed hydrogen on different crystallographic planes, while the two cathodic peaks at the same potentials correspond to deposition of hydrogen atoms onto those same crystallographic planes on the polycrystalline electrode used in the present study. The symmetry of the anodic and cathodic peaks demonstrates the reversibility of the deposition/desorption process (Equation III-2.2) on platinum. As many as three peaks have been resolved in other studies and it is suspected that additional peaks, corresponding to still more crystallographic planes, may be “buried” in the voltammogram in the hydrogen adsorption/desorption region.

As seen from Figure III-2.1, the formation of the “ α -oxide” occurs at potentials starting from about 0.8 V_{SHE} and extends to oxygen evolution, which occurs at $V > 1.4$ V_{SHE}. Within this range, the current attains a plateau between ca. 1.0 to 1.4V_{SHE}. It is also noted that the reduction peak in the first cycle occurs at less positive potentials, and the magnitude of the peak is higher, than those in subsequent cycles. The reason for this is that, in the first cycle, the electrode surface is in the mechanically polished state, and the strain energy and mechanical defects are present on the surface, giving rise to a high surface energy and hence to a high current density. After one cycle, the electrode surface assumes a lower surface energy with less defects, which allows for good reproducibility in the polarization curves. Since

$Q = \int_0^t i dt = \int_{V_0}^V \frac{i}{\nu} dV$, where ν the scan rate in the cyclic voltammetry, the charge densities Q_a for anodic formation of surface oxide and Q_c for cathodic reduction were calculated from the areas under anodic formation potential region of the oxide film and the cathodic peak. The double layer correction is made by subtracting the value of the current in the double layer region. Previous work[11] found that, in properly purified solution, Q_a is exactly equal to Q_c below 1.2V vs. SHE. The ratio of Q_a to Q_c obtained in the current experimental work is 1.37, which is greater than 1. However, in the current work, the potential is swept anodically to 1.4V vs. SHE, which is within the oxygen evolution region. Therefore, this discrepancy arises probably owing to the substantial quantities of oxygen adsorption into platinum or the weak anodic dissolution of oxide film.

Figure III-2.1. Cyclic voltammograms for platinum in 0.5M H₂SO₄ measured at a voltage sweep rate of 50mV/s (T = 20°C). Working electrode surface area = 0.32 cm².

The effect of temperature on the cyclic voltammograms for Pt was also studied. Figures III-2.2 and III-2.3 show cyclic voltammograms for Pt at temperatures of 60°C and 80°C, respectively. Both the anodic polarization plateau (oxide formation) and cathodic peak (oxide reduction) are observed at these two higher temperatures, but the distinct hydrogen adsorption/desorption peaks are lost. These results clearly demonstrate the formation of the anodic oxide film at potentials over the range of 1.2-1.45V_{SHE}. The magnitude of the cathodic peak corresponding to oxide reduction, $I_{p,c}$, is found to increase with increasing temperature, as shown in Figure III-2.4. This probably reflects the effect of temperature on both the rates of oxide formation and reduction.

During the high temperature (60°C and 80°C) work, we also found that if the cyclic voltammogram is swept to a potential that is higher than 1.4V_{SHE}, a second cathodic peak is observed at a potential of about 1.3V_{SHE} (Figure III-2.5 and III-2.6). From the thermal expectation that the higher oxide is reduced at the more positive potential, this new cathodic peak is due to the reduction of Pt(IV). Therefore, the composition of the oxide film at higher potentials must contain two cationic species, Pt²⁺ and Pt⁴⁺. Detailed structural and composition data for the passive film on platinum was characterized by using XPS, as described below.

Figure III-2.2. Cyclic voltammograms for platinum in 0.5M H₂SO₄ measured at a voltage sweep rate of 50mV/s (T=60°C). Working electrode surface area = 0.32 cm².

Figure III-2.3. Cyclic voltammograms for platinum in 0.5M H₂SO₄ measured at a voltage sweep rate of 50mV/s (T=80°C). Working electrode surface area = 0.32 cm².

Figure III-2.4. Cyclic voltammograms for platinum in 0.5M H₂SO₄ measured at a voltage sweep rate of 50mV/s at three different temperatures. Working electrode surface area = 0.32 cm².

Figure III-2.5. Cyclic voltammograms for platinum in 0.5M H₂SO₄ measured at a voltage sweep rate of 50mV/s (T=60°C) with different upper limits of the potential.

Figure III-2.6. Cyclic voltammograms for platinum in 0.5M H_2SO_4 measured at a voltage sweep rate of 50mV/s ($T=80^\circ\text{C}$) with different upper limit of sweep potential.

III-2.2 Steady State Growth of Pt Oxide Film

Potentiostatic experiments were performed to grow the oxide film until the film reached a steady state. This generally occurred after 24 hours of polarization. Figure III-2.7 shows that the logarithm of the steady state current density remains constant as a function of the film formation potential over the potential range of 1.15 to 1.35 V_{SHE} at different temperatures. At higher potentials, particularly for the two highest temperatures, the steady state current is observed to increase. These current-potential relationships are consistent with the diagnostic criteria of PDM [1] for n-type semiconducting oxide films at lower potentials, which predicts that the current should be independent of potential if the dominant defect in the barrier layer is the cation interstitial or the oxygen vacancy, and for p-type films at higher potentials, where the dominant defect is reckoned to be the cation vacancy or if an increase in the oxidation state of the cation occurs upon ejection from the barrier layer, even when the cation interstitial is the dominant defect. The n-type electronic character of the oxide film has been demonstrated by the capacitance measurements (Mott Schottky analysis) performed in the present work. It is also noted that the current density increases with temperature. The increase of the steady state current density with the temperature is consistent with Figure III-2.4, Section 2.1, which also shows that the reaction rate increases while the temperature increases.

Figure III-2.7. Steady state current density as a function of formation potential at different temperatures.

Electrochemical impedance data for platinum in the oxide formation region under steady state conditions were measured as a function of potential across the passive range at different temperatures (Figures III-2.8, III-2.9, and III-2.10). The experimental impedance spectra are plotted in the form of Nyquist plots, in which the imaginary component of the impedance is plotted against the real component for decreasing frequencies. As noted in Figure III-2.8-III-2.10, the complex plane plots at high frequencies are almost linear and are insensitive to the formation voltage. This finding is in agreement with the predictions of PDM for the form of the impedance of a passive film. In terms of the postulates of the PDM, the electric field strength is independent of the formation potential, and the transport of the defects is driven by the electric field strength. Therefore the impedance should be insensitive to the film formation potential [12]. Also, it is observed that the Nyquist plots tend to take the form of semicircles as the temperature increases. The faradic process for oxide film growth was modeled as a space charge capacitance in parallel with the charge transfer impedance and the electronic resistance of the film. When temperature is low, the capacitance is dominant compared with the resistance. This results in an oxide film that is more capacitive and the Nyquist plot is shown in the form of a steep straight line. As the temperature is increased, the number of free electrons and holes increases, which leads to a smaller electronic resistance. Thus, the resistance, which is primarily due to interfacial reactions, starts to have more impact on the growth reaction of the oxide film and the Nyquist plot starts to look like a semicircle.

Since the stability of the system, during EIS measurement, is critical for ensuring that the data are valid, certain precautions were taken. Because a steady state interface should afford the same response regardless of whether the measurements are made in the forward or reverse frequency sweep directions, the frequencies were scanned (stepped) from low to high frequency and then immediately scanned in the reverse direction. Figure III-2.11 reveals that both the Nyquist plot and the Bode plot are in good agreement regardless of the direction of frequency scan frequency scans.

Figure III-2.8. Nyquist plots for oxidized platinum at different oxide formation potentials. $T = 20^\circ\text{C}$.

Figure III-2.9. Nyquist plots for oxidized platinum at different oxide formation potentials. $T = 60^\circ\text{C}$.

Figure III-2.10. Nyquist plots for oxidized platinum at different oxide formation potentials. $T = 80^\circ\text{C}$.

Figure III-2.11. Nyquist plot and Bode plot of oxidized platinum at 1.24V_{SHE}. T= 20°C.

Kramers-Kronig transform were also employed to examine the linearity, causality, and stability of the system. The K-K transforms were first introduced by Kronig [13] and Kramers [14]. These relations, originally developed for the field of optics, establish a connection between the real and imaginary parts of complex physical quantities for the responses of physical systems to conjugate perturbations. Based on the assumption that four physical conditions, causality, stability, linearity, and finity, are fulfilled, the derivation of the K-K relations are a purely mathematical result and do not reflect any physical property or condition of the tested system. Thus, only experimental data satisfying the above four conditions can be used to describe the properties of the systems in terms of linear response theory. In the case of electrochemical impedance, Macdonald and Urquidi-Macdonald [15-16] derived the mathematical relations transforming the real part of impedance into the imaginary part of impedance and vice versa. They explored iron in 1M H₂SO₄ at the open circuit for the sensitivity of the K-K transform to linearity and stability of the electrochemical system. The results show that the K-K transforms are strongly sensitive to the violation of the stability condition of the system. Clearly, the K-K transforms represent a powerful means of detecting violations of these critical constraints in EIS. Here, we applied the K-K relations to experimental impedance data for oxidized platinum, the value of one impedance component (real or imaginary) is calculated when the other component is known over the entire frequency range. Figure III-2.12 shows that the impedance data at room temperature correctly transform according to the

integral K-K transform, demonstrating that the system obeys the constraints of Linear Systems Theory (LST).

Figure III-2.12. K-K transform of EIS data of oxidized platinum at 1.19V_{SHE} at T=20°C.

III-2.3 Electronic Properties

An understanding of local structural and electronic properties of the platinum oxide film is vital in exploring the mechanism of the oxygen reduction reaction on oxidized platinum. Since a large number of defects exist in an oxide film, these defects might be involved in the catalytic process during the oxygen reduction reaction. Mott-Schottky analysis, based upon capacitance measurements, has been employed to determine certain fundamental parameters of the oxide, such as the electronic type, the effective donor or acceptor density (N_D or N_A), and the flat band potential. The basic equations of Mott-Schottky analysis are written as

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon\epsilon_0 N_D A^2} \left(V - V_{fb} - \frac{kT}{e} \right) \quad \text{n-type}$$

$$\frac{1}{C_{sc}^2} = \frac{-2}{\epsilon\epsilon_0 N_A A^2} \left(V - V_{fb} - \frac{kT}{e} \right) \quad \text{p-type}$$

where ϵ is the dielectric constant of the oxide, A is the surface area of the interface, and ϵ^0 is the vacuum permittivity. The interfacial capacitance, C is obtained from $C = -1/\omega Z''$. Assuming that the double layer at the oxide/electrolyte interface can be neglected (i.e., the double layer capacitance is much larger than the space charge capacitance in the film), the measured capacitance C is equal to the space charge capacitance, C_{sc} . On the basis of this relationship, the defect density can be obtained from the slope of the plot if ϵ and A are known.

In the Mott-Schottky experiments reported here, the specimen was first passivated for 24 hrs at a given formation potential, in order to attain a steady state film thickness. The capacitance calculated from the imaginary part of the impedance measured at a fixed, high frequency was recorded as a function of potential, as the potential was swept in the negative direction at a sufficiently high voltage scan rate that the properties of the film (thickness, dopant density) did not change. Thus, if the voltage sweep rate is sufficiently high, the thickness of the passive film will not change significantly, and the vacancy structure and concentration are “frozen in” the film. A Mott-Schottky plot, C^{-2} versus V , measured on oxidized Pt in 0.5 M H_2SO_4 at room temperature is presented in Figure III-2.13. The profile between 1.0-1.3 V_{SHE} is characteristic of n-type semiconductors. This result shows that the dominant defects in the oxide film (barrier layer) over this voltage range are oxygen vacancies and/or platinum interstitials, as invoked in the Point Defect Model (PDM) [1] (see Figure II-8). Interestingly, the slope of the plot is found to change to a negative value at higher potentials ($E > 1.3 V_{SHE}$), which was first considered as indicating a change in electronic character to p-type. However, as described above, the data shown in Figure III-2.13 correspond to a single voltage sweep and hence to a “frozen-in” defect type and concentration, so that a change to cation vacancies as the dominant defect, which would be required for the onset of p-type properties, would seem to be unlikely.

Figure III-2.13. Mott-Schottky plot oxidized platinum at the oxide formation potential of 1.39 V_{SHE} in 0.5M H_2SO_4 solution after polarization for 24 hrs at $T=20^\circ C$. Sinusoidal perturbation frequency = 10^4 Hz. Sinusoidal amplitude = 10mV (peak-to peak). Voltage scan rate = 100 mV/s.

As seen in Figures III-2.14, III-2.15 and III-2.16, regions of negative slope exist in all of the Mott-Schottky plots, but the potentials for the onset for the negative-slope are different for each case. This is contrary to the expectation that p-type should be observed only in the formation potential region where cation vacancies become the dominant defect. A “conventional” Mott-Schottky plot at 20°C (Figure III-2.17) was constructed, in which the capacitance measured under steady-state conditions, measured at a frequency of 10^3 Hz, is plotted against the formation potential. The slope in this plot is positive, which is consistent with n-type characteristic of oxidized platinum, and of importance is that the downward curvature is no longer observed. The calculated donor density here is $3.8 \times 10^{22} / \text{cm}^3$, which is in the range of the donor densities (Figure III-2.21) calculated from the experimental measurements (Figure III-2.14). As we assumed in the capacitance measurements, the passive film must be in the steady state and the voltage sweep rate is sufficiently high, then the vacancy structure and concentration are frozen in the film during the voltage sweep. Figure III-2.18 indicates that the capacitance depends on the voltage scan rate, which indicates the oxide film might not reach a steady state condition, even after 24hrs of passivation.

The capacitance was measured at different frequencies (Figure III-2.19). The curves were shifted to lower values with decreasing frequency. Additionally, non-linearity in the Mott-Schottky plots was also observed.

Figure III-2.14. Mott-Schottky plot of oxidized platinum at different formation potentials in 0.5 MH_2SO_4 solution for 24 hrs at $T=20^\circ\text{C}$. Sinusoidal perturbation frequency = 10^4 Hz. Sinusoidal amplitude = 10mV (peak-to-peak). Voltage scan rate = 100 mV/s.

Figure III-2.15. Mott-Schottky plot of oxidized platinum at different formation potentials in 0.5 MH_2SO_4 solution for 24 hrs at $T=60^\circ\text{C}$. Sinusoidal perturbation frequency = 10^4 Hz. Sinusoidal amplitude = 10mV (peak-to peak). Voltage scan rate = 100 mV/s.

Figure III-2.16. Mott-Schottky plot of oxidized platinum at different formation potentials in 0.5 MH_2SO_4 solution for 24 hrs at $T=80^\circ\text{C}$. Sinusoidal perturbation frequency = 10^4 Hz. Sinusoidal amplitude = 10mV (peak-to peak). Voltage scan rate = 100mV/s

Figure III-2.17. Mott-Schottky plot of oxidized platinum constructed from the capacitance data at 1194 Hz in 0.5 MH_2SO_4 solution at $T=20^\circ C$. Sinusoidal amplitude =10mV (peak-to peak).

Figure III-2.18. Mott-Schottky plot for oxidized platinum at 1.39 V_{SHE} in 0.5 MH_2SO_4 solution for 24 hrs as a function of scan rates at $T=20^\circ C$. Sinusoidal perturbation frequency = 10^4 Hz. Sinusoidal amplitude =10mV (peak-to peak).

Figure III-2.19. Mott-Schottky plot for oxidized platinum at 1.39 V_{SHE} in $0.5 \text{ M H}_2\text{SO}_4$ solution for 24 hrs as a function of frequencies at $T=20^\circ\text{C}$. Sinusoidal amplitude = 10 mV (peak-to peak). Voltage scan rate = 100 mV/s .

As stated by Morrison [17], there are several contributions to the capacity at a semiconductor/solution interface. The measured interfacial capacitance is estimated as follows:

$$C^{-1} = (C_{sc} + C_{ss})^{-1} + C_H^{-1}$$

where C_{sc} is the space charge capacitance, C_{ss} is the surface state capacitance, and C_H is the Helmholtz double layer capacitance. In order to simplify the above equation to $C^{-1} = C_{sc}^{-1}$, the classical Mott-Schottky theory made several assumptions, such as absence of surface states and that the double layer capacitance is much greater than the space charge capacitance in the film (barrier layer). However, as has been shown in many studies, including this work, the anodic oxide film formed on platinum in the oxygen reduction region is only a few monolayers thick, the Debye length is of the same order as the thickness of the depletion layer, thereby negating the assumption that the dimension is infinite in the through-thickness direction. Thus, the assumption that the potential approaches the bulk value asymptotically is not valid. Also, slow transfer of the electrons to/from surface states, due to an insufficiently high sweep frequency applied during the experimental measurements of the capacitance might cause the surface state capacitance C_{ss} not to be negligible compared with C_{sc} , which might then give rise to frequency-dependence of the capacitance in the Mott-Schottky plots. Ion movement could be another source of frequency dependence for the heavily doped platinum oxide film with the very thin space charge region [17].

Classical Mott-Schottky theory also assumes that the defects in the film are doped uniformly. However, as the PDM predicts, the spatial distribution of defects in the oxide film extends from a region very close to the film/solution interface varies exponentially with distance, which is demonstrated by the simulation results from the optimization of PDM on the impedance data (Figure III-2.25). Thus, the appearance of non-linearity in Mott-Schottky plots of oxidized platinum could be associated with the nonuniform doping of defects in the film.

The impact of temperature on the capacitance, as shown in Figure III-2.20, shows that the capacitance decreases with increasing temperature. Since the thickness of the barrier layer is calculated through $L = \epsilon\epsilon_0/C$, where ϵ is the dielectric constant of the film, ϵ_0 is the vacuum permittivity, it is apparent that the thickness of the barrier layer increases with the temperature.

In terms of classical Mott-Schottky theory, the defect concentration can be calculated from the slope of the Mott-Schottky plot. However, on carrying out this calculation, we found that this method failed to yield the expected doping profiles of Pt oxide film, possibly due to the non-linearity and the downward curvature of the plots. Figure III-2.21 show that the donor density increased with the formation potential with neglecting the downward curvature of the plots, in which the donor density is calculated from Mott-Schottky plots by using the parameter value obtained from the optimization of PDM on EIS $\epsilon=30$ (Table III-2.2) and $A=2.25\text{cm}^2$. Furthermore, as the temperature increases the donor density decreases. Since an accurate and robust determination of defect concentration in the oxide film is critical to the outcome of this work, we are examining various methods to improve the analysis of capacitance measurements so that a precise electronic structure of Pt oxide film can be described.

Figure III-2.20. Mott-Schottky plot for oxidized platinum at 1.24 V_{SHE} in 0.5 MH_2SO_4 solution for 24 hrs as a function of temperatures. Sinusoidal perturbation frequency = 10^4 Hz. Sinusoidal amplitude = 10mV (peak-to-peak). Voltage scan rate = 100 mV/s.

Figure III-2.21 Donor density calculated in terms of Mott-Schottky methods as a function of formation potential at three temperatures.

III-2.4 Compositions of Oxide Film

Controversy about the composition of the platinum anodic oxide film formed in sulfuric solution remains and determining the composition as a function of various independent variables remains an active research area in this field. In attempts to clarify the chemical composition of the oxide layer(s), various structural and surface analytical methods have been used to characterize the electrode surface. The most direct way of deducing the chemical identity is by X-ray photoelectron spectroscopy (XPS). Quite a few surface compositions, determined by XPS [17,19], have been suggested for the α -oxide, including PtO, PtO₂, Pt(OH)₂ or Pt(OH)₄. However, most of the interpretations did not integrate the XPS results with published electrochemical literature to support or refute previously proposed oxide surface structural and electrochemical models based on those structures.

As indicated in Figure III-2.1, the formation potential region of the platinum oxide film is between 1.0-1.4V_{SHE}. The oxides are first grown at different formation potentials for 24 hrs, and then rinsed by D.I. water and dried in the air. This is followed by transferring the samples to the sample introduction compartment of the spectrometer. Survey spectra of the surface detect platinum, oxygen, and carbon, with the carbon being attributed to contamination. The platinum 4f spectra of electrodes measured at two takeoff angles and the corresponding simulation curves are shown in Figure III-2.22. It is observed that the oxide film contains only Pt²⁺ peaks at a voltage 1.2V_{SHE}. However at two higher formation potentials, 1.39V_{SHE} and 1.44V_{SHE}, both Pt²⁺ and Pt⁴⁺ peaks exist in the oxide film. The in-depth distribution of these species was established by angle-resolved measurements.

The data presented in Table III-2.1 show that the atomic concentration of these species increases with decreasing takeoff angle. Since at a small takeoff angle the signal is more surface sensitive, these results show that the oxide film contains two species (Pt²⁺ and Pt⁴⁺) at higher potentials, and that Pt⁴⁺ is located in the outer part of the passive film, while Pt²⁺ is located in the inner part of the film. As most of the previous work [20-22] using electrochemical methods suggest, the thin oxide formed in the range of 1.0-1.4V_{SHE} mainly contains the Pt(II) valence, but with an increase in the potential up to 1.4 V_{SHE}, Pt(II) at the outer surface is oxidized to Pt(IV), which results the formation of the outer layer of the thick passive film. The second cathodic peak corresponding to Pt(IV) in the cyclic voltammogram at high temperatures, 60°C and 80°C (Figure III-2.4 and Figure III-2.5) is easily observed at a potential around 1.2V_{SHE} when the upper limit of the sweep potential is over 1.4V_{SHE}. However at room temperature, the

second cathodic peak [20] is usually observed at a potential of 0.2-0.4 V_{SHE} , which is a less positive potential than the first cathodic peak. This observed behavior is probably due to the higher stability of the oxide structures at room temperature. The increase of atomic concentration of these species with the formation potential indirectly indicates that the thickness of the oxide film increases with the formation potential.

Figure III-2.22. XPS spectra of the Pt4f regions recorded at two different takeoff angles for Pt surfaces passivated in 0.5M H_2SO_4 for 24 hrs at different potentials at $T=20^\circ C$.

Table III-2.1. Atomic concentration of the Pt4f regions recorded at two different takeoff angles for Pt surfaces passivated in 0.5M H_2SO_4 for 24 hrs at three different potentials.

Polarization Potential/ V_{SHE}	90° Pt^{2+}	90° Pt^{4+}	90° Pt^0	25° Pt^{2+}	25° Pt^{4+}	25° Pt^0
1.19	2.312	0	97.688	3.820	0	96.18
1.39	4.853	0	95.147	9.156	4.647	86.197
1.44	10.862	11.096	78.042	17.362	16.203	66.435

III-2.5 Growth Mechanism of Pt Oxide Film

Capacitance measurements performed in this work indicate that the Pt oxide film grown in the “oxide formation region” (1.0-1.3V_{SHE}) is a highly defective n-type semiconductor oxide. That the oxide film has a bi-layer structure, where Pt²⁺ exists in the barrier layer and Pt⁴⁺ resides in the outer layer, is also observed by XPS measurements. Therefore, the experimental results carried out in this work are consistent with the postulates of PDM on passive film formed on the surface of metals. In addition, the diagnostic criteria of PDM for n-type oxide films, that the logarithm of the steady state current density is constant as the formation potential increases, is also observed experimentally. Thus, Figure III-2.23 summarizes the physicochemical processes that are envisioned to occur within the barrier layer of the passive film formed on platinum, according to the PDM. The model applied here is a truncated version of the more general PDM. Since, for an n-type oxide film, the dominant defects in the barrier layer on platinum within the passive state will most likely be oxygen vacancies and/or cation interstitials, the generation and annihilation of cation vacancies are excluded [1].

Figure III-2.23. Schematic of physicochemical processes that are envisioned to occur within the barrier oxide (PtO_{χ/2}) layer on passive platinum, according to the truncated Point Defect Model. Pt ≡ platinum atom; Pt_i^{χ+} ≡ interstitial platinum cation; v_{Pt} ≡ platinum vacancy in the Pt; Pt_{Pt} ≡ platinum cation in a normal cation position; Pt^{τ+} ≡ platinum cation in the solution phase; V_O^{••} ≡ oxygen vacancy; O_O ≡ oxygen ion in an anion site.

Reaction (1) describes the injection of the metal interstitial, Pt_i^{χ+}, into the barrier layer. The platinum interstitial is then transmitted through the barrier layer, primarily under the influence of the electric field, and is then ejected into the solution, as described by Reaction (3). Reaction (2) results in the growth of the barrier layer into the bulk platinum via the generation of oxygen vacancies (V_O^{••}), and Reaction (5) leads to the destruction of the barrier layer by dissolution. Reaction (4) represents the annihilation of the oxygen vacancies at the film/solution interface that are produced by Reaction (2) at the

metal/film interface. Note that Reactions (1), (3), and (4) are lattice conservative processes, in that their occurrence does not result in the movement of the corresponding interface with respect to a laboratory frame of reference, while Reactions (2) and (5) are lattice non-conservative processes. A steady state must involve a balance between at least two non-conservative reactions, since only one non-conservative reaction would lead to monotonic growth or thinning of the passive film.

A physico-electrochemical/mathematical model has been developed for the anodic oxide film on Pt for the purpose of interpreting electrochemical impedance spectroscopy (EIS) data. The model employed is a variant of that previously developed for interpreting EIS data for Alloy 22 [23], and is essentially a truncated form of the general PDM discussed elsewhere in this report.

The rate of change of barrier layer thickness involves the two lattice non-conservative reactions, resulting in the following expression:

$$\frac{dL}{dt} = -\frac{2\Omega}{\chi} J_o - \Omega k_5 c_{H^+}^n \quad (\text{III-2.3})$$

where the first term on the right hand side corresponds to barrier layer generation at the alloy/film interface [Reaction (2), Figure III-2.23] and the second term corresponds to the dissolution of the barrier layer at the barrier layer/solution interface [Reaction (5), Figure III-2.23]. The parameter $\Omega=14.97\text{cm}^3\text{mol}^{-1}$ is the molar volume per cation of the barrier layer (PtO), $\chi = 2$ is the oxidation state of platinum in the barrier layer in the passive state, J_o is the flux of oxygen vacancies within the barrier layer, c_{H^+} is the hydrogen ion concentration in the solution at the film/solution interface, n is the kinetic order of the film dissolution reaction with respect to c_{H^+} , and k_5 is the rate constant for Reaction (5), Figure III-2.23.

All interfacial reactions that produce or consume electrons contribute to the total current density, which is described as

$$i = F[-\chi J_i^{m|f} - 2J_o^{m|f} - (\Gamma - \chi)J_i^{f|s} + (\Gamma - \chi)k_5 c_{H^+}^n] \quad (\text{III-2.4})$$

in which $F = 96487 \text{ C mol}^{-1}$ is Faraday's constant, and $\Gamma = 2$ is the oxidation state of platinum in solution in the passive range.

The fluxes of the point defects in the barrier layer may be written as $J_i = -D_i(\partial c_i / \partial x) - \chi K D_i c_i$ and $J_o = -D_o(\partial c_o / \partial x) - 2K D_o c_o$ for platinum interstitials and oxygen vacancies, respectively, where D and c are the diffusivity and concentration, and subscripts i and o designate platinum interstitials and oxygen vacancies. Additionally, $K = \varepsilon F / RT$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the gas constant, T is the absolute temperature, and ε is the electric field strength, which is considered to be a constant, according to the PDM [23]. The continuity equations $\partial c / \partial t = -\nabla J$ then become

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + \chi D_i K \frac{\partial c_i}{\partial x} \quad (\text{III-2.5})$$

and

$$\frac{\partial c_o}{\partial t} = D_o \frac{\partial^2 c_o}{\partial x^2} + 2D_o K \frac{\partial c_o}{\partial x} \quad (\text{III-2.6})$$

These equations are then solved for the initial conditions ($t = 0$) of $c_i(x) = c_i^0(x)$ and $c_o(x) = c_o^0(x)$ and for the boundary conditions ($t > 0$) of: $x = 0$ (the film/solution interface), $J_i(0) = -k_3^0 e^{a_3 V} c_i(0)$ (k_3^0 , cm/s), $J_o(0) = -(\chi/2)k_4^0 e^{a_4 V} c_o(0)$ (k_4^0 , cm/s); at $x = L$ (the metal/film interface), $J_i(L) = -k_1^0 e^{a_1 V} e^{-b_1 L}$ (k_1^0 , mol s⁻¹ cm⁻²), $J_o(L) = -(\chi/2)k_2^0 e^{a_2 V} e^{-b_2 L}$ (k_2^0 , mol s⁻¹ cm⁻²). Note that the fluxes of cation interstitials and oxygen vacancies are negative when the species move from the metal/film (m/f) interface to the film/solution (f/s) interface in the coordinate system adopted in Figure III-2.23. Combined with the rate constants, the rate of change of the barrier layer thickness (Equation (III-2.3)) and the current density (Equation (III-2.4)) then become

$$\frac{dL}{dt} = -\Omega k_2^0 e^{a_2 V} e^{-b_2 L} - \Omega k_5^0 e^{a_5 V} c_{H^+}^n \quad (\text{III-2.7})$$

and

$$i = F [\chi k_1^0 e^{a_1 V} e^{-b_1 L} + \chi k_2^0 e^{a_2 V} e^{-b_2 L} + (\Gamma - \chi) k_3^0 e^{a_3 V} c_i(0) + (\Gamma - \chi) k_5^0 e^{a_5 V} c_{H^+}^n] \quad (\text{III-2.8})$$

where c_{H^+} has units of mol/cm³.

Note that the current density (Equation (III-2.8)) is a function of V , L , and $c_i(0)$. Accordingly, for any arbitrary changes in δV , δL , and $\delta c_i(0)$ we have

$$\delta i = \left(\frac{\partial i}{\partial V} \right)_{L, c_i(0)} \delta V + \left(\frac{\partial i}{\partial L} \right)_{V, c_i(0)} \delta L + \left(\frac{\partial i}{\partial c_i(0)} \right)_{V, L} \delta c_i(0) \quad (\text{III-2.9})$$

The variations in V , L , and $c_i(0)$ are sinusoidal in an EIS measurement, so that we write $\delta V = \Delta V e^{j\omega t}$, $\delta L = \Delta L e^{j\omega t}$, and $\delta c_i(0) = \Delta c_i(0) e^{j\omega t}$; note that ΔX is the amplitude of the variation in X at a frequency $\omega = 0$. From Equation (III-2.10), the Faradic admittance is then defined as

$$Y_f = \frac{\delta i}{\delta V} = i^V + i^L \frac{\Delta L}{\Delta V} + i^{c_i(0)} \frac{\Delta c_i(0)}{\Delta V} \quad (\text{III-2.10})$$

where $i^V = (\partial i / \partial V)_{L, c_i(0)}$, $i^L = (\partial i / \partial L)_{V, c_i(0)}$, and $i^{c_i(0)} = [\partial i / \partial c_i(0)]_{V, L}$. These differentials will be evaluated later from Equation (III-2.8).

We now return to Equation (III-2.7) and determine the response of $\partial L / \partial t$ to δV , δL , and $\delta c_i(0)$ by taking the total differentials. Thus, for the relaxation in film thickness $d(\delta L) / dt = \Omega k_2^0 a_2 e^{a_2 V} e^{-b_2 L} \delta V - \Omega k_2^0 b_2 e^{a_2 V} e^{-b_2 L} \delta L - \Omega k_5^0 a_5 e^{a_5 V} c_{H^+}^n \delta V$. Considering that $d(\delta L) / dt = j\omega \Delta L e^{j\omega t}$, we obtain

$$j\omega \Delta L e^{j\omega t} = \Omega (k_2^0 a_2 e^{a_2 V} e^{-b_2 L} - k_5^0 a_5 e^{a_5 V} c_{H^+}^n) \Delta V e^{j\omega t} - \Omega k_2^0 b_2 e^{a_2 V} e^{-b_2 L} \Delta L e^{j\omega t} \quad (\text{III-2.11})$$

which, upon rearrangement, yields

$$\frac{\Delta L}{\Delta V} = \frac{\Omega(k_2^0 a_2 e^{a_2 V} e^{-b_2 L} - k_5^0 a_5 e^{a_5 V} c_{H^+}^n)}{\Omega k_2^0 b_2 e^{a_2 V} e^{-b_2 L} + j\omega} \quad \text{or} \quad \frac{\Delta L}{\Delta V} = \frac{\Phi_2}{1 + j\omega\tau_2} \quad (\text{III-2.12})$$

where

$$\Phi_2 = \left(\frac{a_2}{b_2} \right) - \left(\frac{k_5^0}{k_2^0} \right) \left(\frac{a_5}{b_2} \right) e^{(a_5 - a_2)V} e^{b_2 L} c_{H^+}^n \quad (\text{III-2.13})$$

and

$$\tau_2 = \frac{1}{\Omega k_2^0 b_2 e^{a_2 V} e^{-b_2 L}} \quad (\text{III-2.14})$$

For platinum interstitials, the relaxation for $c_i(0)$ is determined through the mass balance at the film/solution interface $dc_i(0)/dt = -k_3' c_i(0) = -k_3^0 e^{a_3 V} c_i(0)$ (units of k_3^0 are s^{-1}). The total differential is $d(\delta c_i(0))/dt = -k_3^0 [a_3 e^{a_3 V} c_i(0) \delta V + e^{a_3 V} \delta c_i(0)]$. Inserting the sinusoidal variations for δV and $\delta c_i(0)$ therefore yields

$$j\omega \Delta c_i(0) e^{j\omega t} = -k_3^0 a_3 e^{a_3 V} c_i(0) \Delta V e^{j\omega t} - k_3^0 e^{a_3 V} \Delta c_i(0) e^{j\omega t} \quad (\text{III-2.15})$$

and

$$\Delta c_i(0)(j\omega + k_3^0 e^{a_3 V}) = -k_3^0 a_3 e^{a_3 V} c_i(0) \Delta V. \quad (\text{III-2.16})$$

Therefore,

$$\frac{\Delta c_i(0)}{\Delta V} = \frac{-k_3^0 a_3 e^{a_3 V} c_i(0)}{j\omega + k_3^0 e^{a_3 V}} = -\frac{a_3 c_i(0)}{1 + j\omega\tau_3} \quad (\text{III-2.17})$$

in which

$$\tau_3 = \frac{1}{k_3^0 e^{a_3 V}} \quad (\text{III-2.18})$$

The expression for the Faradaic admittance is finally derived from Equation (III-2.10) as

$$Y_f = j^V + j^L \frac{\Phi_2}{1 + j\omega\tau_2} - j^{c_i(0)} \frac{a_3 c_i(0)}{1 + j\omega\tau_3} + j\omega c \quad (\text{III-2.19})$$

in which the parallel geometric capacitance $C = \hat{\epsilon}\epsilon_0 / L$ (dielectric constant of $\hat{\epsilon} = 30$ for the PtO barrier layer (see later) and with the vacuum permittivity, $\epsilon_0 = 8.85 \times 10^{-14} \text{ F/cm}$) is taken into consideration, and

$$j^V = \left(\frac{\partial j}{\partial V} \right)_{L, c_i(0)} \quad (\text{III-2.20})$$

$$= F[a_1 \chi k_1^0 e^{a_1^V} e^{-b_1^L} + a_2 \chi k_2^0 e^{a_2^V} e^{-b_2^L} + a_3 (\Gamma - \chi) k_3^0 e^{a_3^V} c_i(0) + a_5 (\Gamma - \chi) k_5^0 e^{a_5^V} c_{H^+}^n]$$

$$j^L = \left(\frac{\partial j}{\partial L} \right)_{V, c_i(0)} \quad (\text{III-2.21})$$

$$= F[-b_1 \chi k_1^0 e^{a_1^V} e^{-b_1^L} - b_2 \chi k_2^0 e^{a_2^V} e^{-b_2^L}] = -\chi F[b_1 k_1^0 e^{a_1^V} e^{-b_1^L} + b_2 k_2^0 e^{a_2^V} e^{-b_2^L}]$$

$$j^{c_i(0)} = \left(\frac{\partial j}{\partial c_i(0)} \right)_{V, L} = (\Gamma - \chi) F k_3^0 e^{a_3^V} \quad (\text{III-2.22})$$

In the above expressions, the parameters that appear on the right side [L and $c_i(0)$] are identified with the steady-state quantities. At steady state, Equations (III-2.5) and (III-2.6) become

$$\frac{\partial^2 c_i}{\partial x^2} + \chi K \frac{\partial c_i}{\partial x} = 0 \quad (\text{III-2.23})$$

and

$$\frac{\partial^2 c_o}{\partial x^2} + 2K \frac{\partial c_o}{\partial x} = 0 \quad (\text{III-2.24})$$

The solutions for these equations can be written as

$$c_i(x) = A_i e^{-\chi K x} + B_i \quad (\text{III-2.25})$$

and

$$c_o(x) = A_o e^{-2Kx} + B_o \quad (\text{III-2.26})$$

The expressions for the fluxes therefore become

$$J_i = -\chi K D_i B_i \quad (\text{III-2.27})$$

and

$$J_o = -2K D_o B_o \quad (\text{III-2.28})$$

From the boundary conditions, the coefficients are obtained as

$$B_i = \frac{k_1^0 e^{a_1 V} e^{-b_1 L}}{\chi K D_i} \quad (\text{III-2.29})$$

and

$$B_o = \frac{(\chi/2) k_2^0 e^{a_2 V} e^{-b_2 L}}{2 K D_o} \quad (\text{III-2.30})$$

Because the fluxes for a given species at the two interfaces are equal at steady state:

$-k_3^0 e^{a_3 V} c_i(0) = -k_1^0 e^{a_1 V} e^{-b_1 L}$ and $-(\chi/2) k_4^0 e^{a_4 V} c_o(0) = -(\chi/2) k_2^0 e^{a_2 V} e^{-b_2 L}$. The steady-state concentrations of platinum interstitials and oxygen vacancies at the film/solution interface are

$$c_i(0) = \left(\frac{k_1^0}{k_3^0} \right) e^{(a_1 - a_3)V} e^{-b_1 L} \quad (\text{III-2.31})$$

and

$$c_o(0) = \left(\frac{k_2^0}{k_4^0} \right) e^{(a_2 - a_4)V} e^{-b_2 L} \quad (\text{III-2.32})$$

In the case of the steady state, Equation (III-2.3) becomes

$$J_o(L) = -(\chi/2) k_5 c_{H^+}^n \quad (\text{III-2.33})$$

and from Equations (III-2.28) and (III-2.30), we obtain

$$-(\chi/2) k_5 c_{H^+}^n = -2 K D_o \left(\frac{(\chi/2) k_2^0 e^{a_2 V} e^{-b_2 L}}{2 K D_o} \right) \quad (\text{III-2.34})$$

Therefore, the steady-state barrier layer thickness is

$$L_{ss} = \left(\frac{a_2 - a_5}{b_2} \right) V - \frac{1}{b_2} \ln \left[\left(\frac{k_5^0}{k_2^0} \right) c_{H^+}^n \right] \quad (\text{III-2.35})$$

The parameters, k_1^0 , k_2^0 , k_3^0 , k_4^0 , k_5^0 , in the above equations are a function of solution pH and are not the standard rate constants for the interfacial reactions, since the PDM defines $k_1^0 = k_1^{00} e^{-\alpha_1 \beta \chi \text{pH}} e^{-\alpha_1 \chi \gamma \phi_{fs}^0}$, $k_2^0 = k_2^{00} e^{-\alpha_2 \beta \chi \text{pH}} e^{-\alpha_2 \chi \gamma \phi_{fs}^0}$, $k_3^0 = k_3^{00} e^{\alpha_3 \beta \Gamma \text{pH}} e^{\alpha_3 \Gamma \gamma \phi_{fs}^0}$, $k_4^0 = k_4^{00} e^{\alpha_4 \beta \Gamma \text{pH}} e^{\alpha_4 \Gamma \gamma \phi_{fs}^0}$, and $k_5^0 = k_5^{00} e^{\alpha_5 \beta (\Gamma - \chi) \text{pH}} e^{\alpha_5 (\Gamma - \chi) \gamma \phi_{fs}^0}$, in which α_1 , α_2 , α_3 , α_4 , α_5 are the transfer coefficients, and k_1^{00} , k_2^{00} , k_3^{00} , k_4^{00} , k_5^{00} are the standard rate

constants. The potential drop across the film/solution (f|s) interface is $\phi_{f|s} = \phi_f - \phi_s = \alpha V + \beta \text{pH} + \phi_{f|s}^0$ and that across the metal/film (m|f) interface is $\phi_{m|f} = \phi_m - \phi_s = (1 - \alpha)V - \varepsilon L - \beta \text{pH} - \phi_{f|s}^0$, in which $\alpha = d\phi_{f|s} / dV$ is the dependence of the potential drop across the barrier layer/solution interface on the applied voltage, V , (i.e., α is the polarizability of the barrier layer/outer layer (solution) interface); $\beta = d\phi_{f|s} / d\text{pH}$ is the dependence of the potential drop across the same interface on pH; $\phi_{f|s}^0$ is the value of $\phi_{f|s}$ in the standard state; $\gamma = F / RT$; and $K = \varepsilon \gamma = \varepsilon F / RT$.

The experimental impedance data, and that calculated from the PDM, for different formation potentials for the n-type oxide on platinum are displayed in Figure III-2.24. The commercial DataFit software was employed in this work for optimization of the PDM on the experimental impedance data, in order to obtain the values for the transfer coefficients, α_i , and the standard rate constants, k_i^{00} , for the i elementary interfacial reactions, the polarizability of the film/solution interface, α , the electric field strength, ε , and other parameters, as described below. The values for the kinetic order of the dissolution reaction at the film/solution interface with respect to the $[\text{H}^+]$, and the value for β and $\phi_{f|s}^0$ were assumed. The comparison in Figure III-2.24 shows that the correlation between experimental impedance data and the simulated data is quite good for the Nyquist plots shown.

The model parameters extracted for the oxide film formed on Pt at a potential of 1.24V_{SHE} at 20°C, 60°C and 80°C are presented in Table III-2.2. From Figure III-2.23, we see that Reactions (2) and (5), Figure III-2.23 describe the formation and destruction of the barrier layer oxide film. The parameters k_2^{00} and k_5^{00} are standard rate constants for Reaction (2) and (5) and should be independent of the potential, thickness, and pH, if they are truly model parameters and if the model faithfully describes the properties of the system. However, the kinetic parameters at 20°C, 60°C and 80°C in Table III-2.2, k_2^{00} and k_5^{00} are predicted to increase with the temperature, as described by the Arrhenius equation. This expectation is born out by the data summarized in the table.

Classical Mott-Schottky analysis can only determine an overall film vacancy concentration. In order to determine an actual concentration profile of oxygen vacancies in the film, a relationship between film thickness and vacancy concentration has been developed on the basis of the Point Defect Model. This relationship specifies the vacancy concentration at the film/solution interface, where electrocatalytic oxygen reduction occurs. Therefore, As stated in PDM, the flux of oxygen vacancies, J_o , through the passive film may be written as

$$J_o = -D_o \frac{\partial C_o}{\partial x} - 2D_o \gamma C_o \frac{d\phi}{dx}$$

where $Y=F/RT$, and D_o is the diffusion coefficient of oxygen vacancies.

The concentration profile for oxygen vacancy in the steady state is obtained by solving the Nernst-Planck equation to yield:

$$\begin{aligned} C_o(x) &= A_o e^{-2Kx} + B_o \\ \text{Here } B_o &= \frac{(\chi/2)k_2}{2KD_o}, \quad A_o = k_2 [1/k_4 - 1/(2KD_o)] \end{aligned}$$

where $\chi=2$, k_2 and k_6 are the rate constants for reaction (2) and reaction (4) in Figure III-2.23, respectively, and $K=\varepsilon Y$, ε is the mean electric field strength.

Figure III-2.24. Nyquist plot of experimental and simulated impedance data for oxidized platinum in 0.5M H_2SO_4 at different formation voltage at $T=20^\circ C$.

Table III-2.2. Extracted kinetic parameters from optimization of PDM for n-type platinum oxide formed at potential 1.29V_{SHE} on EIS data at three different temperatures.

	20C	60C	80C
Cdl (F/cm ²)	1.3627e-4	1.1424e-4	1.7941e-4
ε (V/cm)	1200000	1200000	1200000
ε [^]	30.0000	30.0000	30.0000
k ¹⁰⁰ (mol/cm ² s)	2.4082e-16	6.9177e-16	6.7933e-15
k ²⁰⁰ (mol/cm ² s)	4.5997e-17	8.4608e-16	9.3135e-14
k ⁵⁰⁰ (mol ^{0.5} /cm ^{-0.5} s)	1.7336e-11	1.2389e-10	1.0200e-9
α	0.6763	0.7435	0.7438
α1	0.6025	0.4915	0.4070
α2	0.1815	0.2950	0.1965
n	0.5000	0.5000	0.5000
β	-1.0000e-3	-1.0000e-3	-1.0000e-3
φ _{f/s} ⁰ (V)	-0.0100	-0.0100	-0.0100

Therefore, C_O(0) is the concentration of the surface oxygen vacancies at the film/solution interface, where the oxygen reduction reaction occurs. The concentration of oxygen vacancies in the platinum oxide film formed at potential 1.14V vs. SHE, as calculated from the equation (1), is shown in Figure III-2.25. The value of k₂ is calculated from the parameter values in table III-2.2, k₄ is assumed at present time, and D_O = 4e-17 cm²/s [24]. C_O(0) is obtained from the intercept of the plot with the y axis, which is 2.0e21/cm³.

Further work on refining the PDM is underway now. The refined model will be applied to analyze the impedance data and to extract the parameter values for calculating k₂ and k₄ in order that the concentration of the surface oxygen vacancies is described more precisely.

Figure III-2.25 Concentration of Oxygen vacancies vs.the distance within the passive film formed on platinum in 0.5M H₂SO₄ solution at a voltage of 1.14V_{SHE}.

References:

1. D.D. Macdonald, *Pure Appl. Chem.*, **71**, 951 (1999)
2. S.Sze, *The Physics of Semiconductor Devices* (2nd Edit.), Wiley & Sons, N.Y., 1981
3. H.G.Tompkins, *A User's Guide to Ellipsometry*, 1993
4. D.D. Macdonald and S.I. Smedley, *Electrochim. Acta*, **35**, 1949 (1990)
5. M.Urquidi-Macdonald, S. Real, and D.D.Macdonald, *Electrochim. Acta*, **35**, 1559 (1990)
6. B.E. Conway, G.Tremiliosi-Filho and G. Jerkewicz, *J. Electroanal. Chem.* **297**, 435 (1991)
7. P.Ross, *Surf. Sci.* **102**, 463 (1981)
8. B.E. Conway and G. Jerkewicz, *J. Electroanal. Chem.* **339**, 123 (1992)
9. H. Angerstein-Kozłowska, B.E. Conway and W.B.A. Sharp, *Electroanalytical Chemistry and Interfacial Electrochemistry*, **43**, 9 (1973)
10. A. Damjanovic, L.-S.R. Yeh, and J.F. Wolf, *J. Electrochem. Soc.: Electrochemical Science and Technology* 1945 (1980)
11. G. Tremiliosi-Filho, G. Jerkewicz and B.E. Conway, *Langmuir*, **8**, 658 (1992)
12. E. Sikora, D.D. Macdonald, *Electrochimica Acta* **48**, 69 (2003)
13. R.de L. Kronig, *J. opt. Soc. Am.* **12**, 547 (1926)
14. H.A. Kramers, *Z. Phys.* **30**, 521 (1929)
15. D.D. Macdonald, and M.Urquidi-Macdonald, *J. Electrochem. Soc.*, **132**, 2316 (1985).
16. M.Urquidi-Macdonald, S. Real, and D.D. Macdonald, *J. Electrochem. Soc.*, **133**, 2018 (1986)
17. S. R. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, Plenum Press, New York and London, 1980
18. B.R. Chawla and H.K. Gummel, *IEEE Transactions on Electron Devices*, **ED-18**, 178 (1971)
19. M. Peuckert and H.P. Bonzel, *Surface Science*, **145**, 239 (1984)
20. R.Parsons and W. Visscher, *J. Electroanal.Chem.* **36**, 329 (1972)
21. S.J. Xia and V.I. Birss, *Electrochimica Acta* **45**, 3659 (2000)
22. G. Jerkiewicz, G. Vatankhah, J. Lessard, M. P. Soriaga, and Y-S. Park, *Electrochim. Acta* **49**, 1451 (2004)
23. D.D. Macdonald, A. Sun, N. Priyantha, and P. Jayaweera, *J. Electroanal. Chem.*, **572**, 421 (2004)
24. www.pnas.org/cgi/reprint/100/7/3870.pdf

Issues/Concerns: None

III-3. Task 3 and 4: Kinetic Study of Oxygen Reduction and Hydrogen Oxidation on Platinum Electrode (Researcher: Jianer Bao)

In this part, we are experimentally investigating the kinetics of charge transfer reactions on pure and oxidized platinum in order to obtain data to test the theories being developed for electrocatalysis. It was found that the rate of hydrogen oxidation decreased with the formation of an oxide film on platinum[14] (Figure II-1), in keeping with the findings of many other workers [2-4, 9-13], while the rate of the oxygen reduction apparently increases with film formation at high temperatures (275°C) (Figure II-2). The decrease in the rate of oxygen reduction is consistent with rate-limiting quantum mechanical tunneling of charge carriers through the oxide film, but the result for the reduction of oxygen at 275°C would seem to indicate that tunneling is not the rate-limiting process under these conditions. Rather, we postulate that the reaction rate may be limited by the involvement of surface defects (oxygen vacancies); a postulate that satisfies the constraint that the exchange current density of the OER must be much smaller than that for the HER. This yet-to-be-confirmed result is not only of great theoretical interest, but it is of significant practical interest, because second generation proton exchange membrane (PEM) fuel cells are envisioned to operate at temperatures significantly above 100°C. High temperature operation is being considered, in order to reduce the catalyst loading and to alleviate poisoning of the anode by carbon monoxide and other species.

Thus, our approach is to devise experimental systems that can differentiate between the quantum mechanical tunneling of charge carriers across the passive film on platinum and the involvement of surface oxygen vacancies in the reduction of oxygen on the surface of oxidized platinum. Three sets of reaction systems have been designed to explore these issues: pure platinum oxidation and reduction in deoxygenated solutions, oxidation of hydrogen on pure and oxidized platinum, and oxygen reduction on platinum. Preliminary results obtained and theories developed for the cyclic voltammogram of platinum, as well as that for hydrogen oxidation on oxidized platinum, are discussed below.

Task Status:

III-3.1 Cyclic Voltammogram of Platinum

Cyclic voltammogram of platinum both over the full voltage range of kinetic stability of liquid water (from hydrogen evolution reaction to oxygen evolution) and within the platinum oxide formation/reduction region was used to explore the reactions that occur on the metal surface. Figure III-3.1 shows typical cyclic voltammograms for platinum using a rotating ring disk electrode (RRDE) in 0.1M KOH at ambient temperature (20°C). The rotation speed was 900rpm, corresponding to a Reynolds number ($Re = \omega r^2 / \nu$, where ω , r , and ν are the angular velocity, disk radius (0.75cm, including the Teflon sheath), and kinematic viscosity of the solution (dynamic viscosity divided by the density, approximately $9 \times 10^{-3} \text{cm}^2/\text{s}$ [15] at room temperature), respectively, of 5888. This value is less than the critical value of 2×10^5 for transition from laminar to turbulent flow, so that we conclude that the system was operating under laminar flow conditions. The voltage sweep rate used in acquiring the voltammograms was 30mV/s starting from a sufficiently negative potential (-1.0V vs. SCE) that hydrogen was being evolved from the metal surface. The forward-going potential sweep was reversed at progressively more positive potentials, as indicated in Figure III-3.1. Nitrogen gas was bubbled through the solution before each experiment, and then purged above the solution surface during the experiments. The cell comprised three separate compartments, in order to avoid contamination of the working electrode compartment with reaction products from the counter electrode. The cell was designed to achieve dynamic sealing, so that gases other than nitrogen (hydrogen and oxygen in the latter experiments) are not contained within the cell.

Figure III-3.1. Cyclic voltammogram of platinum in 0.1M KOH at 20°C with progressively more positive reversing potentials. Sweep rate = 30mV/s, rotation speed = 900rpm.

As shown in Figure III-3.1, three hydrogen adsorption peaks ($H_2O + e^- \rightarrow H_{ads} + OH^-$) are found on the reverse sweep at potentials prior to hydrogen evolution that are matched by three hydrogen atom oxidation peaks ($H_{ads} + OH^- \rightarrow H_2O + e^-$) on the forward sweep. That the conjugate peaks occur at the same potentials on the forward and reverse sweeps in the hydrogen adsorption/desorption region is predicted by electrochemical adsorption theory[8]. The three peaks are postulated to arise from adsorption onto different crystallographic planes of the polycrystalline platinum surface employed in the present work. In any event, the findings of the present work are consistent with studies reported in the literature[16-21]. Since the primary objective of the present work is to explore the impact of the oxide film on the kinetics of charge transfer reactions on platinum, and not on the adsorption/desorption of hydrogen atoms, little attention will be paid further in this report to the processes that occur in the hydrogen region.

The voltammograms plotted in Figure III-3.1 also shows that platinum oxidation starts at a potentials of about -0.2V (vs. SCE), and as the reversing potential increases, the oxygen reduction peak shifts to more negative potentials and the peak becomes more prominent. This is the expected behavior, in that increasing the potential of sweep reversal results in the formation of a thicker oxide film on the surface.

According to electrochemical thermodynamics calculations, the equilibrium potential for platinum oxidation:

at 25°C is 0.996V and 1.019V (vs. SHE) in pH=0 acid, respectively. In this case, the pH corrected equilibrium potential for platinum oxidation is around 0.213V (vs. SHE, which is -0.03V vs. SCE), which

corresponds well with the experimental result, as it sits within the oxidation peak. The increase of current at potentials more positive than the oxide formation region is primarily due to oxygen evolution.

Substrate oxidation and reduction processes on platinum in nitrogen-deaerated 0.1M KOH at 20°C were examined by cyclic voltammogram within the potential range of -0.05V to 0.4V (vs. SCE) as a function of voltage sweep rate, as shown in Figures III-3.2 and III-3.3. The potential range was chosen so that the electrochemical reduction of PtO at the metal/barrier layer interface

probably does not occur (lowest potential is significantly more positive than the PtO reduction peak shown in Figure III-3.1). Occurrence of the above reaction would significantly complicate the theory (see below), because it would be necessary to include the time dependence of the concentration of oxygen vacancies at the metal/barrier layer interface.

Figure III-3.2. Cyclic voltammograms for the oxidation and reduction of a platinum electrode in 0.1M KOH at 20°C as a function of voltage sweep rate. Rotation speed = 900rpm. Initial voltage sweep direction: negative to positive.

Figure III-3.3. Oxidation and reduction of platinum in 0.1M KOH. Sweep rate: 100mV/s. Sweep direction: positive. Rotation speed: 900rpm.

It is clearly seen that the amount of charge transferred is different between the positive-going sweep and reverse sweep, resulting in the accumulation of oxide on the surface (i.e., a net oxidation of the metal occurs over a potential cycle). This is the direct result of reversing the negative-going sweep at a sufficiently positive sweep that no electro reduction of the oxide occurs at the metal/barrier layer interface. Had the sweep reversal potential been set at a value that is more negative than the peak potential for the oxide reduction peak shown in Figure III-3.1, the net charge would be close to zero as was observed when the potential was swept down to $-0.3V_{SCE}$. The difference is especially clear for the first sweep loop as seen in Figure III-3.3, and decreases with further sweeps.

The theory of platinum oxidation and reduction is developed in terms of the Point Defect Model (PDM)[1, 6], which quantitatively predicts the oxide film growth rate law. As the film thickness L varies with potential, then, at a constant potential sweep rate ν within the potential range V_1 to V_2 , assuming that oxygen reduction is negligible within this range (deaerated solution), the dynamic growth of the platinum oxide film could be written as

$$\frac{dL}{dt} = A'' e^{a_3 V} e^{-b_3 L} - C \quad (\text{III-3.1})$$

where A'' is a constant, and C is the film dissolution rate. By mathematical manipulation (see Appendix II for details), it is derived that during the positive potential sweep

$$V = V_1 + \nu t \quad (\text{III-3.2})$$

the thickness of the oxide film is a function of the sweep rate and time

$$L = \frac{a_3 \nu}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r / A}{1 - e^{-b_3 r(t-t_0)} + \frac{r}{A} e^{-[b_3 r(t-t_0) + a_3 \nu t_0 - b_3 L_0]}} \right\} \quad (\text{III-3.3})$$

where r is a defined parameter as $r = C + \frac{a_3 \nu}{b_3}$, $A = A'' e^{a_3 V_1}$, L_0 is the film thickness at t_0 , and a_3 , b_3 and c_3 come from the rate constant for the third reaction in the PDM model: $m \xrightarrow{k_3} M_M + \frac{\chi}{2} V_O^- + \chi e^-$ (see Appendix I for the reaction scheme and meaning of each parameter)

$$k_3 = k_3^0 e^{a_3 V} e^{b_3 L} e^{c_3 pH} \quad (\text{III-3.4})$$

with $a_3 = \alpha_3(1 - \alpha)\chi\gamma$, $b_3 = \alpha_3\chi K$, and $c_3 = -\alpha_3\beta\chi\gamma$ (α is polarizability of the film/solution interface, α_3 is the transfer coefficient, χ is the metal oxidation state, $K = \frac{\bar{\epsilon}F}{RT}$, $\gamma = \frac{F}{RT}$). For the negative potential sweep, we can similarly derive the film growth equation by replacing ν to $-\nu$, L_0 to L_0' , which is the film thickness at potential V_2

$$L' = L_0' - \frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r' / A'}{1 - e^{-b_3 r'(t-t_0)} + \frac{r'}{A'} e^{-[b_3 r'(t-t_0) - a_3 v t_0 - b_3 L_0']}} \right\} \quad (\text{III-3.5})$$

now $r' = C - \frac{a_3 v}{b_3}$, $A' = A'' e^{a_3 V_2}$. If assume the initial thickness of film at t_0 is zero, then

$$L_0' = \frac{a_3 (V_0' - V_0)}{b_3} - \frac{1}{b_3} \ln \left\{ \frac{r / A}{1 - (1 - r/A) e^{-\frac{b_3 C (V_0' - V_0)}{v}} e^{-a_3 (V_0' - V_0)}} \right\} \quad (\text{III-3.6})$$

The passive current for substrate metal is usually composed of the metal oxidation /reduction and oxide film dielectric charging in terms of the PDM

$$i_p = F \chi k_3^0 e^{a_3 V} e^{a_3 v t} e^{-b_3 L} e^{-c_3 p H} + \frac{\varepsilon \varepsilon_0}{L} v \quad (\text{III-3.7})$$

here ε is the dielectric constant, ε_0 is the permittivity of free space. Thus during the positive potential sweep

$$i_p = F \chi k_3^0 e^{a_3 V_1} e^{-c_3 p H} \frac{r/A}{1 - (1 - r/A) e^{-b_3 r t}} + \frac{\varepsilon \varepsilon_0}{\frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r / A}{1 - (1 - r/A) e^{-b_3 r t}} \right\}} v \quad (\text{III-3.8})$$

and for the negative potential sweep

$$i_p' = F \chi k_3^0 e^{a_3 V_2} e^{-c_3 p H} e^{-b_3 L_0'} \frac{r'/A'}{1 - (1 - r'/A') e^{-b_3 r t} + \frac{r'}{A'} e^{b_3 L_0'}} - \frac{\varepsilon \varepsilon_0}{L_0' - \frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r'/A'}{1 - (1 - r'/A') e^{-b_3 r t} + \frac{r'}{A'} e^{b_3 L_0'}} \right\}} v \quad (\text{III-3.9})$$

Kinetic parameters could be extracted from numerical simulation of the experimental work, which thereafter could be compared with other works like EIS. However, due to the time limitation, the work will not be discussed here.

III-3.2 Hydrogen Oxidation on Oxidized Platinum

As described in the background section (Figure II-1), when increasing the potential from the open potential value of the hydrogen oxidation reaction on platinum, the current first increases to a plateau corresponding to rate control by mass transfer of H_2 to the surface. As the potential is increased further, the logarithm of the current density decreases linearly with increasing voltage, due to quantum

mechanical tunneling of charge carriers through a barrier layer whose thickness increases linearly with voltage. The current decreases at the point where the formation of the platinum oxide film is initiated, as determined by comparing the potential of this point with the equilibrium potential for Pt/PtO. These previous experiments were carried out at elevated temperatures (50°C to 300°C)[14]. The present work on hydrogen oxidation on oxidized platinum is restricted to ambient temperature (20°C).

Figure III-3.4 (a) and (b) show voltammograms for the oxidation of hydrogen on platinum at voltage sweep rates of 5mV/s and 50mV/s, respectively. Hydrogen at a pressure of 1 bar was bubbled through the solution before the experiments for more than 15 minutes, and then blanketed above the surface while the experiments were being conducted. The dissolved concentration of hydrogen in the solution is calculated to be around 1.4ppm. The cell used is the same as previously described in Section III-3.1. The potential was swept from the H₂ open circuit value (around -1.0V_{SCE}) to various oxidation potentials and was then reversed in a negative-going sweep back to the initial potential.

Figure III-3.4. Hydrogen oxidation behavior on platinum in 0.1M KOH. (a) sweep rate: 5mV/s. (b) 50mV/s. Rotating speed: 900rpm. Initial potential sweep direction: negative to positive.

The current density starts is observed to decrease gradually with increasing potential at potentials above -0.2V_{SCE} where the oxide film is formed. At the low sweep rate (5mV/s), the current density decreased greatly and extends to the high potential region. However, at the high sweep rate (50mV/s), after an initial small decrease, the current becomes stable until oxygen evolution occurs.

Furthermore, the hysteresis in the current increases as the reversal potential increases, indicating that the formation and subsequent reduction of the oxide on platinum is only quasi-reversible. Of particular importance is the appearance of a peak on the negative-going sweep immediately after reversal of the potential sweep. This peak, which is attributed to oxide reduction at potentials where the hydrogen oxidation current is suppressed by the low tunneling probability through the film, becomes increasingly prominent as the reversal potential extends into the oxygen evolution region (i.e., as the film becomes thicker and hence as the tunneling probability becomes even smaller), as seen from Figure III-3.4 (b). Finally, as shown in Figure III-3.4 (b) at the high sweep rate, considerable hysteresis between the forward and reverse sweeps persists at potentials as low as -0.90V_{SCE}, suggesting that a phase exists through which charge carriers must tunnel, also persists down to this highly negative potential. This phase remains unidentified, but it apparently exists at sufficiently negative potentials that it might have an impact on hydrogen oxidation under fuel cell operating conditions, but presumably this would only be an issue if the electrode had been subject to prior exposure to very oxidizing conditions.

According to Gurney[3, 2], Vetter[4], Moffat and coworkers[5], and many other workers, the current due to the tunneling of charge carriers across the oxide film can be written as:

$$i = \hat{i}_0 e^{-\beta L} \quad (\text{III-3.10})$$

where β is the tunneling constant, and $\hat{i}_0$ is the “film-free” hydrogen oxidation current density. In the present work, we have developed a theory for hydrogen oxidation on passive metals in terms of the quantum mechanical tunneling or charge carriers (e.g., electrons) across the film and the Point Defect Model, the latter describes the film growth law.

From the above theoretical work, we know that the thickness of the platinum oxide film varies as a function of sweep rate and time during the constant potential sweep, assuming that the film grows quick enough, then the hydrogen oxidation current density on oxide covered electrode during the positive potential sweep is therefore:

$$i(t) = \hat{i} \left\{ \frac{r / A}{1 - e^{-b_3 r(t-t_o)} + \frac{r}{A} e^{-[b_3 r(t-t_o) + a_3 v t_o]}} \right\}^{\beta / b_3} \cdot e^{-\frac{\beta a_3 v t}{b_3}} \quad (\text{III-3.11})$$

if initially there is no film covered on the surface ($L_0=0$). Setting $t_0 = 0$, and substituting $t = \frac{V - V^0}{v}$, then yields:

$$i(V) = \hat{i} \left\{ \frac{r / A}{1 - (1 - \frac{r}{A}) e^{-b_3 r \frac{V - V^0}{v}}} \right\}^{\beta / b_3} \cdot e^{-\frac{\beta a_3 (V - V^0)}{b_3}} \quad (\text{III-3.12})$$

Thus, we have obtained the current density of hydrogen oxidation on the passive platinum film. However, what we collected experimentally is the total of the hydrogen oxidation current, the passive current for platinum oxidation, and the oxide charging current. From PDM, we can describe the passive current as:

$$i_{pass} = F[\chi k_1 C_M^L + \chi k_2 + \chi k_3 + (\delta - \chi)k_4 + (\delta - \chi)k_5 C_i^0 + (\delta - \chi)k_7 (C_{H^+} / C_{H^+}^0)^n] \quad (\text{III-3.13})$$

Assuming that we have only a growth current, the current density for oxide film growth with $\delta = \chi$ is

$$i_{pass} = F \chi k_3^0 e^{a_3 V} e^{-b_3 L} e^{-c_3 p H} \quad (\text{III-3.14})$$

and, finally, for linear voltage sweep conditions,

$$i_{pass} = F \chi k_3^0 e^{a_3 V^0} e^{-c_3 p H} \frac{r / A}{1 - (1 - r/A) e^{-b_3 r \frac{V - V^0}{v}}} \quad (\text{III-3.15})$$

As before, the charging current density can be written as

$$i_{charging} = C_{ox} \frac{dV}{dt} \quad (\text{III-3.16})$$

where $C_{ox} = \frac{\epsilon\epsilon_0}{L}$ is the capacitance of the oxide film, and ϵ the dielectric constant. Thus:

$$i_{charging} = \frac{\epsilon\epsilon_0}{L} v = \frac{\epsilon\epsilon_0 v}{\frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r/A}{1 - (1 - r/A) e^{-b_3 r \frac{V-V^0}{v}}} \right\}} \quad (\text{III-3.17})$$

The total current density is then:

$$i_{total} = \hat{i} R^{\beta/b_3} \cdot e^{-\frac{\beta a_3}{b_3} (V-V^0)} + F \chi k_3^0 e^{a_3 V^0} e^{-c_3 pH} R + \frac{\epsilon\epsilon_0 v}{\frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln R} \quad (\text{III-3.18})$$

where $R = \frac{r/A}{1 - (1 - r/A) e^{-b_3 r \frac{V-V^0}{v}}}.$

The polarization curves, measured under cyclic voltage polarization conditions, for hydrogen oxidation on a passive platinum electrode have been calculated. By optimizing this model on the experimental results (by Matlab constrained optimization), the theory will permit the extraction of values for various parameters in the PDM and tunneling model, which may then be compared with values obtained for the same parameters using Electrochemical Impedance Spectroscopy (EIS).

The current process describes the irreversible formation of the oxide at the metal/film interface, so that film thinning occurs exclusively by dissolution at the film/solution interface. A more comprehensive model that includes oxide reduction at the metal/oxide interface is currently being developed and will be applied to the interpretation of cyclic voltammogram data from oxidized platinum.

Returning now to the data plotted in Figure II-1 (see below), it is evident that in the quantum mechanical tunneling region $\log(i)$ decreases linearly with voltage, as previously noted. The theoretical basis of this behavior is readily accounted for by the Point Defect Model and quantum mechanical tunneling theory, as shown below.

Thus, according to the Point Defect Model [1, 6], the steady state thickness of the barrier oxide layer on the metal surface can be written as

$$L_{ss} = \left(\frac{1 - \alpha}{\epsilon} \right) (V - V_0) \quad (3-19)$$

where α is the polarizability of the film (barrier layer)/solution interface, ϵ is the electric field strength, and V_0 is the voltage of zero thickness of the barrier layer. As previously noted, the tunneling current can be written in the form

$$i = \hat{i}_0 e^{-\beta L_{ss}} \quad (3-20)$$

Figure II-1. Anodic polarization curves for oxidation of H_2 on platinized nickel in 0.1 m NaOH solution at 150°C and 6.9 MPa. The broken line is a fit of Equation (II-3), yielding a tunneling constant of $\beta = 0.75 \times 10^8 \text{ cm}^{-1}$, and indicating that direct quantum mechanical tunneling occurs through the passive oxide film. “RPM” refers to the rotation rate of the flow-activating impeller.

where $\hat{i}_0$ is the tunneling current at zero film thickness and β is the tunneling constant. Combining these two expressions yields

$$\ln(i) = \ln(\hat{i}_0) - \beta \left(\frac{1-\alpha}{\varepsilon} \right) (V - V_0) \quad (3-21)$$

Thus, a linear relationship is predicted between the current density and the voltage with a negative slope of $\beta \left(\frac{1-\alpha}{\varepsilon} \right)$ and an intercept at $V = 0$ of $\ln(\hat{i}_0) + \beta \left(\frac{1-\alpha}{\varepsilon} \right) V_0$. Selecting $\alpha = 0.5$ and $\varepsilon = 2 \times 10^6 \text{ V/cm}$,

as being typical parameter values, the broken line plotted in Figure II-1 corresponds to Equation (3-20) with $\beta = 0.75 \times 10^8 \text{ cm}^{-1}$. This value is typical of tunneling of electrons through passive films on metals (e.g., through Cr_2O_3 on Cr [5] with β ranging from $0.215 \text{ \AA}^{-1}$ to $0.164 \text{ \AA}^{-1}$). Excellent agreement is observed between theory and experiment (Figure II-1, above). We conclude, therefore, that the PDM combined with quantum mechanical tunneling theory, provides a robust and accurate account of charge transfer across passive films on metal surfaces. It is also evident that the tunneling current is a very sensitive probe for measuring the thickness of very thin oxide films; films that are so thin that traditional techniques, such as ellipsometry, are ineffective, because of surface roughness. We are now using the

tunneling current as an accurate probe for measuring the thickness of anodic oxide films on platinum that range in thickness up to 1-3nm.

III-3.3 Measurement of Film Thickness via Tunneling Spectroscopy

The accurate measurement of the thickness of very thin oxide films on metal surfaces has proven to be extremely difficult, unless the surface is atomically smooth (as in the case of liquid mercury). Thus, if the surface roughness is significantly greater than the thickness of the film, capacitance measurements, with the thickness being calculated from the parallel plate capacitor expression

$$L = \epsilon \epsilon^0 A / C \quad (3-22)$$

where ϵ is the dielectric constant, ϵ^0 is the permittivity of free space, A is the true surface area, and C is the measured capacitance (not the specific capacitance). Thus, not only does the uncertainty in the area of a rough surface limit the precision of the calculated thickness, so does the uncertainty in the dielectric constant. Note that it is customary to use the bulk oxide value for ϵ , but, of course, the true value may be greatly different, because of the presence of a high electric field. In the case of ellipsometry, which has been used extensively for measuring the thickness of oxide films on metal and semiconductor substrates, surface roughness ultimately limits the ability of the method to measure very small film thicknesses. Thus, a rough surface appears as a composite film having a refractive index that is different from the solid substrate and from the bulk solution. A priori knowledge of the form and amplitude of the roughness, would of course allow resolution of the problem of calculating the true film thickness. In the case of very thin oxide films, such as that on platinum, the apparent thickness of the film, as measured by ellipsometry, appears to be voltage-independent when, in fact, the true film thickness is expected to vary linearly with applied voltage. This is exactly the problem that was encountered in the present work, when an attempt was made to measure the thickness of the oxide film using a high quality, spectroscopic ellipsometer. Polishing with finer abrasives is unlikely to solve the problem, because the minimum roughness amplitude that can be achieved is of the order of 100nm, whereas the oxide film thickness is of the order of one thousandths to one hundredths of this value. It is therefore evident that ellipsometry is of limited value for studying the growth of very thin anodic oxide films on platinum in the oxygen reduction region.

Our work on the kinetics of redox reactions (oxidation of hydrogen) suggests an alternative method based upon the tunneling of charge carriers (e.g., electrons or holes in the reverse direction) to a reaction center (redox species) from the metal. The current for this process is adequately expressed in the form

$$i = \hat{i}_0 e^{-\beta L} \quad (3-23)$$

where, as before, $\hat{i}_0$ is the tunneling current at zero film thickness, β is the tunneling constant, and L is the film thickness. Rearranging this equation yields

$$L = \frac{1}{\beta} \ln \left(\frac{\hat{i}_0}{i} \right) \quad (3-24)$$

Since β is known (or can be calculated from quantum mechanical tunneling theory) and because $\hat{i}_0$ can be measured, L can be determined unequivocally. Note that knowledge of the true area of the electrode is not a determining factor in the accuracy of the calculation, since the ratio of current densities is the same as the ratio of the currents, and that, because tunneling occurs over a dimension that is very small compared with any roughness, the calculated thickness should be independent of the roughness amplitude.

We have applied this technique to the data shown in Figure III-3.4 and calculated the thickness versus voltage using a β value equal to $0.215\text{\AA}^{-1}$ got by Moffat et.al[5], the results are shown in Figure III-3.5.

Figure III-3.5. Calculated potential dependence of film thickness. Data are based on the results obtained with potential sweep rate of 5mV/s and reversal potential of $0.5V_{SCE}$.

Comparison of our results with the ellipsometric study by Reddy et. al.[27] shows good agreement except the slope they got for the film growth is 1nm/V. But the limitation of the ellipsometric study of the film thickness is that the instrument is not sensitive enough, so that the film is usually invisible to the ellipsometer when the film is less than 1 angstrom thick. However, our approach of identifying the oxide film thickness is proved to be very sensitive, and free of the roughness effect as the current density at each potential is divided by the film free current density.

III-3.4 Oxygen Reduction on Passive Platinum

As is well known, the cathodic reduction of oxygen is generally the performance-limiting factor in H_2/O_2 fuel cells, as stated previously in this report. However, although the oxygen electrode reaction has been studied for more than half a century, and enormous efforts have been made to find a better electrocatalyst than platinum, platinum and its alloys (e.g., with Ru) remains at the top of the “volcano” relation between catalytic activity ($\log K$) and the Gibbous energy of adsorption (ΔG) of all of the metals tested. Furthermore, the mechanism for the reduction of oxygen has not been established with any certainty and, indeed, it is fair to conclude that our present knowledge of the mechanism of this important reaction is such that it cannot be used in a quantitative manner to guide catalyst development. Our previous findings suggested that at elevated temperature, the rate of oxygen reduction is faster on oxidized platinum than on bare platinum, although this previous finding needs to be confirmed using an experimental system that is currently under development. From the PDM, the oxide layer formed on platinum has a highly defective structure that contains high concentrations of cation vacancies, cation interstitials, and anion vacancies. It is a postulate of the present work that surface oxygen vacancies ($V_{O,s}^{\bullet\bullet}$) are involved in the oxygen reduction reaction in the catalytic sense, as summarized by the overall reaction

Thus, the principal goal of the work described in this section is to determine experimentally the role (if any) played by surface oxygen vacancies in the reduction of oxygen on oxidized platinum.

Some preliminary experiments at room temperature have been carried out on the cathodic reduction of oxygen using the linear potential sweep method in 0.1M KOH, with the potential being swept from the positive to negative direction. The experiments are being carried out using a rotating ring-disk electrode (RRDE) with both the ring and the disk being fabricated from platinum. The results are shown in Figure III-3.6. The disk electrode was held at 0.4V (vs. SCE) for 1 second so that a thin layer of platinum oxide was formed before the potential was swept in the negative direction to the hydrogen evolution region (-1.1V vs. SCE). Various sweep rates were chosen to test the rate at which the platinum oxide film could be reduced at low temperatures. The disk electrode was always set at 0.3V (vs. SCE) to collect any peroxide formed as an intermediate product. The potentiodynamic curves shown in Figure III-3.6 demonstrate that at potentials over the range of $-0.45V_{SCE}$, which is close to the calculated equilibrium potential for the oxygen electrode reaction, to $-0.2V_{SCE}$, which coincides with the potential at which PtO forms on the metal surface, both the disk current and the ring current are very small and it is not until the potential is displaced to values that are more negative than $-0.2V_{SCE}$ that a significant oxygen reduction current is observed. Likewise, over the same 0.45 to $-0.2V_{SCE}$ range, the ring current is also small; this is expected, because H_2O_2 , which is oxidized at the ring under the present experimental conditions, is produced by the oxygen reduction reaction in a two-electron process. However, once the potential is displaced to a value more negative than the PtO formation value ($-0.2V_{SCE}$), the ring current increases in magnitude and passes through a prominent peak at about $-0.3V_{SCE}$. This finding indicates that hydrogen peroxide formation occurs at relatively low overpotentials by the two electron reduction path but at higher (more negative) overpotentials the H_2O_2 intermediate is either reduced immediately at the disk to water, or the four electron path to water becomes increasingly predominant over the two electron path to hydrogen peroxide. Two distinct Tafel slope regions for oxygen reduction were also observed by Damjanovic et.al.[22-25] under potentiostatic conditions on platinum with oxide films of various thickness at the surface, the Tafel slope also varies greatly at different film thickness.

Figure III-3.6 Linear potential sweep voltammograms for the cathodic reduction of oxygen on platinum as a function of voltage sweep rate. Rotation speed: 900rpm, sweep direction: negative. Ring potential was held at 0.3V (vs. SCE) to oxidize any peroxide produced.

Negative-going potentiodynamic polarization curves for the reduction of oxygen on platinum in 0.1M KOH at 20°C are displayed in Figure III-3.7 for three different voltage sweep rates: (a) 100mV/s, (b) 30mV/s, (c) 0.1mV/s. In all three cases, a “Tafel” region is observed at high overpotentials with the Tafel constant ranging from 0.056V/dec for the lowest sweep rate of 0.1mV/s to 0.132mV/dec for the highest sweep rate of 100mV/s. At more negative potentials, the current reaches a plateau, corresponding to the mass transfer limited supply of oxygen to the metal surface. Extrapolation of the Tafel region to the equilibrium potential for the oxygen electrode reaction ($0.46V_{SHE}$), as calculated from thermodynamics, yields exchange current densities of 3.98×10^{-11} , 1.00×10^{-7} , and $7.94 \times 10^{-7} A/cm^2$ for voltage sweep rates of 0.1, 30, and 100mV/s, respectively. No doubt, this sweep rate dependence of the kinetic parameters for the oxygen electrode reaction is partly responsible for the large scatter of values for the kinetic parameters reported in the literature, because of the frequent use of potentiodynamic methods for their measurement.

Figure III-3.7 Tafel plots for oxygen reduction on platinum in 0.1M KOH at 20°C. The voltage sweep rates are: (a) 100mV/s, (b) 30mV/s, (c) 0.1mV/s. The equilibrium potential for the oxygen electrode reaction is shown by the dotted line in each figure and the apparent exchange current densities are indicated. Note the pseudo Tafel region at low overpotentials.

At lower overpotentials, and especially for high voltage sweep rates, a second Tafel region becomes evident, with Tafel slopes of 0.377V/dec and 0.357V/dec for voltage sweep rates of 30mV/s and 100mV/s, respectively. We postulate that this region corresponds to the reduction of oxygen on the oxide-covered surface and that the origin of the larger Tafel constant lies in the fact that only part of the applied voltage appears across the barrier layer/solution interface; the rest of the applied voltage drop appears as a

voltage drop across the metal/barrier layer interface and as a voltage drop across the film. However, this region is not detected at the lowest voltage sweep rate, which argues that it arises from pseudo capacitance rather than from a redox reaction (oxygen reduction) at the film/solution interface. If the reaction is really oxygen reduction on the oxide, then extrapolation of the Tafel relationship to the equilibrium potential for the oxygen electrode reaction yields exchange current densities of $2 \times 10^{-5} \text{ A/cm}^2$ and $5.01 \times 10^{-5} \text{ A/cm}^2$ for voltage sweep rates of 30mV/s and 100mV/s, respectively, indicating that the reduction of oxygen is faster on the oxide covered Pt surface than on the bare surface. This conclusion is in keeping with unpublished data obtained by the author at the Ohio State University two decades ago, which showed that the reduction of oxygen at 275°C in 0.1M LiOH solution is apparently faster on the oxidized surface than on the bare surface. As noted above, we regard this observation as being highly tentative, because of the significant implications that it would have on fuel cell technology, if proven to be correct. An apparatus is currently being fabricated that should allow resolution of this important issue.

The interpretation of data from potentiodynamic experiments is often complicated by relaxation processes involving adsorbed intermediates, and the oxygen electrode reaction is no exception. Thus, the reduction of oxygen involves adsorbed OH radicals at least, and their relaxation gives rise to pseudo capacitive currents in addition to the current that arises from simple charge transfer. Thus, the danger exists, when determining kinetic parameters for a multi-step electrochemical reaction using potentiodynamic methods, that artifacts arising from the relaxation of the adsorbed intermediates will distort the values obtained. It is for this reason that polarization under steady state conditions is the preferred method for acquiring kinetic parameters for charge transfer reactions. A typical polarization curve for platinum in oxygenated 0.1M KOH at 20°C obtained under potentiostatic conditions is shown in Figure III-3.8. The Tafel slope for oxygen reduction of 0.07V/dec approaches that in Figure III-3.7(c), corresponding to the lowest sweep rate in the potentiodynamic study. However, within the potential range 0.27V to 0.45V (vs. SHE), the net current is positive (green points), so that if oxygen reduction occurs on the oxidized surface, it is obscured by substrate oxidation. Indeed, the polarization characteristics are those for a normal corroding system, with the open circuit potential (E_{corr}) being simply a mixed potential involving oxygen reduction on the oxidized surface and substrate oxidation. We see no evidence that hydrogen peroxide is involved in the establishment of the mixed potential, as has been proposed by others (e.g., J.P. Hoare[26]). Finally, extrapolation of the Tafel relationship to the equilibrium potential for the oxygen electrode reaction yields an exchange current density of $2.04 \times 10^{-10} \text{ A/cm}^2$, which is very close to the result obtained from the sweep rate of 0.1mV/s (Figure III-3.7 (c)).

Figure III-3.8. Tafel plot for the potentiostatic reduction of oxygen. The current values in triangles for $E > E_{\text{corr}}$ are positive (anodic oxidation); all other current values are negative (cathodic reduction).

III-3.4 Possible Role of Surface Defects in the Oxygen Electrode Reaction

As noted elsewhere in this report, the involvement of surface defects in gas-phase heterogeneous catalysis is well established as providing reaction sites for the reaction at the surface. Indeed, a fruitful line of research that has resulted in significant advances in gas-phase catalysis has been to modify the surface defect structure to optimize the rate and specificity of a reaction, to the extent that the chemical industry has undergone a revolution in the economics of producing vital commodities. We postulate, in this work, that a similar strategy should be enacted in electrocatalysis, including that of the oxygen electrode reaction. Accordingly, we have initiated a theoretical study of how surface defects might be involved in the oxygen electrode reaction, with our initial emphasis being placed on the role possibly played by oxygen vacancies.

For the oxygen reduction reaction on the oxidized platinum, we propose two mechanisms that have the oxygen vacancy playing a dominant role (see below). Mechanism I considers an oxygen divacancy at the surface to be the reaction site, while Mechanism II considers a single oxygen vacancy only. Figure III-3.9 explains schematically the postulated mechanisms for the oxygen electrode reaction on passive metals involving surface oxygen vacancies. Before proceeding further, we emphasize that an important goal of this work is to devise analytical methods for detecting and characterizing the involvement of oxygen vacancies in this important reaction, because it must first be established that the vacancies are indeed involved in the reaction mechanism in the catalytic sense.

Mechanism I

Mechanism II

Figure III-3.9. Proposed mechanisms for the oxygen electrode reaction on passive metals involving surface oxygen vacancies.

Figure III-3.10 depicts a possible multi-step reaction schemes for the oxygen electrode reaction on the platinum oxide film surface. If the oxygen vacancy does play a important catalytic role on the oxygen reduction reaction, control of the vacancy concentration could control the rate of the reaction. The rate constants for each reaction may also be calculated by optimizing the models on electrochemical impedance spectroscopy (EIS) data, which also is capable on distinguishing between closely related mechanisms[7]. For this reason, EIS will be the primary experimental tool that will be employed in future work.

Mechanism I

Mechanism II

Figure III-3.10. Multi-step reaction schemes on platinum oxide film surface involving oxygen vacancies.

References:

1. D.D. Macdonald, *J. Electrochem. Soc.*, **139**, 3434 (1992).
2. R. W. Gurney and E. U. Condon, *Phys. Rev.*, **33**, 127 (1929).
3. R. W. Gurney, *Proc. Roy. Soc.*, **A134**, 137 (1931).
4. V.K.J. Vetter and J.W. Schultze, *Ber. Bunsen. Phys. Chem.*, **77**, 945 (1973).
5. T.P. Moffat, H. Yang, F-R. F. Fan, and A. J. Bard, *J. Electrochem. Soc.*, **139**, 3158 (1992).
6. D.D. Macdonald, *Pure Appl. Chem.*, **71**, 951 (1999).
7. C. Gabrielli, *Identification of electrochemical processes by frequency response analysis.*, Solatron Instruments 1984.
8. D. D. Macdonald, *Transient Techniques in Electrochemistry*. Plenum Press, N.Y 1977.
9. J.W. Schultze and V.K.J. Vetter, *Electrochim. Acta*, **18**, 889 (1973).
10. J.W. Schultze and U. Stimming, *Z. Phys. Chem. N.F.*, **98**, 285 (1975).
11. W. Schmickler, *J. Electroanal. Chem.*, **82**, 65 (1977).
12. W. Schmickler, *J. Electroanal. Chem.*, **134**, 167 (1982).
13. J. O'M. Bockris and S.U.M. Khan, *Quantum Electrochemistry.*: Plenum Press, N.Y 1979.
14. D.D. Macdonald R. Biswas, Z. Ahmed, and S. Lvov, *to be published*, (2005),
15. D.D. Macdonald J. Mankowski, M. Karaminezhad-Ranjbar, and Y-H. Hu, *Corrosion-NACE*, **44**, 186 (1988).
16. P.N. Ross, *J. Electrochem. Soc.*, **126**, 67 (1979).
17. P.N. Ross, in *Structure of Electrified Interfaces*, P.N.R. J. Lipkowski, Editor. 1993, NY: VCH Publishers: New York. p. Chapter 2.
18. E.B. Yeager, W. O'Gready, M.Y.C. Woo, and P. Hagans, *J. Electrochem. Soc.*, **125**, 1348 (1978).
19. D. Armand and J. Clavilier, *J. Electroanal. Chem.*, **225**, 205 (1987).
20. D. Armand and J. Clavilier, *J. Electroanal. Chem.*, **233**, 251 (1987).
21. L. Gao and B.E. Conway, *Electrochim. Acta*, **39**, 1681 (1994).
22. D.B. Seps, M.V. Vojnovic, Lj. M. Vracar, A. Damjanovic, *Electrochim. Acta*, **31**, 91 (1986).
23. D.B. Seps, M.V. Vojnovic, Lj. M. Vracar, A. Damjanovic, *Electrochim. Acta*, **31**, 97 (1986).
24. A. Damjanovic, *J. Electrochem. Soc.*, **138**, 2315 (1991).
25. D.B. Seps, M.V. Vojnovic, and A. Damjanovic, *Electrochim. Acta*, **26**, 781 (1981).
26. J.P. Hoare, *The Electrochemistry of Oxygen, chapter 4*. 1968: Interscience Publishers.
27. A.K.N. Reddy, M.A. Genshaw, and J. O'M Bockris, *J. Chem. Phys.*, **48**, 671 (1968).

Issues/Concerns: None

III-5 Task 5: The Evidence of the Involvement of Oxygen Vacancies in Oxygen Electrode Reaction (Researcher: Bumwook Roh)

The goal of this work is to study the kinetics of the oxygen electrode reaction on passive titanium. Previous work indicates that the oxygen electrode reaction may occur at a higher rate (has a higher exchange current density) on the oxide-covered platinum surface than it does on the oxide-free surface at very elevated temperatures (275°C in 0.1M LiOH – see Introduction). As noted above, this result cannot be accounted for by the classical quantum mechanical tunneling of charge carriers across the oxide film as being the rate-limiting process. However, it is also important to stress that the high temperature result referred to above has yet to be confirmed; these experiments are now underway and we expect that the results will be available within the next two months. Also, the work now being performed should ascertain the impact of temperature on the kinetics and mechanism of oxygen reduction over the technologically-important range of 20°C to 200°C. Assuming that the high temperature result is confirmed, it is clearly necessary to ascertain the role of the oxide film on this important reaction. That oxygen vacancies could be involved in this important reaction is not surprising, in that these species are known to be involved in gas phase catalysis [1], but to our knowledge their involvement in an aqueous media oxygen electrode reaction has never previously been proposed. In this work, titanium is being used as a substrate, because the oxygen vacancy concentration in the titanium oxide film can be varied over a wide range by chemical or electrochemical means [2]. Oxygen deficient TiO_{2-x} consists of several sub-oxides of titanium oxide, collectively known as Magneli phases, and generally contains the most conductive compounds of the series, Ti_4O_7 and Ti_5O_9 , as its main components. An important feature of the Magneli phases is that the oxygen vacancy concentration can be varied over a wide range resulting in significant changes in material properties, such as the electrical conductivity (see Figure III-5.1).

Figure III-5.1. Phase diagram of the titanium-oxygen system, showing stoichiometry of the titanium oxides against the log of conductivity of oxide phases [3].

In the present work, the role of surface oxygen vacancies on the kinetics of the oxygen electrode reaction on passive titanium was investigated by comparing the oxygen electrode reaction rate with the oxygen vacancy density of the oxide film, in order to ascertain how the vacancies affect the rate of oxygen reaction. The dependence of the reaction rate on the defect concentration in the oxide film may be explained by the specific involvement of oxygen vacancies in oxygen electrode reaction mechanism or by facilitating charge carrier transport across the passive film. This will be studied in further

investigations by determining whether the reaction rate depends on the vacancy concentration exposed at the surface, or whether the reaction rate is controlled by the transfer of charge carriers via oxygen vacancies in the bulk of the film.

We have examined how these two possibilities might be differentiated, and we conclude it is necessary to either measure the concentration of oxygen vacancies at the surface, in situ, or establish relationships between the bulk vacancy concentration, which can be readily measured using Mott-Schottky analysis, and the kinetics of the reaction in which the dominant factors are the surface vacancy concentration or the inter vacancy distance in the bulk of the oxide film. That delineation of these factors is necessary, in order to resolve the role of surface defects is obvious, but the methodology of doing so is not. Resolution of this issue is regarded as being a key challenge in the present program.

Task Status:

Determination of the donor density in the oxide film formed by the anodic oxidation of titanium in 0.5M sulfuric acid solution, was affected by Mott-Schottky analysis. In Mott-Schottky analysis [4], as used in this research, it is assumed that the capacitance of the double layer on the solution side of the interface is much larger than the space charge capacitance of the oxide film and that these capacitances exist in series. Accordingly, the measured capacitance, C , is equal to the space charge capacitance, C_{sc} . Plots of C^{-2} versus V_{sce} for oxygen deficient passive films on metal surfaces display a positive slope that is characteristic of an n-type semiconductor (see Figure III-5.4). The dominant defect in the oxide film on titanium over the voltage range of measurement is well-known to be the oxygen vacancy and the defect structure is well accounted for in terms of the Point Defect Model (PDM)[5, 6]. Evidence for this defect assignment can be found elsewhere [7, 8].

The space charge capacitance of an n-type semiconductor is given by Equation (III-5.1),

$$C^{-2} = \frac{2}{e\epsilon_r\epsilon_0 N_d A^2} \left(V - V_{fb} - \frac{kT}{e} \right) \quad (III-5.1)$$

where A , ϵ_0 , ϵ_r , and N_d are, respectively, the geometrical surface area, the vacuum permittivity, the dielectric constant of the oxide, and the donor concentration. V is the applied potential, V_{fb} is the flat band potential, and e is the charge of the electron (1.6×10^{-19} C).

Typical Bode plot of the impedance of passive titanium is shown in Figure III-5.2. The spectrum was recorded at a potential of $1.0V_{sce}$, with an AC amplitude of 10mV. In the figure at frequencies higher than ~600Hz, the real part of the impedance reveals little dependence on the frequency and approaches a constant value at limitingly high frequencies. Accordingly, at sufficiently high frequencies, the frequency dependence of the impedance was assumed to be governed by the imaginary component, from which the capacitance was calculated for Mott-Schottky analysis. In this work, the Mott-Schottky analysis was performed using the capacitance calculated from the imaginary component measured at a frequency of 1000Hz, as the potential was swept to the negative direction from the formation potential (from 1.5 to 0.0 V_{sce}), and the capacitance was measured as a function of voltage. This procedure was adopted to circumvent one of the major objections to Mott-Schottky analysis of passive films; that the defect concentration varies with voltage. Thus, if the voltage sweep rate in the negative direction is sufficiently high, the defect concentration is “frozen in” at the value of the formation potential.

III-5.1 Titanium Oxide Formation and Semiconductive Properties

Passive anodic oxide films were grown on titanium initially at various current densities ranging from 10 to 110 mA/cm², and to a maximum potential of $20V_{sce}$. The first stage of film growth was at constant current, and after attaining the potential of $20 V_{sce}$ the mode was shifted to constant voltage, where the sample was maintained under the potentiostatic control for 2min. Figure III-5.3 shows the oxide film

thickness as a function of current density for oxide film formation on titanium in 0.5M H₂SO₄ solution at room temperature (20°C) after the final growth stage at 20V_{sce}. The thickness decreases slightly with increasing film formation current density, but the thickness is almost constant within the range of 42-47nm.

Figure III-5.2. Electrochemical impedance spectrum of the titanium oxide film formed at 10mA/cm² on pure titanium, recorded at a potential 1.0V_{sce} with an AC amplitude of 10mV. (○) Z', (■) Z''

Figure III-5.3. Variation of anodic oxide film thickness on titanium with formation current density, with the final stage of growth being carried out potentiostatically at 20V_{sce}.

Using Mott-Schottky analysis (Figure III-5.4), the donor density, N_d , was evaluated for each film formation current density and the results are plotted in Figure III-5.5. These data show that the donor density decreases with increasing film formation current density. These results are in general agreement with the findings of previous researchers, Blackwood et al.[9] and Ohtsuka et al. [10].

Figure III-5.4. Mott-Schottky plots obtained from the titanium oxide films formed with various film formation current densities at a frequency of 1000Hz; film formation current density ($\blacklozenge$) 25 mA/cm^2 , ($\bullet$) 20 mA/cm^2 , ($\blacktriangledown$) 15 mA/cm^2 , and ($\blacktriangle$) 10 mA/cm^2 .

Figure III-5.5. Variation of the donor density in anodic oxide film formed on titanium in 0.5M sulfuric acid solution with formation current rate

III-5.2. Anodic Processes in Deoxygenated Solution (Oxygen Evolution Reaction)

To investigate the possible role of surface oxygen vacancies in oxygen evolution, the voltage of samples prepared with different donor densities at constant film thickness, as described above, was swept linearly at a known rate (5mV/sec) to an upper limiting potential of 5 V_{sce} in a deoxygenated solution of 0.5M H₂SO₄. Figure III-5.6 and Figure III-5.7, respectively, present the potentiodynamic curves measured on an anodic oxide film in a deoxygenated solution of 0.5M H₂SO₄ and the peak current density as a function of donor density in the oxide film at the upper vertex potential. Without further analysis, these data are consistent with the crystallographic defects (oxygen vacancies) being active sites for oxygen evolution or acting to enhance the conductivity of the passive film[11, 12]. Electron transfer through an oxide film (from the metal to an acceptor state in a redox species in solution) proceeds by the quantum tunneling, revealing that the electron transfer rate is exponentially dependent on the tunneling distance, d ,

$$k_{ET}^o = A(T)e^{-\beta d}$$

where $A(T)$ and β are, respectively, the pre-exponential factor that includes rate-determining effects like temperature [11]. If we consider that the vacancies in the oxide film play a role as intermediate electron-relay stations, then the electron-tunneling distance of one step decreases and the number of tunneling steps from the metal to the solution increases, however according to the above quantum-tunneling electron transfer expression, the tunneling effect does not depend on how many “jumps” occur, but only on the thickness of the film. This conclusion is valid only if there exist donor and acceptor states at the same energy. However, a very high electric field exists within the film (of the order of 2×10^6 V/cm), so that the energies of the quantum wells of neighboring vacancies are displaced and an acceptor state may not be available. In this case, the electron or hole tunnels to a virtual state and must then lose energy to the lattice until a stationary state is reached and the process starts over again. The physics of this indirect tunneling case has been dealt with earlier in this report. In any event, the simple arguments that the total probability of electron transfer across the film is simply the product of the probabilities of the individual steps no longer applies, because of the finite dwell times during which energy is transferred to the lattice. The alternative is that the oxygen vacancies participate in the reaction as catalysts; that is, the vacancies impact the rate of the reaction, but they do not appear in the stoichiometry of the reaction. It is the delineation of these two processes that is the principal goal of this work.

Figure III-5.6. Potentiodynamic curves(i-E) recorded from 0 to 5 V_{sce} in nitrogen purged 0.5M hydrosulfuric acid solution with the anodic oxide films formed on titanium, scan rate 5 mV/s

Figure III-5.7. Variation of the peak current density at the upper vertex potential, 5.0 V_{sce}, with donor density of the oxide film, as determined by potentiodynamic polarization, for the oxygen evolution reaction in nitrogen purged, 0.5M sulfuric acid solution at 20°C.

III-5.3 Cathodic Processes in Oxygen Saturated Solutions (Oxygen Reduction Reaction)

In the cathodic potential range, cyclic voltammetry was used to measure the oxygen reduction rate (from 0.0 to $-0.7V_{sce}$, at a voltage scan rate of 5mV/s) on passivated titanium in sulfuric acid solution. In this case, as the potential is swept in the negative direction, hydrogen evolution can interfere with the study of oxygen reduction, as evidenced by previous research [7, 12]. To distinguish these two reactions, the background current for hydrogen evolution was measured in a solution deoxygenated with pure nitrogen and it was confirmed that the hydrogen evolution reaction does not contribute significantly, compared with the current due oxygen reduction, to the current observed in the external surface. Furthermore, in the cathodic potential range, some amount of the current can be considered to originate from the reduction of the oxide itself; however, this current was also found to be negligible compared with the current measured in the external circuit [13]. Figure III-5.8 shows that the current density corresponding to the reduction of oxygen at the negative vertex potential, $-0.7V_{sce}$, in 0.5M sulfuric acid solution. As with the oxygen evolution reaction, which is promoted by the defect density (see Section 5.2), an oxide film having a higher donor density displays a peak current of greater magnitude than does an oxide film of lower density. While this is powerful *prima facie* evidence that oxygen vacancies are involved in the oxygen reduction reaction, and that the mechanism involves oxygen vacancies in the catalytic sense (i.e., the vacancies do not appear in the stoichiometric equation for the reaction, but their concentration appears in the rate expression), it is not possible, at this stage, to dismiss the role of the vacancies acting to promote charge transfer across the oxide film, thereby reducing the potential drop across the substrate. As noted above, delineation of these processes (catalytic involvement of oxygen vacancies and electron transfer in the bulk of the oxide film) remains a principal goal of this research.

Figure III-5.8. Variation of the peak current density at the lower vertex potential, $-0.7V_{sce}$ with donor density of the oxide film, as determined by the potentiodynamic polarization, for the oxygen reduction reaction on passivated titanium of constant passive film thickness, in oxygen saturated, 0.5M sulfuric acid solution.

References:

1. W. S. Epling, C. H. Peden, M. A. Henderson, U. Diebold, *Surface Science*, **412/413**, 333 (1998).
2. J. R. Smith, F. C. Walsh, R. L. Clarke, *J. Appl. Electrochemistry*, **28**, 1021 (1998).
3. R. L. Clarke and S. K. Harnsburger, *Am. Lab.*, **20**, 6 (1998).
4. S. R. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, (1980).
5. D. D. Macdonald, *J. Electrochem. Soc.*, **139**, 3434 (1992).
6. D. D. Macdonald, *Pure Appl. Chem*, **71**, 951 (1999).
7. R. M. Torresi, O. R. Camara, C. P. De Pauli, *Electrochim. Acta*, **32**, 1291 (1987).
8. K. Leitner, J. W. Schultze, U. Stimming, *J. Electrochem. Soc.*, **133**, 1561 (1986).
9. D. J. Blackwood, L. M. Peter, *Electrochim. Acta* **34**, 1505 (1989).
10. T. Ohtsuka, T. Otsuki, *Corr. Sci.*, **40**, 951 (1998).
11. N. P. Lebedeva, M. T. M. Koper, J. M. Feliu, and R. A. van Santen, *J. Phys. Chem. B*, **106**, 12938 (2002).
12. N. P. Lebedeva, A. Rodes, J. M. Feliu, M. T. M. Koper, and R. A. van Santen, *J. Phys. Chem. B*, **106**, 9863 (2002).
13. T. P. Moffat, H. Yang, F.-R. Fan, A. J. Bard, *J. Electrochem. Soc.*, **139**, 3158 (1992).
14. R. M. Torresi, O. R. Camara, C. P. de Pauli, M. C. Giordano, *Electrochim. Acta*, **32**, 1357 (1987).
15. V. B. Baez, J. E. Graves, D. Pletcher, *J. Electroanal. Chem.*, **340**, 273 (1992).

Issues/Concerns: none

III-6 Task 6: Experimental Investigation of the Role of Substitutional Defects in the Oxidation of Hydrogen on Defective Tungsten Carbide (Researcher: LaSalle Swenson)

The surface state of a solid material is generally a function of the bulk material properties, in addition to the environment to which it is exposed. This fact is made manifest in solid-state heterogeneous catalysis, where catalytic activity is known to increase as structure and stoichiometry deviate from the perfectly ordered material [1]. As the surface processes occurring in many electrochemical systems are similar to their non-electrochemical counterparts (e.g., the disassociative adsorption of molecular hydrogen), the role of defects in electrocatalysis is similarly important [2]. This task investigates the role of substitutional point defects in base metal electrocatalysis, and is expected to produce generally applicable results with respect to engineered base metal catalysts for PEM fuel cell applications.

Our initial focus is on tungsten carbide (WC), which disassociatively adsorbs hydrogen[3], is not poisoned by carbon monoxide[4], and is stable in highly acidic environments[5]; properties which have motivated sporadic investigations of the material as a PEM fuel cell anode beginning from the 1960s. While the material has shown activity for hydrogen [6-9] and methanol [10-11] electro-oxidation, the current levels are insufficient for practical application. Prior investigations have noted a strong relationship between catalytic activity and non-stoichiometry (WC_xO_{1-x}) [11-14], a relationship that has not been explored in a systematic manner. We consider such an investigation the natural starting point of an inquiry into the role of substitutional point defects in electrocatalysis by base metals. Our approach thus centers on varying substitutional defect concentration (d_c) in a systematic manner in connection with a series of electrochemical and surfaces studies, including: (i) Voltammetric investigations of hydrogen oxidation, oxygen reduction, and material oxidative stability, (ii) electrochemical impedance spectroscopic investigations of the same, and (iii) XPS/AES studies of the chemical state and composition of the surface. The key fundamental questions to be addressed in the initial phase of this study include:

1. What is the functional relationship between activity, oxidative stability, and bulk material defect concentration?
2. What is the functional relationship between the surface chemical state, surface composition, and bulk material defect concentration?
3. In anticipation of advanced PEM fuel cell operating at elevated temperatures ($T > 100^\circ\text{C}$): What is the temperature dependence of the activity and oxidative stability relationships of question 1 (above)?

The ultimate objective of this inquiry, as with our work on oxide films, is a mechanistic understanding of underlying physical processes, capable of providing a theoretical basis for the specification of more effective PEM fuel cell electrocatalysts. In that regard, mechanistic and theoretical modeling is anticipated following the initial phase, which is mainly a phenomenological investigation.

The initial phase subtasks are, in broad outline:

1. Systematic synthesis of defective tungsten carbide (WC_xO_{1-x}).
2. Characterization of broad defect state and determination of substitutional defect concentration of the synthesized materials.
3. Gas-phase catalytic testing of the materials, including catalytic activity and surface areas.
4. Fabrication of electrodes suitable for electrochemical and impedance studies.
5. Electrochemical and impedance spectroscopic testing.
6. Surface analysis by XPS/AES.

III-6.1 Initial Results Concerning Subtask 1: Systematic Synthesis of Defective Tungsten Carbide (WC_xO_{1-x})

Defective tungsten carbide is typically synthesized by gas-phase carburization of a tungstic acid precursor, a method that is known to produce oxygen substitution at carbon vacancies [5,15]. Ross and Stonehart describe a method of producing the white form of the tungstic acid precursor ($WO_3 \cdot xH_2O$) with varying levels of crystalline irregularity [13]. Kulcický and Petrdlik showed that, at carburization temperatures below 1000 °C, characteristic irregularities of the precursor tungstic acid are transferred to the final tungsten carbide material [16]. Our initial synthesis efforts have focused on establishing a systematic procedure of producing varying levels of crystalline irregularity by the method of Ross and Stonehart, and confirming that those irregularities transfer to the carburized material, as indicated by Kulcický and Petrdlik.

Figure III-6.1 shows the results of three initial trials of the tungstic acid precursor precipitation procedure. Slight procedural variations were made in each of these initial attempts. The x-axis, “saturation concentration fraction,” is the controlling independent variable of the precipitation procedure. The y-axis indicates the location (2-theta) of the most prominent peak in the XRD pattern of the resulting tungstic acid samples. The shift in peak location along a series represents variation in d-spacing, indicating a variation in crystalline irregularity. The precipitation procedure predicts an inverse relationship between peak position (d-spacing) and saturation concentration fraction, which is seen generally in the data.

The Trial 3 samples of the precipitation were carburized at 850°C and the prominent peak locations of the resulting XRD patterns were examined and compared to those found for the precursor precipitation in an effort to ascertain whether the crystalline irregularities of the precursor would transfer in a systematic way to the final product on carburization. Results are shown in Figure III-6.2. Note that the magnitude of the range on each y-axis is equivalent. The data are encouraging, although not conclusive. We intend to repeat these experiments to obtain more quantitative data. We emphasize, again, that the overarching goal of our work is to obtain as carefully characterized electrocatalytic material as possible, in order that the results of the electrochemical experiments can be related in a quantitative manner to materials properties, in particular to the defect structure.

Figure III-6.1. Tungstic acid precipitation trials: “26”-peak location vs. saturation fraction.

Figure III-6.2. 850°C carburization of Trial 1 tungstic acid

References:

1. P. H. Emmet, in *Catalysis*, Reinhold, New York, 278 (1954).
2. P. Stonehart, P. N. Ross, *Catalysis Reviews - Science and Engineering*, **12**, 1 (1975).
3. H. Boehm, *Electrochimica Acta*, **15**, 1273 (1970).
4. V. S. Palanker, R. A. Gajjev, D. V. Sokolsky, *Electrochimica Acta*, **22**, 133 (1977).
5. L. E. Toth, *Transition Metal Carbides and Nitrides*, Vol. 7, Academic Press, New York, (1971).
6. D. V. Sokol'skii, V. S. Palanker, E. N. Baibat'yrov, *Electrochimica Acta*, **20**, 71 (1975).
7. R. D. Armstrong, A. F. Douglas, D. E. Keene, *Journal of the Electrochemical Society*, **118**, 568 (1971).
8. G. Brondel, E. Museux, G. Leclercq, L. Leclercq, N. Tassin, *Electrochimica Acta*, **36**, 1543 (1991).
9. R. B. Levy, M. Boudart, *Science* (Washington, DC, United States), **181**, 547 (1973).
10. H. Okamoto, G. Kawamura, A. Ishikawa, T. Kudo, *Journal of the Electrochemical Society*, **134**, 1649 (1987).
11. H. Okamoto, G. Kawamura, A. Ishikawa, T. Kudo, *Journal of the Electrochemical Society*, **134**, 1645 (1987).
12. P. N. Ross, Jr., J. MacDonald, P. Stonehart, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **63**, 450 (1975).
13. P. N. Ross, Jr., P. Stonehart, *Journal of Catalysis*, **48**, 42 (1977).
14. P. N. Ross, Jr., P. Stonehart, *Journal of Catalysis*, **39**, 298 (1975).
15. E. K. Storms, *The Refractory Carbides*, Vol. 2, Academic Press, New York, 1967.
16. M. P. I. Kulcickij, in *IIIrd Intern. Conf. on Powder Metallurgy*, Vol. 4, 1970.

Issues/Concerns: None

III-7 Task 7: Mechanistic Analysis and the Prediction of Electrocatalytic Activity

The work outlined in the six tasks outlined above is being focused in this task to provide a mechanistic explanation and prediction of the electrocatalytic activities of noble metals and noble metal and defective tungsten carbide toward the oxidation of hydrogen and reduction of oxygen under prototypical PEM fuel cell conditions. Of particular interest is the development of mechanistic explanations of the apparently different roles played by quantum mechanical tunneling in the hydrogen oxidation and oxygen reduction reactions, particularly at elevated temperatures (275°C). Two important factors are being considered: (1) The impact of the electron tunneling probability for bare and oxide-covered surfaces on the rates of these reactions, and (2) the role of the oxygen vacancies that are postulated to contribute to the increase in the catalytic activity for the oxygen reduction reaction. Once the models have been found to account for the existing data, they will be used (where possible) in sensitivity analyses to identify those factors that have greatest impact on the reaction rate and hence on catalytic activity. We expect that this analysis will lead to the establishment of theory-based rules for designing new electrocatalysts, particularly alloy systems, that can be evaluated using combinatorial techniques of the type being practiced at Penn State University under the direction of Professor Tom Mallouk.

Task Status:

Progress is being made in the individual tasks described earlier. The roles played by charge carrier tunneling and oxygen vacancies in the hydrogen oxidation and oxygen reduction reactions are being investigated. Once these factors have been properly defined, the information will be assembled to formulate strategies based upon fundamental principles for improving electrocatalyst performance. One such strategy identified to date is outlined below:

The current work shows that the open circuit potential of the OER on Pt is a simple, conventional mixed potential resulting from the simultaneous operation of a partial anodic reaction (Pt oxidation) and a partial cathodic reaction (oxygen reduction). The large difference between the OCP and the OER equilibrium potential represents a major loss in the practical energy density of any fuel cell that employs an air electrode. For example, this difference in voltage may be as much as 0.35V (see Figure III-3.8), so that the power loss for a cell operating at a current density of 1A/cm² would be 0.35W/cm². In cells that typically deliver power densities of 0.6W/cm² at this current density, this is a substantial loss. Much of this loss could be avoided by moving the OCP to higher values and the present work shows that this can be done by decreasing the electro oxidation current density of Pt or by increasing the oxygen reduction current. According to tunneling theory, the only way for the latter to be achieved is by reducing the thickness of the oxide film, but the theory developed in this work for the passive film on Pt suggests that this would result in a concomitant increase in the Pt oxidation current density, with there likely being little impact on the OCP. However, the current work strongly suggests that increasing the oxygen vacancy concentration in the film is an alternate strategy for increasing the rate of oxygen reduction without incurring a parallel increase in the Pt oxidation rate. We are currently exploring methods by which this may be achieved, but the reader is reminded that the dependence of the rate of the OER on oxygen vacancy concentration in the oxide film has yet to be demonstrated for platinum.

Issues/Concerns: None.

IV. STATUS SUMMARY OF PERSONNEL

The current status of students working on the project is summarized below:

Name of Students/Researchers	Degree Sought	Current Status	Expected Completion Date
Adan Sun	PhD	Successfully completed candidacy and comprehensive exam.	Fall 2006
Jianer Bao	PhD	Successfully finished candidacy exam	Fall 2007
Bum-Wook Roh ¹	PhD	Successfully finished candidacy exam.	Fall 2007
LaSalle Swenson ²	PhD	Taking candidacy exam in April 2005.	Summer 2008

¹. Stipend and academic fee partially supported by Hyundai Motor Company, Korea.

². Support shared with Professor T. Mallouk, Chemistry Department, Pennsylvania State University

V. PUBLICATIONS AND PRESENTATIONS

Presentations:

1. D. D. Macdonald, A. Sun, Growth and Properties of Oxide Films on Platinum: I. EIS and XPS Studies, 207th Meeting of The Electrochemical Society, Quebec city, Canada, May 2005
2. B.-W. Roh, D. D. Macdonald, Evidence for the Involvement of Oxygen Vacancies in the Oxygen Electrode Reaction on Passive Titanium, 207th Meeting of The Electrochemical Society, Quebec city, Canada, May 2005
3. J. Bao, D. D. Macdonald, The Oxidation of Hydrogen on Oxidized Platinum, 207th Meeting of The Electrochemical Society, Quebec city, Canada, May 2005
4. A. Sun, J. Bao, and D. D. Macdonald. Properties and electrocatalysis effects of oxidized platinum on redox reactions in fuel cell, Gordon Research Conference on Electrochemistry, Aventura, CA, Feb 2005
5. A. Sun, J. Franc and D. D. Macdonald. Characterization of the Oxide Film that Forms on Platinum under Oxygen Reduction Reaction, Gordon Research Conference on Corrosion-Aqueous, New London, NH, July 2004
6. A. Sun, D. D. Macdonald, Study of Growth and Properties of Thin Anodic Oxide Films on Platinum, 204th Meeting of The Electrochemical Society, Orlando, FL, October 2003
7. D.D. Macdonald, A. Sun, N. Priyantha and P. Jayaweera, Analysis of Electrochemical Impedance Data for Alloy 22 in Prototypical High Level Nuclear Waste Environments, 204th Meeting of The Electrochemical Society, Orlando, FL, October 2003

Publications:

1. G. Chen., C. C. Waraksa, H. Cho, D. D. Macdonald, and T. E. Mallouk, "EIS Studies of Porous Oxygen Electrodes with Discrete Particles: I: Impedance of Catalyst Oxide Supports", *J. Electrochem. Soc.* **150**, E423 (2003).
2. Waraksa, C. C., G. Chen, D. D. Macdonald, and T. E. Mallouk, "EIS Studies of Porous Oxygen Electrodes with Discrete Particles: II, Transmission Line Modeling", *J. Electrochem. Soc.*, **150**, E429 (2003).
3. D. D. Macdonald, A. Sun, N. Priyantha and P. Jayaweera, An Electrochemical Impedance Study of Alloy 22 in NaCl Brine at Elevated Temperature: II. Impedance Analysis, *J. Electroanal. Chem.*, **572**, 421 (2004)
4. N. Kamrun, J. Bao, and D. D. Macdonald, "Future Challenges in Electron Transfer Theory", *Corros. Sci.*, Special Issue Commemorating the Development of Tafel's Law, in review (2005).
5. A. Sun, J. Franc, D. D. Macdonald, "Growth and Properties of Oxide Films on Platinum: I. EIS and XPS Studies", *Electrochim. Acta*, in preparation (2005).
6. B.-W. Roh and D.D. Macdonald, "Evidence of the Involvement of Oxygen Vacancies in Oxygen Electrode Reaction", *Electrochim. Acta*, in preparation (2005).
7. J. Bao and D. D. Macdonald, "Theory of Hydrogen Oxidation on Oxidized Platinum", *Electrochim. Acta*, in preparation (2005).
8. D. D. Macdonald, "The Theory of Partial Charge Transfer in Describing the Kinetics of Charge Transfer Reactions at Interfaces", *Electrochim. Acta*, in preparation (2005).

Four additional papers are currently being prepared and are expected to be submitted to peer-reviewed journals within the next six months. Please note that the work described in Presentation 2 and Paper 3 was developed on this project for interpreting electrochemical impedance data for passive films. The techniques were qualified on the current project by analyzing available data for Alloy 22 from another DOE project related to the disposal of High Level Nuclear Waste in the Yucca Mountain Repository. These same techniques were subsequently used to analyze the impedance data for platinum reported above (Task II).

Appendix I

Rate Constants for the PDM

The generalized Point Defect Model for a passive film on a metal substrate can be represented in terms of a set of defect generation and annihilation reactions that occur at the interfaces between the film and the metal and the film and the solution. These reactions are summarized in Figure III-4.1 below.

Figure AI-1. Interfacial defect generation/annihilation reactions that occur in the growth of anodic barrier oxide films according to the Point Defect Model [3]. m = metal atom, $V_M^{\chi'}$ = cation vacancy on the metal sublattice of the barrier layer, $M_i^{\chi+}$ = interstitial cation, M_M = metal cation on the metal sublattice of the barrier layer, $V_O^{\cdot\cdot}$ = oxygen vacancy on the oxygen sublattice of the barrier layer, O_O = oxygen anion on the oxygen sublattice of the barrier layer, $M^{\Gamma+}$ = metal cation in solution.

Using the method of partial charge transfer, the rate constants can be defined in terms of the voltage, barrier layer film thickness (reactions at the metal/film interface only), and pH, as summarized in Tables A1.1 and A1.2 below. Note that the reactions are written only in the forward sense.

Table AI-1. Rate constants $k_i = k_i^0 e^{a_i V} e^{b_i L} e^{c_i pH}$ for the interfacial defect generation and annihilation reactions employed in the Point Defect Model. $K = \frac{\overline{\varepsilon F}}{RT}$, $\gamma = \frac{F}{RT}$

Reaction	a_i (V^{-1})	b_i (cm^{-1})	c_i	Units of k_i^0
(1) $m + V_M^{\chi'} \xrightarrow{k_1} M_M + v_m + \chi e'$	$\alpha_1(1-\alpha)\chi\gamma$	$-\alpha_1\chi K$	$-\alpha_1\beta\chi\gamma$	$\frac{l}{s}$
(2) $m \xrightarrow{k_2} M_i^{\chi+} + v_m + \chi e'$	$\alpha_2(1-\alpha)\chi\gamma$	$-\alpha_2\chi K$	$-\alpha_2\beta\chi\gamma$	$\frac{mol}{cm^2 s}$
(3) $m \xrightarrow{k_3} M_M + \frac{\chi}{2} V_{\ddot{O}} + \chi e'$	$\alpha_3(1-\alpha)\chi\gamma$	$-\alpha_3\chi K$	$-\alpha_3\beta\chi\gamma$	$\frac{mol}{cm^2 s}$
(4) $M_M \xrightarrow{k_4} M^{\Gamma+} + (\Gamma - \chi)e'$	$\alpha_4\alpha\Gamma\gamma$		$\alpha_4\beta\Gamma\gamma$	$\frac{mol}{cm^2 s}$
(5) $M_i^{\chi+} \xrightarrow{k_5} M^{\Gamma+} + (\Gamma - \chi)e'$	$\alpha_5\alpha\Gamma\gamma$		$\alpha_5\beta\Gamma\gamma$	$\frac{cm}{s}$
(6) $V_{\ddot{O}} + H_2O \xrightarrow{k_6} O_O + 2H^+$	$2\alpha_6\alpha\gamma$		$\alpha_6\beta\Gamma\gamma$	$\frac{cm}{s}$
(7) $MO_{\chi/2} + \chi H^+ \xrightarrow{k_7} M^{\Gamma+} + \frac{\chi}{2} H_2O + (\Gamma - \chi)e'$	$\alpha_7\alpha(\Gamma - \chi)\gamma$		$\alpha_7\beta(\Gamma - \chi)$	$\frac{mol}{cm^2 s}$

Table AI-2. Definition of the standard rate constants for the interfacial defect generation and annihilation reactions employed in the Point Defect Model. Note that the base rate constant for the i^{th} reaction is designated k_i^{00} .

Reaction		k_i^0
(1)	$m + V_M^{\chi'} \xrightarrow{k_1} M_M + v_m + \chi e'$	$k_1^{00} e^{-\alpha_1 \chi \gamma \phi_{f/s}^0}$
(2)	$m \xrightarrow{k_2} M_i^{\chi+} + v_m + \chi e'$	$k_2^{00} e^{-\alpha_2 \chi \gamma \phi_{f/s}^0}$
(3)	$m \xrightarrow{k_3} M_M + \frac{\chi}{2} V_O^{\cdot\cdot} + \chi e'$	$k_3^{00} e^{-\alpha_3 \chi \gamma \phi_{f/s}^0}$
(4)	$M_M \xrightarrow{k_4} M^{\Gamma+} + (\Gamma - \chi) e'$	$k_4^{00} e^{\alpha_4 \Gamma \gamma \phi_{f/s}^0}$
(5)	$M_i^{\chi+} \xrightarrow{k_5} M^{\Gamma+} + (\Gamma - \chi) e'$	$k_5^{00} e^{\alpha_5 \Gamma \gamma \phi_{f/s}^0}$
(6)	$V_O^{\cdot\cdot} + H_2O \xrightarrow{k_6} O_O + 2H^+$	$k_6^{00} e^{\alpha_6 \Gamma \gamma \phi_{f/s}^0}$
(7)	$MO_{\chi/2} + \chi H^+ \xrightarrow{k_7} M^{\Gamma+} + \frac{\chi}{2} H_2O + (\Gamma - \chi) e'$	$k_7^{00} e^{\alpha_7 (\Gamma - \chi) \gamma \phi_{f/s}^0}$

$$K = \frac{\overline{\varepsilon F}}{RT}, \gamma = \frac{F}{RT}$$

Appendix II

Potential Dynamic Current Behavior on Passive Platinum

This appendix outlines the derivation of the current density for the oxidation of hydrogen on a passive film, where the hydrogen oxidation current is controlled by quantum mechanical tunneling of charge carriers across the film and the current due to the growth/dissolution of the film is described by the Point Defect Model. Neglecting the double layer charging, the total current density is composed of three parts:

$$i_{total} = i_{electron} + i_{passive} + i_{charging}$$

As outlined earlier, the Point Defect Model describes the anodic oxide film that forms on platinum in the oxygen reduction region at high potentials in terms of interfacial reactions that generate and annihilate point defects.

Figure AII-1. Point Defect Model for the anodic oxide film on platinum.

The rate constants for the interfacial defect generation and annihilation reactions are expressed as

$$k_i = k_i^0 e^{a_i V} e^{b_i L} e^{c_i p H}, \text{ where } a_3 = \alpha_3 (1 - \alpha) \chi \gamma, \text{ } b_3 = -\alpha_3 \chi K, \text{ and } c_3 = -\alpha_3 \beta \chi \gamma, \text{ with } \gamma = F/RT,$$

$K = \frac{\bar{\epsilon} F}{RT}$, and α is the polarizability of the film/solution interface. The parameter $\bar{\epsilon}$ is the electric field strength and α_3 the transfer coefficient for the generation of oxygen vacancies at the metal/film interface. Using the PDM, we can now resolve the current density item by item, beginning with the current due to the dynamic growth of film thickness.

A. Growth of the Platinum Oxide Film During Hydrogen Oxidation

The Point Defect Model predicts that the rate of thickening of the barrier layer of the passive film on a metal is given by:

$$\frac{dL}{dt} = A' e^{a_3 V} e^{-b_3 L} - C \quad (\text{AII-1})$$

where C is the dissolution rate of the film. Assuming that the dissolution rate is independent of voltage (i.e., no change occurs in the oxidation state of the cation upon dissolution) and assuming that the voltage is swept at a constant rate

$$V = V^0 + vt$$

where V^0 is the equilibrium potential for the formation of PtO , the rate of film growth becomes

$$\frac{dL}{dt} = A'' e^{a_3 V^0} e^{a_3 vt} e^{-b_3 L} - C$$

$$\frac{dL}{dt} = A e^{a_3 vt} e^{-b_3 L} - C$$

where $A = A'' e^{a_3 V^0}$. By variable substitution:

$$Z = e^{a_3 vt} e^{-b_3 L}$$

we get

$$dZ = a_3 v e^{a_3 vt} e^{-b_3 L} dt - b_3 e^{a_3 vt} e^{-b_3 L} dL$$

$$dZ = a_3 v Z dt - b_3 Z dL$$

$$\frac{dZ}{dt} = a_3 v Z - b_3 Z \frac{dL}{dt}$$

$$\frac{dL}{dt} = (a_3 v Z - \frac{dZ}{dt}) / b_3 Z$$

Accordingly,

$$(a_3 v Z - \frac{dZ}{dt}) \frac{1}{b_3 Z} = AZ - C$$

and hence

$$\begin{aligned} \frac{a_3 v}{b_3} - \frac{1}{b_3 Z} \frac{dZ}{dt} &= AZ - C \\ -\frac{1}{b_3 Z} \frac{dZ}{dt} &= AZ - C - \frac{a_3 v}{b_3} \end{aligned}$$

Defining $r = C + \frac{a_3 v}{b_3}$ we obtain

$$-\frac{1}{b_3 Z} \frac{dZ}{dt} = AZ - r$$

and hence

$$-\frac{dZ}{dt} = b_3 Z (AZ - r)$$

or

$$\int_{Z_0}^Z \frac{dZ}{Z(AZ - r)} = -b_3 \int_0^t dt \quad (\text{AII-2})$$

Expanding the integrand on the left side as a partial fraction, we write

$$\frac{1}{Z(AZ - r)} \equiv \frac{X}{Z} + \frac{Y}{AZ - r}$$

and hence

$$X(AZ - r) + YZ \equiv 1$$

Putting $Z = 0$ yields

$$-rX = 1$$

and therefore

$$X = -\frac{1}{r}$$

On the other hand, setting $Z = \frac{r}{A}$ we obtain

$$Y \cdot \frac{r}{A} = 1$$

and

$$Y = \frac{A}{r}$$

Accordingly,

$$\therefore \frac{1}{Z(AZ - r)} = -\frac{1}{rZ} + \frac{1}{r(Z - r/A)}\}$$

and integrating yields:

$$\int_{Z_0}^Z \frac{1}{Z(AZ - r)} dZ = -\frac{1}{r} \ln(Z) \Big|_{Z_0}^Z + \frac{1}{r} \ln(Z - r/A) \Big|_{Z_0}^Z = -\frac{1}{r} \ln\left(\frac{Z}{Z_0}\right) + \frac{1}{r} \ln\left(\frac{Z - r/A}{Z_0 - r/A}\right)$$

and hence

$$\therefore -\frac{1}{r} \ln\left(\frac{Z}{Z_0}\right) + \frac{1}{r} \ln\left(\frac{Z - r/A}{Z_0 - r/A}\right) = -b_3(t - t_0)$$

or

$$\ln\left[\frac{Z_0(Z - r/A)}{Z(Z_0 - r/A)}\right] = -b_3 r(t - t_0)$$

$$\frac{Z_0(Z - \frac{r}{A})}{Z(Z_0 - \frac{r}{A})} = e^{-b_3 r(t - t_0)} = \theta$$

$$Z_0(Z - \frac{r}{A}) = \theta Z(Z_0 - \frac{r}{A})$$

$$ZZ_0 - Z_0 \frac{r}{A} = \theta ZZ_0 - \theta Z \frac{r}{A}$$

$$Z(Z_0 - \theta Z_0 + \frac{\theta r}{A}) = Z_0 \frac{r}{A}$$

and

$$Z = \frac{Z_0 r / A}{Z_0 - \theta Z_0 + \frac{\theta r}{A}}$$

Recalling that $Z = e^{a_3 vt} e^{-b_3 L}$ we therefore obtain

$$Z_0 = e^{a_3 vt_0} e^{-b_3 L_0} \quad (L_0 \text{ is the thickness at } t_0, \text{ if } L_0 = 0, \text{ then } Z_0 = e^{a_3 vt_0})$$

Further recalling that $\theta = e^{-b_3 r(t - t_0)}$ we then find that

$$e^{a_3 vt} e^{-b_3 L} = \frac{r / A}{1 - e^{-b_3 r(t - t_0)} + \frac{r}{A} e^{-[b_3 r(t - t_0) + a_3 vt_0 - b_3 L_0]}}$$

$$a_3 vt - b_3 L = \ln \left\{ \frac{r / A}{1 - e^{-b_3 r(t - t_0)} + \frac{r}{A} e^{-[b_3 r(t - t_0) + a_3 vt_0 - b_3 L_0]}} \right\}$$

$$b_3 L = a_3 \nu t - \ln \left\{ \frac{r / A}{1 - e^{-b_3 r(t-t_0)} + \frac{r}{A} e^{-[b_3 r(t-t_0) + a_3 \nu t_0 - b_3 L_0]}} \right\}$$

and hence

$$L = \frac{a_3 \nu}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r / A}{1 - e^{-b_3 r(t-t_0)} + \frac{r}{A} e^{-[b_3 r(t-t_0) + a_3 \nu t_0 - b_3 L_0]}} \right\}$$

If $L_0 = 0$, then

$$L = \frac{a_3 \nu}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r / A}{1 - e^{-b_3 r(t-t_0)} + \frac{r}{A} e^{-[b_3 r(t-t_0) + a_3 \nu t_0]}} \right\} \quad (\text{AII-3})$$

The variation of the film thickness during the negative potential sweep is similar to that of the positive sweep. Set the time to the start time t_0 again, and replace the sweep rate ν to $-\nu$, V^0 to $V^{0'}$, which is the up limit for the potential sweep. Thus $r' = C - \frac{a_3 \nu}{b_3}$, $A' = A'' e^{a_3 V^{0'}}$, and L_0' is the thickness at potential $V^{0'}$. The thickness is then:

$$L' = L_0' - \frac{a_3 \nu}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r' / A'}{1 - e^{-b_3 r'(t-t_0)} + \frac{r'}{A'} e^{-[b_3 r'(t-t_0) - a_3 \nu t_0 - b_3 L_0']}} \right\}$$

If $L_0 = 0$ (the initial thickness of film at t_0 is zero), then

$$L_0' = \frac{a_3 (V_0' - V_0)}{b_3} - \frac{1}{b_3} \ln \left\{ \frac{r / A}{1 - (1 - r/A) e^{-\frac{b_3 C (V_0' - V_0)}{\nu}} e^{-a_3 (V_0' - V_0)}} \right\}$$

B. Current Density for Hydrogen Oxidation on Oxidized Film

Equation (AII-3) yield the thickness of the barrier layer as the potential varies linearly with time. We are now in the position to calculate the current density for the oxidation of hydrogen, assuming that the current is limited by the direct quantum mechanical tunneling of charge carriers across the film. As noted previously in this report, the tunneling current is given by:

$$i(t) = \hat{i} e^{-\beta L}$$

where $\hat{i}$ is the film free hydrogen oxidation current density. Substitution for the film thickness therefore yields

$$\begin{aligned}
 i(t) &= \hat{i} e^{-\beta \left[\frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r/A}{1 - e^{-b_3 r(t-t_o)} + \frac{r}{A} e^{[b_3 r(t-t_o) + a_3 v t_o]} \right\} \right]} \\
 &= \hat{i} e^{-\frac{\beta a_3 v}{b_3} t} \cdot e^{\frac{\beta}{b_3} \ln \left\{ \frac{r/A}{1 - e^{-b_3 r(t-t_o)} + \frac{r}{A} e^{[b_3 r(t-t_o) + a_3 v t_o]} \right\}} \\
 &= \hat{i} e^{-\frac{\beta a_3 v}{b_3} t} \cdot \left\{ \frac{r/A}{1 - e^{-b_3 r(t-t_o)} + \frac{r}{A} e^{-[b_3 r(t-t_o) + a_3 v t_o]} \right\}^{\beta/b_3}
 \end{aligned}$$

Hence

$$i(t) = \hat{i} \left\{ \frac{r/A}{1 - e^{-b_3 r(t-t_o)} + \frac{r}{A} e^{-[b_3 r(t-t_o) + a_3 v t_o]} \right\}^{\beta/b_3} \cdot e^{-\frac{\beta a_3 v}{b_3} t}$$

Putting $t_0 = 0$ yields

$$i(t) = \hat{i} \left\{ \frac{r/A}{1 - (1 - \frac{r}{A}) e^{-b_3 r t}} \right\}^{\beta/b_3} \cdot e^{-\frac{\beta a_3 v}{b_3} t}$$

and substituting

$$t = \frac{V - V^0}{v}$$

we obtain

$$i(V) = \hat{i} \left\{ \frac{r/A}{1 - (1 - \frac{r}{A}) e^{-b_3 r \frac{V - V^0}{v}}} \right\}^{\beta/b_3} \cdot e^{-\frac{\beta a_3}{b_3} (V - V^0)}$$

Now recalling that $r = C + \frac{a_3 v}{b_3}$ we obtain the following expression for the hydrogen oxidation current on oxidized platinum electrode

$$i(V) = \hat{i} \left\{ \frac{C/A + a_3 v / b_3 A}{1 - e^{-\left(\frac{C b_3}{v} + a_3\right)(V - V^0)}} \left[1 - \frac{C}{A} - \frac{a_3 v}{b_3 A} \right] \right\}^{\beta / b_3} e^{-\beta \frac{a_3}{b_3} (V - V^0)} \quad (\text{AII-4})$$

The hydrogen oxidation current density derived above must be added to the current density for the growth of the oxide film. The expression for the latter is given by the PDM as

$$i_{pass} = F[\chi k_1 C_M^L + \chi k_2 + \chi k_3 + (\delta - \chi)k_4 + (\delta - \chi)k_5 C_i^0 + (\delta - \chi)k_7 (C_{H^+} / C_{H^+}^0)^n]$$

For the specific case where no change in oxidation state occurs upon dissolution of the film we get:

$$i_{pass} = F \chi k_3^0 e^{a_3 V} e^{-b_3 L} e^{-c_3 p H}$$

For linear voltage sweep conditions, $V = V^0 + vt$, and hence

$$i_{pass} = F \chi k_3^0 e^{a_3 V^0} e^{a_3 vt} e^{-b_3 L} e^{-c_3 p H}$$

Recalling that $L = \frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r / A}{1 - e^{-b_3 r(t-t_0)} + \frac{r}{A} e^{-[b_3 r(t-t_0) + a_3 vt_0]}} \right\}$, and setting $t_0 = 0$, we obtain

$$i_{pass} = F \chi k_3^0 e^{a_3 V^0} e^{-c_3 p H} \frac{r / A}{1 - (1 - r/A) e^{-b_3 r t}}$$

$$i_{pass} = F \chi k_3^0 e^{a_3 V^0} e^{-c_3 p H} \frac{r / A}{1 - (1 - r/A) e^{-b_3 r \frac{V - V^0}{v}}}$$

The final contribution to the current is that due to charging of the film during the potential sweep

$$i_{charging} = C_{ox} \frac{dV}{dt}$$

where $C_{ox} = \frac{\varepsilon \varepsilon_0}{L}$, ε is the dielectric constant of the oxide film, and ε_0 is the vacuum permittivity.

$$i_{charging} = \frac{\mathcal{E}\mathcal{E}_0}{L} v = \frac{\mathcal{E}\mathcal{E}_0 v}{\frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left[\frac{r/A}{1 - (1 - r/A) e^{-b_3 r \frac{V-V^0}{v}}} \right]} \quad (\text{AII-5})$$

We are now in the position to write the total current density as

$$i_{total} = \hat{i} \left[\frac{r/A}{1 - (1 - r/A) e^{-b_3 r \frac{V-V^0}{v}}} \right]^{\beta/b_3} \cdot e^{-\frac{\beta a_3}{b_3} (V-V^0)} + F \chi k_3^0 e^{a_3 V^0} e^{-c_3 pH} \frac{r/A}{1 - (1 - r/A) e^{-b_3 r \frac{V-V^0}{v}}} + \frac{\mathcal{E}\mathcal{E}_0 v}{\frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left[\frac{r/A}{1 - (1 - r/A) e^{-b_3 r \frac{V-V^0}{v}}} \right]}$$

We now define $R = \frac{r/A}{1 - (1 - r/A) e^{-b_3 r \frac{V-V^0}{v}}}$. Accordingly, the total current becomes

$$i_{total} = \hat{i} R^{\beta/b_3} \cdot e^{-\frac{\beta a_3}{b_3} (V-V^0)} + F \chi k_3^0 e^{a_3 V^0} e^{-c_3 pH} R + \frac{\mathcal{E}\mathcal{E}_0 v}{\frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln R} \quad (\text{AII-6})$$

C. Calculation of Cyclic Voltamogram for Platinum

Let the potential be swept within the range V_1 to V_2 at a rate of v . Further assume that platinum oxidation and reduction are reversible within this range, then, during the positive sweep:

$$V = V_1 + vt$$

$$i_p = F \chi k_3^0 e^{a_3 V_1} e^{a_3 vt} e^{-b_3 L} e^{-c_3 pH} + \frac{\mathcal{E}\mathcal{E}_0}{L} v$$

During negative sweep, when $V = V_2 - vt$, the current becomes:

$$i_p' = F \chi k_3^0 e^{a_3 V_2} e^{-a_3 vt} e^{-b_3 L} e^{-c_3 pH} - \frac{\mathcal{E}\mathcal{E}_0}{L} v$$

With

$$L = \frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r/A}{1 - (1 - r/A)e^{-b_3 r t}} \right\}$$

$$L' = L_0' - \frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r'/A'}{1 - (1 - r'/A')e^{-b_3 r' t} + \frac{r'}{A'} e^{b_3 L_0'}} \right\}$$

Here $L_0' = \frac{a_3(V_0' - V_0)}{b_3} - \frac{1}{b_3} \ln \left\{ \frac{r/A}{1 - (1 - r/A)e^{-\frac{b_3 C(V_2 - V_1)}{v} e^{-a_3(V_2 - V_1)}}} \right\}$. Thus, the passive current density

during the positive potential sweep is

$$i_p = F \chi k_3^0 e^{a_3 V_1} e^{-c_3 p H} \frac{r/A}{1 - (1 - r/A)e^{-b_3 r t}} + \frac{\varepsilon \varepsilon_0}{\frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r/A}{1 - (1 - r/A)e^{-b_3 r t}} \right\}} v$$

During the negative potential sweep, the current is given by

$$i_p' = F \chi k_3^0 e^{a_3 V_2} e^{-c_3 p H} e^{-b_3 L_0'} \frac{r'/A'}{1 - (1 - r'/A')e^{-b_3 r t} + \frac{r'}{A'} e^{b_3 L_0'}} - \frac{\varepsilon \varepsilon_0}{L_0' - \frac{a_3 v}{b_3} t - \frac{1}{b_3} \ln \left\{ \frac{r'/A'}{1 - (1 - r'/A')e^{-b_3 r t} + \frac{r'}{A'} e^{b_3 L_0'}} \right\}} v$$