FUNDAMENTAL ASPECTS OF ELECTROCATALYSIS OF THE HYDROGEN ELECTRODE REACTION AND OXYGEN ELECTRODE REACTION ON PLATINUM

A Thesis in
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by
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ABSTRACT

This dissertation work studies the fundamental aspects of the electrocatalysis of the hydrogen electrode reaction (HER) and oxygen electrode reaction (OER) on platinum over a wide temperature range from ambient up to 220°C. Previously, the majority of the work reported was restricted to temperatures below 70°C due to apparatus constraints, whereas the current operation temperature for proton exchange membrane fuel cells is around 100°C and is envisioned to operate at even higher temperatures. In this work, a special apparatus for controlled hydrodynamic study was constructed, which can keep the system in a single aqueous phase at elevated temperatures.

The growth kinetics and mechanism of the anodic oxide film on platinum are studied under potential sweep conditions. By fitting the current equation derived based on the framework of the point defect model (PDM) on the linear polarization curves, the kinetic parameters for film growth and dissolution are extracted, which agree well with other findings.

The kinetics and mechanism of the HER are investigated both at ambient temperature with a rotating ring disk electrode and at elevated temperatures with a platinized nickel electrode. Ambient results by micropolarization analysis agree well with findings in literature, and yield an exchange current density on the order of mA/cm². An activation energy of 17.3kJ/mol is determined. This is comparable with that of a bulk platinum electrode, and is lower than sputtered platinum and single crystal platinum electrodes in alkaline solutions. Surprisingly, the apparent Tafel slope of the hydrogen evolution reaction is almost temperature independent. The most probable reason is that two parallel reactions with different activation energy and transfer coefficients are occurring at the interface.

The OER on platinum is also studied by potential sweep method and potentiostatic polarization method. The sluggish nature of this reaction is postulated to be due to the existence of a thin oxide layer on the electrode surface so that the electrons resides in the metal have to quantum mechanically tunnel (QMT) through this layer in order to reach the oxygen species in the solution or adsorbed on the surface.
The exponential decay of the current with potential (the inverse Tafel’s law) upon the formation of an oxide film can be accounted for by combining QMT theory for charge transfer across an interface and the PDM for film growth and dissolution. A new method for extremely thin oxide film thickness measurement is also developed by combining these two theories. This method employs the tunneling current of the hydrogen oxidation reaction as a probe and is demonstrated to be a very sensitive and convenient \textit{in situ} technique. However, currently the thickness range that can be measured is limited to 1-2nm, since the passive current of platinum imposing a lower limit of the tunneling current that can be measured.

The tunneling constant, which defines the blocking character of the film, is measured to be $(0.57 \pm 0.035) \times 10^8 \text{cm}^{-1}$, and is temperature independent. A barrier height of 0.31eV at the film/solution interface is then yielded. Theoretical interpretation is implemented by developing a model for the electronic structure of the metal/barrier layer/solution interphase utilizing the Boltzmann’s distribution law for the distribution of the energy states of the redox species in the solution phase and by noting that the barrier layer is a highly doped (and probably degenerate) defect (oxygen vacancy) semiconductor, having a Debye length that is the same order as the thickness of the film.
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### ROMAN SYMBOLS

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<td>$a_j$</td>
<td>activity for species $j$</td>
</tr>
</tbody>
</table>
| $A$ | (a) surface area of the electrode, chap.2, chap.5  
(b) film growth rate constant, chap.4 & Appendix A |
| $b_a$ | Tafel slope for an oxidation reaction |
| $b_c$ | Tafel slope for a reduction reaction |
| $C$ | (a) capacitance, chap.2  
(b) potential independent film dissolution rate, chap.4 & Appendix  
(c) concentration, chap.3 |
| $C_{dl}$ | Helmholtz double layer capacitance |
| $C_{ox}$ | geometric capacitance of the oxide film, $C_{ox} = \frac{\varepsilon \varepsilon_0 L}{L}$ |
| $C_{H^+}$ | hydrogen ion concentration in the solution at the film/solution interface |
| $C_{H^+}^0$ | standard state hydrogen ion concentration, defined as being 1.0mol/l |
| $D$ | diffusivity |
| $E$ | (a) energy  
(b) electrode potential, chap.5, 6 |
| $E^0$ | standard electrode potential |
| $E^*$ | equilibrium potential of a redox couple |
| $\Delta E$ | barrier height |
| $E_C$ | conduction band energy |
| $E_F$ | Fermi energy |
| $E_V$ | valence band energy |
| $f$ | (a) fugacity of gas  
(b) rotation frequency in rpm, chap.5 |
| $F$ | Faraday’s constant |
| $\Delta G^0$ | standard gibbs free energy change |
| $\Delta G_{ad}$ | adsorption energy |
$H$ Planck constant
$\Delta H$ enthalpy energy of change/activation energy
$i$ current density
$\hat{i}_0$ “film-free” (bare metal electrode surface) redox reaction current density
$i_{l,a}$ limiting current for the hydrogen oxidation reaction
$i_{l,c}$ limiting current for the hydrogen evolution reaction
$I_L$ limiting current density
$I_{ss}$ steady state current density
$k$ Boltzmann’s constant
$k_{i}$ rate constants for reaction (i)
$k_{i}^0$ standard rate constants independent of potential and thickness for reaction(i)
$k_{i}^{00}$ base rate constant independent of potential, thickness and pH for reaction(i)
$K$ Henry’s constant
$K_L$ mass transfer coefficient
$K_{sp}$ solubility product of the KCl solution
$L_D$ Debye length
$L$ thickness of the oxide film
$L^+$ growth of the oxide film
$L^-$ dissolution of the oxide film
$m/M$ metal atom
$m_{H2}$ amount of dissolved hydrogen
$m_e$ the effective electron mass
$M_{i^{*\star}}$ cation interstitial
$n$ (a)kinetic order of the film dissolution reaction with respect to $C_{H^+}$, chap.2
(b) number of electrons transferred, chap.3, 4
$n(E,V)$ density of empty electron states having energy $E$ in the metal electrode at the applied voltage $V$
$N_D$  donor density  

$N(E,x)$  density of donor species having energy $E$ at a distance $x$ from the metal surface in the solution phase or adsorbed at the oxide film surface  

$P$  pressure in Torr  

$P_{T}(E,x)$  probability of tunneling of an electron from the reduced species in the solution/at the surface to an acceptor state in the metal at the same energy  

$Q$  charge density  

$R$  gas constant  

Re  Reynolds numbers  

Sh  Sherwood numbers  

St  Stanton numbers  

$t$  time  

$T$  temperature  

$U$  vibrational-rotational energy of ion-solvent bonds  

$U_0$  ground state vibrational-rotational energy of ion-solvent bonds  

$v$  voltage scan rate in the cyclic voltammetry  

$V$  potential  

$V$  voltage of zero thickness of the barrier layer  

$V_{\text{abs}}$  potential of the electrode at equilibrium on the absolute (vacuum) scale  

$\Delta V$  potential away from the film free potential for platinum  

$x$  distance from the metal surface  

$x_j$  mole fraction of gas type $j$  

**GREEK SYMBOLS**  

$\alpha$  polarizability of the barrier layer/outer layer (solution) interface  

$\alpha_i$  transfer coefficient, subscript $i$ represents the $i$-th elementary interfacial reaction  

$\alpha_a$  transfer coefficient of the hydrogen oxidation reaction  

$\alpha_e$  transfer coefficient of the hydrogen evolution reaction
\( \beta \) dependence of the potential drop across the same interface on pH
\( \hat{\beta} \) tunneling constant
\( \Gamma \) oxidation state of platinum in solution in the passive range
\( \delta \) (a) effective (Nernstian) diffusion layer thickness, chap.3
(b) measure of the efficiency of electrical energy used to increase the energy states of the species
\( \gamma_j \) activity coefficient for species \( j \)
\( \varepsilon \) dielectric constant of the oxide
\( \varepsilon^0 \) permittivity of free space
\( \hat{\varepsilon} \) electric field strength within the oxide film
\( \eta \) overpotential
\( \bar{\mu}_e \) Fermi energy of an electron in the redox couple in the solution
\( \nu \) kinematic viscosity
\( \rho \) density
\( \phi_{ls} \) potential drop at the barrier layer/solution interface
\( \phi^0_{ls} \) value of \( \phi_{ls} \) in the standard state
\( \phi_{mf} \) potential drop at the metal/barrier layer interface
\( \Delta \phi \) potential drop across the barrier layer
\( \phi^s \) potential at the solution side of the interface
\( \Phi \) work function of platinum
\( \Omega \) molar volume per cation of the barrier layer
\( \chi \) oxidation state of platinum in the barrier layer in the passive state
\( \omega \) rotation rate

STANDARD ABBREVIATIONS

AFC  alkaline fuel cell
CV  cyclic voltammogram
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>DMFC</td>
<td>direct methanol fuel cell</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
</tbody>
</table>
| HER     | (a) hydrogen electrode reaction, chap. 2  
          (b) hydrogen evolution reaction |
| HFM     | high field model |
| HOR     | hydrogen oxidation reaction |
| HPLC    | high pressure liquid chromatography |
| IEM     | interfacial equilibrium model |
| IHP     | inner Helmholtz plane |
| LEED    | low energy electron diffraction |
| MCFC    | molten carbonate fuel cell |
| OER     | oxygen electrode reaction |
| OHP     | outer Helmholtz plane |
| ORR     | oxygen reduction reaction |
| PAFC    | phosphoric acid fuel cell |
| PEM     | place exchange model |
| PEMFC   | proton exchange membrane fuel cell |
| PDM     | point defect model |
| QMT     | quantum mechanical tunneling |
| RRDE    | rotating ring disk electrode |
| RHE     | reversible hydrogen electrode |
| SCE     | saturated caramel electrode |
| SEM     | scanning electron microscopy |
| SHE     | Standard hydrogen electrode |
| SOFC    | solid oxide fuel cell |
| XRD     | x-ray diffraction |
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Chapter 1
Overview

The increasing importance and popularity of the fuel cells are partly due to the oil crisis, and partly due to the increasing concern over global warming as consequences of fossil fuel used in the propulsion of vehicles and in electricity generation. The dramatic increase of the world population during the last half century led to a rapid consumption of energy and the global awareness of how human activities in the industrialized countries affect the environment. Now, the challenge is how a sustainable energy future can be achieved.

Fuel cells are currently the most promising solution for the sustainable energy future. The recent success of road vehicles powered by proton exchange membrane fuel cells (PEMFCs) developed by General Motor, DaimlerChrysler, and Ballard Power Systems has indicated the coming of the fuel cell age[1]. Using pure hydrogen, the only product of this energy conversion system is drinkable water, thus eliminating all the poisonous emissions otherwise caused by heat engines and other electricity generation methods. Moreover, fuel cells have great flexibility and compatibility within the existing fuel infrastructure for various scale power requirements, with notably higher electrical energy conversion efficiency than any other conventional systems.

With the increasing commercial interest in fuel cells, considerable research effort has been invested over the past several decades in improving the performance of current electrocatalysts and searching for new electrocatalysts, developing reliable membranes for use in PEMFCs and direct methanol fuel cells (DMFC), as well as developing other components of fuel cells[2]. However, besides the complex interactions in stacking the system, some basic aspects of the anodic and cathodic reactions in fuel cells are still not resolved. Platinum-group based alloys remain as the only practical catalysts for both reactions in low (<120°C) and medium temperature (100°C-400°C) fuel cells, although progress has been made through the development of platinum/non-noble metal alloy
electrocatalysts (e.g. Pt/Cr) and through better methods of depositing nano-scale platinum on carbon supports. There are still two Achilles’ Heels waiting to be solved, before the fully commercialization of PEMFC technology: the sluggish nature of the oxygen electrode reaction (OER) and the lack of a viable high temperature (>400°C) proton exchange membrane.

The rate of the OER, even on platinum, is 6 orders of magnitude lower than that of the hydrogen electrode reaction (HER)[3], resulting in high overpotential loss that limit the fuel cell efficiency, and the reaction does not always occur via the desired four-electron pathway. Hydroxyl radicals and hydrogen peroxide generated via the undesired two-electron pathway result in severe degradation of the current membranes, thereby limiting the membrane electrode assembly (MEA) life. Controversy exists with respect to the role of catalyst structure on catalyst activity, due to experimental difficulties in resolving structures at the nanometer scale. It is generally agreed that small particles have higher specific surface area, thus providing better performance (higher activity). However, an optimum particle size for the specific activity was found to be around 4-5nm[4-7]—though it is disputed that the reactivity depends on electrocatalyst loading, that the intercrystalline distance is important to the oxygen reduction reaction (ORR)[8], and that larger particles have higher specific exchange current densities than smaller particles[1].

Researchers have gradually recognized that, even in the case of a “noble” metal, such as platinum, the ORR still occurs on an oxide film covered surface, not on a bare metal surface at low overpotentials[9-12]. Thus, charge transfer between metal and oxygen species must involve the transfer of electrons or electron holes through a film whose thickness depends upon the applied voltage. Therefore, the defect structure and the film thickness are very important in determining the rate of the ORR. Yet, surprisingly, only a little information could be found regarding these properties in literature.

Despite the fast character of the hydrogen oxidation reaction (HOR) on platinum, with a rate constant of about 10⁻⁵ mols⁻¹cm⁻²[13], poisoning of the electrocatalyst is still a crucial problem mainly due to the CO impurity in the hydrogen fuel obtained via stream
reforming or the partial oxidation of carbonaceous fuels. Scientists endeavor to increase the operation temperature of PEMFCs (currently it is still limited to below 100°C as the membrane requires humidification for good proton conduction[2,14-16]), so that not only the kinetics of the reactions are greatly enhanced, but also the poisoning problem is mitigated, thereby rendering the design of the fuel cell MEA much simpler.

Partly due to the apparatus restrictions, mechanistic studies of both reactions at elevated temperatures are seldom published in literature, and most of work was limited to below 70°C. However, as the proton exchange membranes are envisioned to operate at temperatures above 100°C, it is of great importance as well as interest to explore the behavior of both reactions at elevated temperatures. This dissertation work on the hydrogen electrode reaction, oxygen electrode reaction, as well as charge carriers tunneling across anodic oxide films on platinum covers a wide range of temperature up to 220°C using a specially designed, controlled hydrodynamic apparatus. Therefore, it is expected to unveil the properties of these reactions and the oxide film over this temperature range.

Some specific efforts in this dissertation are that we:

1. Studied the growth kinetics of the anodic oxide film on platinum under potential dynamic conditions and extracted kinetic parameter values based on the framework of the point defect model (PDM)[17-19]. The structural properties of the oxide film are also portrayed.

2. Explored the kinetics and mechanism of the HER on platinum over a wide temperature range using cyclic and potentiostatic polarization methods. Kinetic parameter values of the reaction are extracted by micropolarization analysis and optimization on Butler-Volmer equation. Temperature dependence of the exchange current density, Tafel slopes, and transfer coefficients are obtained.

3. Studied the ORR on both bare and oxide covered platinum electrode using a rotating ring disk electrode. The probable reason for the sluggish nature of the reaction is postulated.
4. Investigated the impact of the thin oxide layer on the rate of redox reactions, and measured the thickness of the oxide layer utilizing the method we developed combining the PDM and quantum mechanical tunneling (QMT) theory. This method employs the tunneling current of the HOR as a probe, and measures the film thickness down to an angstrom.

5. Illustrated the electronic structures at the metal/oxide barrier layer/solution interphase. Explained the tunneling behavior employing the Boltzmann’s law for the distribution of the energy states in solution. The barrier height at the oxide/solution interface, through which the charge carriers have to tunneling in order for the reaction to occur, is also obtained.

The materials in this dissertation are divided into 7 chapters. Chapter 1 (this chapter) unfolds an energy sustainable future powered by the fuel cell technology, presents the remaining technical problems, and introduces the thesis work and organization of this dissertation. Chapter 2 is intended to provide some pertinent background information on the fuel cells: kinetics and mechanism of HER and OER, and the electrocatalysis. Theories of QMT for charge carriers transfer across an oxide barrier layer, the PDM for film growth and dissolution under steady state and transient conditions, as well as the development of the film thickness measurement method combining the above two theories, are also introduced in chapter 2. Chapter 3 gives the layout of experimental apparatuses used both for ambient temperature and high temperature experiments, including the hydrodynamic/mass transport analysis of the designed flow channel. Preparation methods for the working electrode (electroplating) and the reference electrode are also introduced. Chapters 4 to 6 expand the experimental results and discussions. The general properties of the platinum electrode and growth kinetics of the platinum oxide film under transient conditions are discussed in chapter 4. Chapter 5 is focused on the electrocatalytic aspects of platinum for the kinetics and mechanism of the HER over a wide temperature range, as well as the ORR. Chapter 6 explores the impact of the oxide film on the rate of redox reactions, how effectively the newly developed technique can measure the film thickness, and the electronic structure at
the metal/barrier layer/solution interphase is also revealed. Chapter 7 summarizes this dissertation, and discusses some possible future work.

References


Chapter 2

Background

The idea of the fuel cell turns out to be a quite early one. The first fuel cell was made by Grove in 1839[1], but the development lacked drive for almost a century due to some economic factors, and the study of the electrode reaction kinetics did not begin until the 1950s. The concept of electrodes as catalysts—in fact, there is a great dependence of the reaction rate on the chosen electrode surface (over 10 orders of magnitude variation), was first introduced by Grubb in 1963[2]. Discover of the proton exchange Nafion® membrane in 1972[3] promised to revolutionize transportation systems by eliminating emissions of CO₂ and other poisonous gases from the combustion of carbonaceous fuels. Therefore, over the past six decades, there has been a wide variety of fuel cell research, not only on the fundamental aspects, but also on other components. This chapter provides some basic information regarding the fundamental aspects of the fuel cell technology, theory of quantum mechanical transfer of the charge carriers across an oxide film which inhibits the rate of the redox reactions, and also the point defect model (PDM) for oxide film growth and dissolution.

2.1 Types of Fuel Cells

Fuel cells are energy producing devices which continuously convert chemical energy of a reaction into electricity and at the same time release some heat, but without any combustion, as long as the fuel is supplied. For the case of a hydrogen/oxygen fuel cell, which is the most popular, the overall chemical reaction is:

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \]  
(Eq. 2.1)
with the Gibbs energy change of -237 kJ/mole, and hence the standard equilibrium cell voltage of 1.23V. By appropriate assembly, fuel cells can be scaled for various purpose uses. There are mainly five types of fuel cells usually classified by the electrolyte employed in the cell or the cell operating temperature: proton exchange membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). All types of fuel cells function in the same basic way that hydrogen fuel or hydrocarbons are oxidized at the anode and oxygen is reduced at the cathode. Direct methanol fuel cell (DMFC) is somehow an exception to the classification, as methanol, instead of hydrogen, is directly oxidized in the fuel cell, but it also uses the same type of Nafion© membranes as the PEMFC. Table 2-1 provides an overview of the properties of these six fuel cell types that are currently under active development[3-5].

Table 2-1: Fuel cell types that are under active development and their characteristics and applications

<table>
<thead>
<tr>
<th></th>
<th>PEMFC</th>
<th>DMFC</th>
<th>PAFC</th>
<th>AFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating</td>
<td>60-100°C</td>
<td>60-120°C</td>
<td>160-220°C</td>
<td>60-220°C</td>
<td>600-800°C</td>
<td>600-1000°C</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Solid polymer</td>
<td>Solid polymer</td>
<td>H3PO4</td>
<td>KOH</td>
<td>Na2CO3</td>
<td>Y-ZrO2</td>
</tr>
<tr>
<td>Carrier</td>
<td>H+</td>
<td>H+</td>
<td>H+</td>
<td>OH-</td>
<td>CO3^2-</td>
<td>O2^-</td>
</tr>
<tr>
<td>Fuel compatibility</td>
<td>H2, methanol</td>
<td>Methanol</td>
<td>H2</td>
<td>H2</td>
<td>Hydrocarbons</td>
<td>Hydrocarbons, CO</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Pt alloys</td>
<td>Pt alloys</td>
<td>Pt alloys</td>
<td>Pt alloys</td>
<td>Ni</td>
<td>Perovskites</td>
</tr>
<tr>
<td>Efficiency &amp;</td>
<td>35-45%, 5- 250kW</td>
<td>5kW</td>
<td>40%, 50kW-11MW</td>
<td>35-55%, 5-150kW</td>
<td>&gt;50%, 200kW-2MW</td>
<td>&gt;50%, 2kW-MW</td>
</tr>
<tr>
<td>Power range</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applications</td>
<td>Transportation, portable, small power plants</td>
<td>Portable, small power plants</td>
<td>Small-medium plants</td>
<td>Space, military</td>
<td>Small-medium power plants</td>
<td>Small power plants</td>
</tr>
</tbody>
</table>
From the table, it is clearly seen that platinum/platinum based alloy is still the best electrocatalyst choice for low to medium temperature applications due to its superior activity. With the technological advances, cost of the catalyst loading is greatly reduced (though it is still the major barrier for commercialization) by means of reducing the particle size of the catalyst, and hence, increasing the specific surface area for the reactants to adsorb on.

The electrolyte used in this thesis work is alkaline. The advantage of alkaline based H₂/O₂ fuel cell is that the activity of oxygen reduction reaction (ORR) is much higher in alkaline than in acid media, thus, significantly reducing the cost as non-noble metals can be used as electrocatalysts while they will dissolve in acid medium. People are now looking for polymer membranes that use alkaline media[6-10]. With the application of this alkaline, anion-exchange membranes in fuel cells, several problems associated with traditional DMFCs and AFCs are going to be potentially resolved and significant performance enhancement and cost reduction are predicted.

### 2.2 Hydrogen Electrode Reaction

As the anodic reaction in the fuel cell components, the hydrogen electrode reaction (HER) on platinum or platinum based alloys is one of the most intensively investigated electrochemical processes[11-24] and has served as a model for electrocatalysis studies over the past six decades. The reaction rate of the HER on platinum is very fast with the exchange current density on the order of mA/cm²[25] when pure hydrogen gas is fed, and the reaction is usually controlled by the mass transport of hydrogen at the electrode/electrolyte interface. This reaction, nevertheless, still deserves further investigation, as new aspects of the mechanism are continually being discovered. Moreover, with the progressive increasing operation temperature for low to medium temperature fuel cells, it is becoming more and more important to study this reaction at elevated temperatures, as it is known that the kinetics and mechanism of the HER change when the conditions at the electrode interface change. Therefore, it is the goal of this work to explore the behavior of this reaction at elevated temperatures.
The overall HER can be written as (reduction reaction is provided here following the Stockholm convention, but in fuel cell operation, this reaction proceeds in the oxidation direction):

\begin{align*}
2H_2O^+ + 2e^- &\rightarrow H_2 + 2H_2O \quad \text{(in acid)} \quad \text{(Eq. 2.2)} \\
2H_2O + 2e^- &\rightarrow H_2 + 2OH^- \quad \text{(in alkaline)} \quad \text{(Eq. 2.3)}
\end{align*}

Choice of the electrode or electrolyte as well as variation of other conditions at the electrode and solution interface can cause the change of the Tafel slopes for hydrogen oxidation and evolution reactions due to the different mechanism dominating in the given system. As the overall HER involves transfer of two electrons, it can therefore be divided into two elementary steps involving the participation of adsorbed H atoms. So far, two reaction pathways are considered as the most probable for the hydrogen evolution reaction\cite{25}: discharge-recombination path and discharge-electrochemical desorption path. In case of alkaline solution, the discharge-recombination path, which is also well known as the Volmer-Tafel mechanism, can be expressed as:

\begin{align*}
M + H_2O + e^- &\rightarrow MH + OH^- \quad \text{(Volmer Reaction)} \quad \text{(Eq. 2.4)} \\
2MH &\rightarrow 2M + H_2 \quad \text{(Tafel Reaction)} \quad \text{(Eq. 2.5)}
\end{align*}

where M indicates the metal electrode, and MH is the adsorbed state of the hydrogen atom on metal electrode surface. The discharge-electrochemical desorption path, also known as the Volmer-Heyrovsky mechanism, can be expressed as:

\begin{align*}
M + H_2O + e^- &\rightarrow MH + OH^- \quad \text{(Volmer Reaction)} \quad \text{(Eq. 2.6)} \\
MH + H_2O + e^- &\rightarrow H_2 + M + OH^- \quad \text{(Heyrovsky Reaction)} \quad \text{(Eq. 2.7)}
\end{align*}
The first discharge step that water discharges on the metal electrode surface and forms an adsorbed H atom is common to both paths, but the mode of the removal of the adsorbed H atom is different. Each step can be rate determining (assuming that the reaction is activation controlled and not by mass transport), and the theoretical forecast of the criteria for kinetic parameters of each mechanism was provided by Bockris[25], which is also used as a reference for the present work. When noble metal electrodes like platinum are used, the exchange current density reaches as high as $10^{-3}$ A/cm$^2$, then the overall reaction can be governed by the diffusion of the molecular hydrogen away from the electrode surface:

$$H_{2,a} \rightarrow H_{2,b}$$  \hspace{1cm} (Eq. 2.8)

where $H_{2,a}$ and $H_{2,b}$ are the molecular hydrogen at the electrode surface and in the bulk of the solution, respectively.

Kinetics of the HER has been investigated on a wide variety of electrodes. However, when pure hydrogen is used, platinum is still the best electrocatalyst at low to medium temperatures, not only because of its stability (most other metals dissolve in acid) and availability, but also its superior catalytic power. As indicated from the reaction pathways, the heat of H adsorption on metal or the bond strength between the metal and H atom M-H, is crucial to the kinetics of the HER. So that if we plot the exchange current density of the HER against the M-H bond strength of a series of catalysts (the well known “volcano plot”) [26-28], then platinum sits on top of the volcano, and the activity of the HER varies by 5-6 orders of magnitude depending on the electrode material. Meanwhile, the diffusivity of the adsorbed H atom on the metal electrode surface and the coverage of the surface by the adsorbed H atoms determines which pathway the reaction proceeds with. At low temperatures, the diffusivity of the adsorbed H atoms may be the rate determining step for the reaction.
To date, most of the work on the HER has been carried out at ambient temperature and, surprisingly, only sparse work has been reported for elevated temperatures, especially at temperatures above 70°C, where PEMFCs are envisioned to operate. Only a few mechanistic studies of the HER have been carried out at elevated temperatures, e.g. the HER on mercury in HCl solutions up to temperature 300°C by Tsionsky et al[29]. The HOR has been studied in this lab by Biswas[30] at elevated temperatures, but mechanistic information was not achieved since only the HOR was studied. In this thesis work, both the anodic and cathodic branches are explored, therefore, some important kinetic parameters and mechanism of the reaction can be revealed.

2.3 Oxygen Electrode Reaction

The electrochemical reduction of oxygen is a reaction of great practical importance not only because of its role in the kinetics of corrosion mechanisms, but also because that it is the rate controlling reaction in electrochemical energy conversion systems, particularly in fuel cells. The kinetics of the ORR is sluggish on any electrode material with the exchange current density less than \(10^{-10}\)A/cm\(^2\) at room temperature. Even for the most catalytically active noble metal electrodes, measurable currents could not be obtained at the potentials near the equilibrium value, and only under high overpotentials (>250mV) are the reduction currents measurable. Despite the great amount of efforts invested, advances in finding a new, better catalyst remain hesitant. Although progress has been made through the development of platinum alloy electrocatalysts (e.g. Pt/Cr) and through better methods for depositing nano-scale platinum particles on carbon supports, it is still not certain, at the fundamental level, how an electrocatalyst works for the ORR, and as a result, no principle has evolved which would lead to radical improvement of the electrocatalysis design for the ORR.

The mechanism of the ORR is much complex than that of the HOR as it involves transfer of 4 electrons that may include several elementary steps during which bonds are
broken and formed. A number of reaction schemes have been proposed, Wroblowa et al. [31] gave the simple, generalized version of the $O_2$ reduction pathways as

$$\begin{align*}
&k_1 \\
&O_2 \xrightarrow{k_2} O_{2,\text{ad}} \xrightarrow{k_3} H_2O_{2,\text{ad}} \xrightarrow{k_4} H_2O \\
&\text{H}_2O_2
\end{align*}$$

where $k_i$ is the rate constant for the $i$-th reaction. Based on this reaction scheme, $O_2$ can be reduced either directly to $H_2O$ with a rate constant of $k_1$ (the so called direct 4-electron path), or to an adsorbed intermediate $H_2O_2$ with a rate constant of $k_2$ (series 2-electron pathway)[32]. If the adsorbed peroxide is further reduced to $H_2O$ ($k_3$), then it completes the series 4-electron pathway. However, the hydrogen peroxide can also chemically decompose on a catalytic electrode surface ($k_4$), or desorb and then diffuse into the bulk of the solution ($k_5$), rendering a decrease in the electrical efficiency, and also the degradation of the membrane assembly. The desirable 4-electron pathway, however, also consists of a number of steps involving oxygen bond dissociation and electron, proton transfer. It is still not clear whether the electron and proton transfer step starts before the cleavage of the O-O bond or after the dissociation[33]. Experimental evidence indicates that there is no O-O bond splitting before the formation of a peroxide species[32,34,35], and the rate determining step is the transfer of the first electron to the adsorbed $O_2$ molecule.

Platinum is by far the best electrocatalyst known for the ORR in low temperature PEMFCs—though the exchange current density of the oxygen electrode reaction on platinum is still 6 orders of magnitude lower than that of the HER[25], which results in the high cost of the commercialization of this technology and is responsible for about 60% overpotential loss of the fuel cell. It is very interesting, that, although the “oxide theory” was used at the beginning of last century to explain the open circuit potential of the hydrogen-oxygen fuel cell being lower than 1.229V[36-39], a lot of researchers are not aware of the fact that the ORR occurs on an oxide covered platinum electrode, not on
a bare platinum metal electrode. According to the thermodynamics calculation (using the 
Chemical Reaction and Equilibrium Software with Extensive Thermochemical Database 
(Version 5.1) by Outokumpu HSC\textsuperscript{®} Chemistry), the equilibrium potentials for the 
formation of PtO/PtO\textsubscript{2} are 0.996V and 1.019V respectively with the reaction paths:

\begin{align*}
PtO + H_2 & \leftrightarrow Pt + H_2O \quad E^0 = 0.996V \\
PtO_2 + 2H_2 & \leftrightarrow Pt + 2H_2O \quad E^0 = 1.019V
\end{align*}

(Eq. 2.9) (Eq. 2.10)

With the existence of a thin platinum oxide, charge transfer between the metal and 
adsorbed oxygen species must involve the quantum mechanical transfer of electrons or 
electron holes through a film whose thickness depends upon the applied voltage. The 
fact that measurable currents are obtainable only below 1V_{RHE}\textsuperscript{1} is a proof of the existence 
of the oxide layer, and its inhibiting effect. Extensive work by some researchers has 
shown that the rate of oxygen reduction decreases exponentially with increasing film 
thickness when the potential is held constant[40-43]. The decrease of the tunneling 
current can be attributed to a decrease in the quantum mechanical tunneling (QMT) 
probability for transfer of charge carriers (electrons and/or holes) through the film. Study 
for the kinetics of the ORR therefore must not be carried out without considering the 
structural and electronic properties of this thin oxide layer, and its impact to the rate of 
the reaction. This then became the interest of this work. Recent work in our lab has 
defined the crystallographic point defect and electronic structures of the film based on the 
framework of the PDM[44]. Briefly, the passive film forms as a bi-layer structure 
comprising a defective PtO barrier layer, and an outer Pt(IV) oxide or hydroxide layer 
that forms at high potentials. The barrier layer is thin (0.1 – 1.0 nm, depending upon the 
voltage) and is n-type in electronic character, with the dominant point defect being 
identified as the oxygen vacancy[44]. The PDM[45,46] quantitatively predicts the steady

\textsuperscript{1} To differentiate the RHE from the SHE, we note that the Reversible Hydrogen Electrode (RHE) refers to 
a hydrogen reference electrode under the same conditions of pH and temperature as in the solution of the 
studied electrode, and at the same H\textsubscript{2} pressure (Ref.[55], p1207).
state thickness of a barrier oxide layer on a metal as a function of the applied potential. Based on QMT theory and the PDM, a new method was developed to measure the thickness of thin films down to angstroms[47-50]. The following sections introduce some fundamental aspects of QMT theory and the PDM.

### 2.4 Electron Transfer across a Passive Film

The exponential decrease of the tunneling current with increasing film thickness at the metal/barrier layer/solution interphase is in accordance with the elastic tunneling theories originally developed by Gurney[51,52] in the early 1930s, and furthered by Weiss[53], Marcus[54-56], Levich[57,58], and Gerischer[59,60] in the 1950s, 1960s, and 1970s, among others, for the transfer of charge carriers from its bound states to acceptor states through the electrode/solution interface. Gurney was the founder of quantum electrode kinetics[61]. After 1970, the development of quantum electrode kinetics is mainly furthered by Bockris and Khan et al.[61-63] stressing molecular level contributions, i.e. vibrational-rotational energy levels of the ion-solvent bonds. The theory treats a redox reaction at an oxidized metal electrode/solution interface as involving the QMT of an electron from an occupied state in one phase (e.g., a reduced specie in solution or adsorbed at the surface) to an unoccupied state in the other phase (e.g. metal) with the energy levels of two states being equal. The current density for an anodic charge transfer reaction is therefore given by

\[
i \propto \int \int n(E,V)N(E,x)P_T(E,x) dEdx
\]

(Eq. 2.11)

where \(n(E,V)\) is the density of empty electron states having energy \(E\) in the metal electrode at the applied voltage \(V\), \(N(E,x)\) is the density of donor species having energy \(E\) at a distance \(x\) from the metal surface in the solution phase or adsorbed at the oxide film surface, and \(P_T(E,x)\) is the probability of tunneling of an electron from the reduced
species in the solution/at the surface to an acceptor state in the metal at the same energy. The tunneling probability \( P_T(E, x) \) can be calculated by solving the Schrödinger equation for a specific shape of potential barrier using the WKB approximation. The quantity \( n(E, V) \) is the product of the density of states in the metal and the Fermi-Dirac distribution function[64] for the empty states in this case. When the oxide film on the metal electrode acts as a barrier to the direct (“resonant”) tunneling of charge carriers, the tunneling probability depends on the barrier thickness \( L \) and the barrier height \( \Delta E \) [59] as:

\[
P_T(E, x) \propto \exp\left[-\frac{4nL}{h} \sqrt{\frac{2m_e \Delta E}{\hbar^2}} \right]
\]

(Eq. 2.12)

for a rectangular shape barrier, where \( m_e \) is the effective electron mass and \( h \) is Planck’s constant. A schematic electronic band diagram at the metal/barrier layer/solution interface and QMT of an electron from a reduced species \( R \) in the solution to the metal in case of an anodic reaction is shown in Figure 2-1.

![Figure 2-1: Quantum mechanical tunneling of an electron from a reduced species \( R \) at the oxide/solution interface to an empty state in the metal.](image-url)
Since the oxide film on platinum is generally very thin (perhaps smaller than the Debye length of the semi-conductor junction)[44,65], the film is reckoned to be completely depleted under high field conditions and, hence, the oxide thickness may be taken as the barrier layer thickness, and the direct ("resonant") tunneling is reckoned to be the prevailing tunneling mode. Furthermore, the barrier height is determined by the difference of the Fermi level of electrons associated with the vibrational-rotational levels of the ion-solvent bonds of the redox couple in the solution (or at the surface) and the energy level at the conduction band edge of the oxide phase. The Fermi energy of an electron in the redox couple in the solution $\mu_e^S$, which is actually the electrochemical potential of electrons associated with the vibrational-rotational levels of redox ion-solvent bonds at equilibrium, can be defined as[63,66]

$$\mu_e^S = -FV_{\text{abs}} - F\phi^S$$

(Eq. 2.13)

where $F$ is Faraday’s constant, $V_{\text{abs}}$ is the potential of the electrode at equilibrium on the absolute scale (or on the “vacuum scale”, note that the vacuum potential scale for the standard hydrogen electrode (SHE) is $4.6 \pm 0.2\text{V}$[63,67]), and $\phi^S$ is the potential at the solution side of the interface. The concept is that the electrons tunnel from the uppermost occupied states of the redox couple in the solution to the available states in the metal at the same energy. Unlike metal and semiconductor materials, for which the partition function of electrons in the various energy states are well defined (Fermi-Dirac distribution), controversy (or, perhaps, misunderstanding) has existed for decades with respect to the appropriate distribution function of the energy states in solution. The controversy arises because the electrons with Fermi level energy in the metal are free to move, whereas, the electrons in the solution are bound to the ions, and their energy is related with the vibrational and rotational states of the bonds of the ion-solvent in the solution. In this thesis work, Boltzmann’s distribution law for the distribution of the vibrational-rotational energy states of the redox species in the solution is used, therefore,
the availability of a state with energy $E$ above the ground state of the ion-solvent fluctuation is proportional to $\exp(-E/RT)$. However, it should be noted that the vibrational-rotational levels of ion-solvent bonds in solution are appreciably blurred by the interactions with the adjacent solvent molecules, so that each energy level has a continuous band of levels in accordance with Gaussian distribution[2,62,63].

Briefly, the theory for QMT of charge carriers across a thin oxide film of thickness $L$ on a metal electrode surface yields a tunneling current density $i$, that can be expressed in the following simple form

$$i = i_0 e^{-\beta L} \quad \text{(Eq. 2.14)}$$

where $\beta$ is the tunneling constant, which defines the blocking character of the film[68-71], and $i_0$ is the “film-free” (bare metal electrode surface) redox reaction current density. In this formula, it is evident that $\beta$ is mainly determined by the barrier height, $\Delta E$. However, an accurate calculation of $\beta$ requires a detailed picture of the potential distribution across the passive film, in order to determine $\Delta E$.

In developing an electrochemical theory for charge transfer at oxide-covered metal surfaces, it is necessary to recognize that the independent variable that is available for experimental manipulation is generally the applied voltage, not the film thickness as expressed in Eq. (2.14). Thus, in order to render a theory for charge transfer compatible with experiment, it is necessary to develop a theoretical relationship between the passive film thickness and the applied voltage, recognizing that the accurate experimental determination of the thickness of a thin film across which direct (“resonant”) QMT
occurs is exceedingly difficult, if not impossible, employing the conventional techniques (e.g. an ellipsometer is able to measure the film thickness accurately only when the film is significantly thicker than the roughness of the surface so that the refractive index of the film can be differentiated from the composite comprising the substrate, oxide and water). The required relationship between the film thickness and applied voltage is readily provided by the PDM[45,46].

2.5 The Point Defect Model

The phenomenon of passivity, that a reactive metal is protected from the environment with a passive oxide layer, has been known for 170 years as it is the enabler of our current, metals-based civilization[72]. The conditions under which the passive films can exist is of great theoretical and practical interest, and many theories and models for the passive state have been developed, including the high field model (HFM) of Verwey[73], and the variants by Mott et al.[74,75], the place exchange model (PEM) of Sato and Cohen[76], the interfacial equilibrium model (IEM) of Vetter et al.[77,78], and the PDM of Macdonald et al.[45,46,79]. All the prevailing models, except PDM, describe the growth law for an already existing film without addressing the conditions under which the film may form or disappear. A comprehensive review of the literature, with emphasis on oxide growth via the PEM, has been published later by Conway[80]. It is of interest to note that the PDM and the PEM yield almost identical rate laws for oxide film growth, except that the former incorporates dissolution whereas the latter does not. This section briefly introduces the PDM, and the rate laws it predicts for the passive film growth under both transient and steady state conditions.

First of all, for any successful model for the passive film, it must account for the following observed properties:

1. Passive films generally form as bilayer structures, with a highly disordered “barrier” layer adjacent to the metal, and an outer layer comprised of a precipitated phase.
2. Steady states are observed in the barrier layer thickness and the current, given sufficient time. The steady state film thickness generally varies linearly with the applied voltage.

3. The defects within the oxide film are important in determining the electronic character of the film.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Barrier Oxide Layer</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) (m + V_M^{x'} \xrightarrow{k_1} M_M + v_m + \chi e')</td>
<td>(4) (M_M \xrightarrow{k_2} M^{\Gamma+} + V_M^{x'} + (\Gamma - \chi)e')</td>
<td></td>
</tr>
<tr>
<td>(2) (M \xrightarrow{k_2} M_i^{x'} + v_m + \chi e')</td>
<td>(5) (M_i^{x'} \xrightarrow{k_3} M^{\Gamma+} + (\Gamma - \chi)e')</td>
<td></td>
</tr>
<tr>
<td>(3) (M \xrightarrow{k_4} M_M + \frac{x}{2} V_o^{x'} + \chi e')</td>
<td>(6) (V_o^{x'} + H_2O \xrightarrow{k_5} O_O + 2H^+)</td>
<td></td>
</tr>
<tr>
<td>[x=0]</td>
<td>[x=L]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(V_o^{x'})</td>
<td></td>
</tr>
</tbody>
</table>
| \(x=L\) | | \(V_o^{x'}\) \(x=0\)

Figure 2-2: Interfacial defect generation-annihilation reactions that are postulated to occur in the growth of anodic barrier oxide films according to the PDM. \(m = \) metal atom in bulk metal lattice, \(V_M^{x'} = \) cation vacancy on the metal sublattice of the barrier layer, \(v_m = \) metal vacancy in the bulk metal, \(M_i^{x'} = \) interstitial cation, \(M_M = \) metal cation on the metal sublattice of the barrier layer, \(V_o^{x'} = \) 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. \(\chi\) and \(\Gamma\) are the oxidation state of the cation in the barrier layer and solution, respectively.

A general theory for the passive film growth and dissolution has been developed in the form of PDM by Macdonald et al[45,46,72]. The PDM postulates that passive
films are bi-layer structures consisting of a highly defective inner “barrier” layer that grows into the metal and an outer porous layer that forms via the hydrolysis of cations ejected from the barrier layer. In many systems, the barrier layer appears to be responsible for the passivity. The PDM also postulates that the defects present in the barrier layer are cation vacancies ($V_M^{\chi}$), oxygen vacancies ($V_O^{\bullet\bullet}$), and cation interstitials ($M_i^{\chi\bullet}$), as designated by Kroger-Vink notation. The cation vacancies are electron acceptors, thus doping the oxide film p-type, whereas cation interstitials and oxygen vacancies are electron donors, thus resulting in the n-type character of the film. The PDM further postulates that the electric field strength is independent of distance through the barrier layer, and because that the steady state film thickness varies linearly with the applied voltage, it is also concluded that the electric field strength within the film is independent of the applied voltage (this can also be predicted as a consequence of the Esaki tunneling within the oxide film).

The microscopic picture of the formation and dissolution of the barrier layer, in terms of sets of defect generation and annihilation reactions at the metal/barrier layer interface and at the barrier layer-outer layer/solution interface, is depicted in Figure 2-2. It is seen that during the film growth, there is no thermodynamic equilibrium for this interphase, instead, the process is determined by kinetics, and when a steady state is reached, a kinetic equilibrium is established.

In developing an understanding of the growth of the barrier layer based on this model, it is important to differentiate the interfacial reactions as to whether they are lattice conservative (no movement of the boundary of the barrier layer) or non-conservative processes (movement of the boundary) upon their occurrence. Reactions (1), (2), and (4)-(6) are lattice conservative processes, whereas reaction (3), oxygen vacancy generation, and (7), barrier layer dissolution, are lattice non-conservative processes. Reaction (3) causes the boundary to move into the metal substrate, thus, thickening of the barrier layer, and reaction (7) results in the dissolution of the barrier layer. Reaction (1) and (4), and reaction (2) and (5) simply result in the transmission of cations through the barrier layer via cation vacancies or cation interstitials, respectively. Therefore, only reaction (3) and (7) are responsible for the growth and destruction of the
barrier layer, and the rate of change of the thickness for a barrier layer grown on a metal or alloy surface can then be expressed as[72]

$$\frac{dL}{dt} = \frac{dL^{+}}{dt} - \frac{dL^{-}}{dt} = \Omega k_{3}^{0} e^{-a_{+}V} e^{b_{+}L} e^{c_{+}pH} - \Omega k_{7}^{0} \left( \frac{C_{H^+}^{0}}{C_{H^+}^{0}} \right)^{n} e^{-a_{-}V} e^{c_{-}pH} \quad (Eq. \ 2.16)$$

where $\Omega$ is the mole volume of the barrier layer per cation, $a_{3} = \alpha_{3}(1 - \alpha) \chi \gamma$, $a_{7} = \alpha_{7}(\Gamma - \chi) \chi \gamma$, $b_{3} = -\alpha_{3} \chi \hat{e} \gamma$, $c_{3} = -\alpha_{3} \chi \beta \gamma$, and $c_{7} = \alpha_{7} \beta(\Gamma - \chi) \gamma$. $k_{i}^{0}$ and $\alpha_{i}$ are the standard rate constant and transfer coefficient of the $i$-th reaction depicted in Figure 2-2. $\alpha$ is the polarizability of the barrier layer/solution interface (the dependence of the voltage drop across the interface, $\phi_{f/s}$, upon the applied voltage $V$), $\hat{e}$ is the electric field strength within the barrier layer, $\beta$ is the dependence of the $\phi_{f/s}$ on pH. $\gamma = \frac{F}{RT}$, $C_{H^+}^{0}$ is the concentration of the $H^+$, $C_{H^+}^{0}$ is the standard state concentration (an ideal 1mol/cm$^3$ solution), and $n$ is the kinetic order of the barrier layer dissolution reaction with respect to $H^+$. Hence, the potential drop across the barrier layer/solution interface, $\phi_{f/s}$, is assumed to vary linearly with applied voltage $V$ and pH

$$\phi_{f/s} = \alpha V + \beta pH + \phi_{f/s}^{0} \quad (Eq. \ 2.17)$$

where $\phi_{f/s}^{0}$ is a constant. Note that the rate of dissolution is voltage independent only when $\Gamma = \chi$. For the sake of convenient discussion in later chapters, the expressions of these parameters and their identities are listed in Table 2-2 and Table 2-3 for reference.
When a steady state is reached, the film growth rate equals zero. Then from Eq. (2.16), the steady state film thickness, \( L_{ss} \), is readily derived as

\[
L_{ss} = \left[ \frac{1 - \alpha}{\varepsilon} - \frac{\alpha a_\gamma}{\alpha_5 \varepsilon} \left( \frac{\Gamma}{\chi} - 1 \right) \right] V + \left[ \frac{2.303n}{\alpha_5 \varepsilon \chi \gamma} - \frac{\alpha_5 \beta \left( \frac{\Gamma}{\chi} - 1 \right) - \beta}{\varepsilon} \right] pH
\]

(Eq. 2.18)

When no change of the oxidation state occurs upon the ejection of the cation from the barrier layer to solution, i.e., \( \Gamma = \chi \), a simpler form is then obtained for the above equation

\[
L_{ss} = \left[ \frac{1 - \alpha}{\varepsilon} \right] V + \left[ \frac{2.303n}{\alpha_5 \varepsilon \chi \gamma} - \frac{\beta}{\varepsilon} \right] pH + \frac{1}{\alpha_5 \varepsilon \chi \gamma} \ln \left( \frac{k_1^{0}}{k_7^{0}} \right)
\]

(Eq. 2.19)
The steady state current density can also be derived by considering that the fluxes of a given defect at the two interfaces are equal under steady state conditions:

\[
I_{ss} = \Gamma F \left[ k_2^0 e^{-\alpha_{V}^i} e^{\phi_{fss}} + k_4^0 e^{-\alpha_{V}^i} e^{\phi_{fss}} + k_7^0 e^{-\alpha_{V}^i} e^{\phi_{fss}} (C_{H^+} / C_{H^+}^0)^\alpha \right] \quad \text{(Eq. 2.20)}
\]

where the first, second and third terms represent the generation and transport of cation interstitials, cation vacancies, and oxygen vacancies, respectively, with the latter being expressed in terms of the equivalent rate of dissolution of the barrier layer. In this way, the defect concentrations at the interfaces can be avoided in the expression of the current.

Table 2-3: Identity/Origin of the parameters employed in the PDM

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Identity/Origin</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Omega)</td>
<td>Mole volume of the barrier layer per cation</td>
<td>(\text{cm}^3/\text{mol})</td>
</tr>
<tr>
<td>(\phi_{fss})</td>
<td>Potential drop at the barrier layer/solution interface</td>
<td>(\text{V})</td>
</tr>
<tr>
<td>(\phi_{0fss})</td>
<td>Constant</td>
<td>(\text{V})</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>Polarizability of the barrier layer/solution interface</td>
<td></td>
</tr>
<tr>
<td>(\beta)</td>
<td>Dependence of the (\phi_{fss}) on (pH)</td>
<td>(\text{V})</td>
</tr>
<tr>
<td>(\alpha_i)</td>
<td>Transfer coefficient for reaction ((i))</td>
<td>(\text{mol/cm}^2\text{s}, \text{or s}^{-1})</td>
</tr>
<tr>
<td>(k_i^0)</td>
<td>Standard rate constant independent of potential and thickness for reaction ((i))</td>
<td>(\text{mol/cm}^2\text{s}, \text{or s}^{-1})</td>
</tr>
<tr>
<td>(k_i^{(0)})</td>
<td>Base rate constant independent of potential, thickness and (pH) for reaction ((i))</td>
<td>(\text{mol/cm}^2\text{s}, \text{or s}^{-1})</td>
</tr>
<tr>
<td>(\chi)</td>
<td>Oxidation state of cation in barrier layer</td>
<td></td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>Oxidation state of cation in solution</td>
<td></td>
</tr>
<tr>
<td>(\hat{\varepsilon})</td>
<td>Electric field strength within the barrier layer</td>
<td>(\text{V/cm})</td>
</tr>
<tr>
<td>(n)</td>
<td>Kinetic order of dissolution with respect to ([H^+])</td>
<td></td>
</tr>
</tbody>
</table>
The PDM successfully predicts in Eq. (2.19), that the steady state film thickness will vary linearly with the applied voltage, which is a ubiquitous observation in the anodic oxidation of metals. The PDM also states that the ultimate thickness of the passive film is determined by the standard rate constant for film formation and film dissolution. Furthermore, from Eq. (2.20), it is predicted that the logarithm of the steady state current will vary linearly with applied voltage when one type of the defects dominate the transport of the charge flux within the barrier layer, which is also commonly found to be true experimentally. In fact, Eq. (2.19) and Eq. (2.20) led to the diagnostic criteria for identifying the majority charge carrier in the film and characterizing the kinetic nature of the interfacial reactions[45]. Validity of the diagnostic criteria has already been manifested on several types of passive films[81,82].

2.6 Derivation of the Film Thickness Measurement Method

Now we are at the stage of derivation of the film thickness measurement method based on the above introduced QMT and the PDM. QMT predicts that the tunneling current decays exponentially with the thickness of the oxide film at the interface, while the PDM provides quantitative relation of the film thickness with applied voltage. Therefore, a relationship between the observed current density and applied voltage, which is what electrochemical experiments commonly observe, can be developed combining the two theories. For metals like Pt[44], W[81], and Ti[83], etc., Mott-Schottky analysis has determined that the electronic properties of these passive films are n-type in character, with the dominating defects being the oxygen vacancies. Therefore, reactions (2) and (5) can be crossed out from the 7-reaction scheme of the PDM, rendering a simpler version of the 5-reaction PDM (This is also the model that will be often referred to in later chapters). At a given pH solution, the steady state film thickness is then
where \( V_0 \) is the voltage of zero thickness of the barrier layer. Substituting Eq. (2.21) into Eq. (2.14), and taking logarithm on both sides yield

\[
\ln(i) = \ln(i_0) - \beta \left( \frac{1 - \alpha}{\hat{\varepsilon}} \right) (V - V_0)
\]

Thus, a linear relationship, having a negative slope of \(-\beta (1 - \alpha)/\hat{\varepsilon}\), is predicted to exist between the tunneling current density and applied voltage. Since the anodizing constant, \((1 - \alpha)/\hat{\varepsilon}\), which has a value of about 2.5nm/V for a wide variety of metals (within 10% error bar)[44,45], can be determined experimentally, if either a reliable method (e.g. ellipsometry, capacitance method, or galvanostatic charging methods, etc.) is available for characterizing the dependence of barrier layer thickness on applied voltage (generally not the case for very thin films[65]), or by using electrochemical impedance spectroscopic optimization techniques[44], an unequivocal value for the tunneling constant can then be determined from the slope. Once the tunneling constant is known, the film thickness can then be calculated from a rearrangement of Eq. (2.14)

\[
L = \frac{I}{\beta} \ln \left( \frac{i_0}{i} \right)
\]

Advantages of this QMT-PDM method developed for measuring film thickness over other conventional techniques have been discussed in previous papers[47-49]. Conventional techniques usually become problematic when applied to extremely thin oxide films (e.g. a few monolayers thick). Ellipsometry, for example, requires that the oxide surface be “mirror-like”, so that the refractive index of the substrate metal and the
oxide film on surface can be differentiated. However, the roughness of the polished electrode, when the film is only of a few monolayers thick, gives rise to a composite (water and the film) refractive index, thereby rendering the determination of the film thickness inaccurate. It has been found[65] that oxide films grown on platinum at potentials more negative than 0.95V_{RHE} in 0.1N H_2SO_4, and hence thinner than a few angstroms, were invisible to an ellipsometer. In fact, the true film thickness is expected to vary linearly with applied voltage. In fact, this is exactly the problem that was encountered in our work, when attempts were made to measure the thickness of the oxide film on Pt using a high quality, spectroscopic ellipsometer[84].

The use of capacitance method to determine film thickness employs the parallel plate capacitor expression

$$L = \varepsilon \varepsilon_0 A / C$$  \hspace{1cm} (Eq. 2.24)

where $\varepsilon$ is the dielectric constant of the oxide film, $\varepsilon_0$ is the permittivity of free space ($8.854 \times 10^{-12}$ F/m), $A$ is the true surface area, and $C$ is the measured capacitance. Thus, not only does the uncertainty in the true area of a rough surface limit the precision of the calculated thickness, so does the uncertainty in the dielectric constant, as it is customary to use the bulk oxide value for $\varepsilon$, but, of course, the true value may be greatly different, because of the amorphous nature of the extremely thin film, and the presence of a high electric field.

The galvanostatic growth of oxide films[85] or determination of the thickness of oxide films previously grown at high anodic potentials by cathodic reduction at constant current[86-89], which relate the film thickness to the amount of charge used to grow or reduce the oxide, also has limitations, due to the uncertainty in the coulombic efficiency of the film growth and reduction processes and again in the true surface area.

Whereas, with the developed new method, 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 in Eq. (2.23) 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. Experimentally, the tunneling current for the HOR on platinum is used as a probe to detect the thickness of the oxide film grown on platinum electrode surface, as mentioned before, that the HOR is a relatively fast reaction and has been extensively studied. This method has been demonstrated to be a very sensitive and convenient in situ method for very thin film thickness measurement[47-49].

2.7 Conclusions

Six types of fuel cells have been briefly introduced in this chapter, and redox reactions at the anode (HOR) and cathode (ORR) of a fuel cell have been reviewed. The superiority and drawback of platinum as electrocatalysts are discussed, that though platinum gives best performance for fuel cell operation, high over-voltage loss remains a challenge at the cathode for the ORR, due to the formation of a thin oxide layer on platinum electrode surface at high voltages. The thickness of this extremely thin oxide film is very important in determining the rate of the charge transfer at the metal/oxide film/solution interphase, since that the oxide film acts as a potential barrier, and that the probability of the charge carrier quantum mechanically tunnel through the potential barrier decays exponentially with the barrier width. The development of quantum electrode kinetics for charge transfer reactions, and the PDM for quantitative description of the film thickness as a function of applied voltage are introduced. Combining QMT with the PDM, a new method for thin film thickness measurement is yielded. This new method is advantageous compared with conventional techniques for measuring extremely thin film thickness.
References


Chapter 3
Experimental

Two sets of experimental apparatus were used in this thesis work, one for the regular, ambient temperature experiments, and the other for high pressure, elevated temperature experiments. This chapter introduces the preparation method for all the electrodes, solutions used, and layout of the equipment for the experiments. Because of the great difference in ambient temperature and high temperature experiments, this chapter is mainly divided into two parts.

3.1 Ambient Temperature Experimental Apparatus

A glass electrochemical cell with three separate compartments was used for the ambient temperature (22 ± 2°C) study. The working electrode (WE) is a rotating ring disk electrode (RRDE) from Pine Instrument with disk area of 0.283 cm² and that of the platinum ring 0.126 cm². The collection efficiency of this RRDE is 24%. Either a pure platinum disk insert or a nickel disk electroplated by platinum (by Technic Inc.) was used as the disk electrode. The reference electrode (RE) is a standard saturated caramel electrode (SCE) equipped with a Luggin probe located closely under the WE so as to eliminate the IR drop in the solution. The counter electrode (CE) is a high purity platinum wire with the surface area over 5 times that of the WE. To secure the desired cell environment with the WE still spinning at high rotation rates, a ChemGlass® stirrer bearing matched exactly with the shaft size of the RRDE is used between the rotating electrode and the cell wall (This grease-free Teflon stirrer bearing is designed for use under moderate vacuum applications), and at the same time, gas is constantly purged on top of the solution. The experimental setup of the cell used in the work is shown in Figure 3-1. Before each experiment, the solution was deoxygenated with nitrogen or
saturated with hydrogen or oxygen by sparging the solution in the cell with the appropriate gas at a pressure of 1.0 atm (760 Torr).

Solubility for slightly soluble gas is usually described in the form of Henry’s law constant. From Henry’s law

\[ P_{O_2} = K_{O_2} x_{O_2} \]  \hspace{1cm} (Eq. 3.1)

where \( P_{O_2} \) is partial pressure of oxygen in Torr, \( x_{O_2} \) is mole fraction of oxygen in oxygen saturated water, and \( K_{O_2} \) is the Henry’s constant for oxygen in water (around \( 3.30 \times 10^7 \).
K/Torr at 298K[1]), the solubility of oxygen in water at 298K is then calculated to be 0.26 x 10^{-3} M (equivalent to 8.32ppm). Similarly, the amount of hydrogen dissolved in the solution, \( m_{H_2}^T \) (mol/kg water, or m), is determined by the temperature dependent Henry’s law coefficient, \( K_{H_2}^T \) (m/atm) and the fugacity of hydrogen, \( f_{H_2}^T \) (atm)

\[
 m_{H_2}^T = K_{H_2}^T f_{H_2}^T = K_{H_2}^T f_{H_2}^{T_0}
\]

(Eq. 3.2)

The Henry’s law coefficient for hydrogen in water is given as[2]

\[
 \log(K_{H_2}^T) = \frac{1321}{T} - 10.703 + 0.010468T
\]

(Eq. 3.3)

Therefore, at ambient temperature (298K) and atmospheric pressure, the Henry’s law coefficient is calculated to be 7.1x10^{-4} mol/kg-atm, and the saturated hydrogen concentration in water is 0.7 x 10^{-3}m (equivalent to 1.4ppm). The electrolyte used in most of the experiments is freshly prepared 0.1M KOH solutions from triple-distilled deionized water (resistivity: 18.2MΩ·cm).

Some of the experiments carried out at ambient temperature and all the experiments carried out at elevated temperatures used platinized nickel electrodes. Electroplating of platinum on mirror finish nickel electrodes was implemented at a professional electroplating company: Technic Inc., using a neutral plating solution (Platinum AP #240651). Below is the sequence used for plating provided by Technic Inc.

1) Electroclean-TEC-1001-8ozs./gal.-140F-2 minutes
2) Rinse
3) Acid Activate-30% HCl-RT-45 seconds
4) Rinse
5) Technic Acid Gold Strike-3 Volts-45 second-Room Temp.
6) Rinse
7) Platinum AP Plating Solution-180F-10 Asf- 45 minutes.
8) Rinse
9) Aqua Shed 1-RT-2%v/v-1 minute
10) Hot Rinse
11) Dry

The thickness of the electroplated platinum layer is approximately 5-6μm, so that the structure and electronic properties of the plated platinum tantamount to that of a bulk platinum. Surface morphologies of the platinized nickel electrode and a bulk platinum electrode were examined using a Philips XL-20 Scanning Electron Microscope (SEM). All the electrodes and glassware used in the experiments are first cleaned with acetone, then methanol, followed by deionized water rinsing to remove organic contaminations and other impurities.

Both potential sweep and potentiostatic polarization methods were employed in the experiments using either a bi-potentiostat from Pine instruments Co. or Gamry instruments. All the potentials are converted into the standard hydrogen electrode (SHE) scale, unless noted.

3.2 Elevated Temperature Experimental Apparatus

3.2.1 High Temperature High Pressure Apparatus

The apparatus used at elevated temperature is mainly for the kinetic and mechanistic study of hydrogen electrode reaction, and also quantum mechanical tunneling of charge carriers across an oxide covered metal electrode. The designed apparatus is similar to that originally described by Macdonald, et al.[3] and later by Biswas[4], and comprises a high temperature/high pressure hydrodynamic
electrochemical cell based upon a Parr Instruments Model 4560 reactor, a recirculation flow loop, a high pressure liquid chromatography (HPLC) pump, a pressure control valve, a regenerative heat exchanger and a cooler, and a sealed solution reservoir containing facilities for gas sparging, as shown schematically in Figure 3-2.

Figure 3-2: Schematic of the high temperature/high pressure flow loop used for studying the hydrogen oxidation reaction (HOR) on platinum in KOH solutions at temperatures up to 220°C.

The solution tank is maintained at ambient temperature, and is sparged with hydrogen at the appropriate pressure to establish the desired concentration of dissolved hydrogen in the solution. The hydrogen-saturated solution is pumped into the autoclave via the regenerative heat exchanger by the HPLC pump. The solution exiting from the autoclave is heat exchanged with the incoming solution in the regenerative heat exchanger and is then cooled to ambient temperature via the cooler. The pressure is then reduced to that in the reservoir via the pressure control valve before being returned to the solution tank (“recirculating” mode) or being discharged to waste (“once-through” mode).
The electrochemical cell, shown in Figure 3-3, comprises an autoclave of 0.6L volume, containing a magnetically driven impeller, an annular flow channel used to direct the flowing solution over the specimen, a type J thermocouple (in a 1/8” diameter stainless steel sheath, which was installed in a nickel thermowell), a working electrode mounted on the inner surface of the annulus formed by a nickel rod, a nickel counter electrode connected to the flow channel, and an internal, saturated silver/silver chloride [Ag/AgCl, KCl(sat.)] reference electrode with the liquid junction being located within the flow channel opposite to the working electrode surface. In order to avoid corrosion in the alkaline solution at high temperatures, all wetted surfaces exposed to the high temperature solution are fabricated from nickel, except the working electrode, which is a nickel cylinder electroplated with bright platinum to a thickness of 5 ± 0.5 um. The geometrical surface area of the working electrode is 1.994cm$^2$. The specimen is electrically isolated from the nickel autoclave by PTFE washers and ceramic tubes of a Conax Buffalo packing gland.

The reference electrode is prepared by anodically plating a silver wire with AgCl in 0.1M HCl solution for over 15hs at a constant current density of 0.8mA/cm$^2$. The electrode is then housed in a heat shrink PTFE tube, which is fitted with a porous zirconia plug at one end. The reference electrode compartment is filled with saturated KCl solution and sufficient KCl crystals to ensure saturation at all temperatures studied. To provide good electrolytic communication between the liquid junction and the Ag/AgCl reference element, glass fibers were inserted into the PTFE tube. The stability of the reference electrode is checked at ambient temperature against a standard SCE before and after each experiment. All measured potentials are converted to the Standard Hydrogen Electrode (SHE) scale for good comparability with thermodynamic data, unless otherwise indicated.

The pressure and temperature within the system are controlled via a pressure relief valve and a proportional controller, respectively, and the rotation speed of the impeller is controlled by a variable speed motor and is recorded using a sensitive tachometer. Freshly prepared KOH solutions, with concentrations of 0.1M and 0.01M at ambient temperature, equivalent to 0.1006m and 0.01001m (note unit m means mol
solute/kg solvent), respectively, at any temperature or pressure, are used as the electrolytes, and appropriate amount of K$_2$SO$_4$ solution (0.03M, equivalent to 0.03016m) is added to the 0.01001m KOH solution to equalize the ionic strengths. Note that because the experiments are carried out at a series of temperatures, and that the density of the electrolyte varies with temperature, unit m is used here instead of the generally accepted M. With unit m, the same concentration can be used at any temperature. Several hydrogen concentrations are explored by adjusting the H$_2$ gas pressure in the solution reservoir. The reaction vessel, working electrode, solution tank, and glassware used for preparing the solutions are all scrupulously cleaned with acetone, then methanol, followed by deionized water prior to initiate an experiment.

Figure 3-3: Schematic of the controlled hydrodynamic test cell showing the flow channel; the working, reference, and counter electrodes; and the flow-inducing impeller.
A potentiostat from Gamry Instruments operating in the floating mode, and Solatron 1250 frequency response analyzer were used in the experiments.

### 3.2.2 Hydrodynamic Properties Analysis

Because the mass transfer effects are very important in determining the kinetics of the redox reactions, it is important to analyze the hydrodynamic properties of designed apparatus, so that the experiments are carried out under controlled hydrodynamic conditions at high temperatures. The annular flow channel is adopted in this study and it is so designed because that this system has been extensively analyzed both experimentally and theoretically, and that the flow of the solution at the working electrode surface is fully developed with laminar, transitionary, and turbulent regimes being accessible[3].

In this study, the top entrance diameter for the channel is 5.25cm, transitioning to 2.05cm immediately downstream of the impeller. The total length of the channel is 17cm, and the entrance length-to-annular gap ratio is 7.1. This flow channel is capable of yielding Reynolds numbers over the range of $10^2$ to $10^5$. Properties of the annular flow channel are list in Table 3-1. The hydrodynamic property analysis is similar to that of a previous study[3].

Anodic polarization curves for the HOR on platinized Ni electrode with a sweep rate of 2mV/s in 0.1M KOH solution at 25°C, as a function of the rotation speed of the impeller, are shown in Figure 3-4. Due to its fast kinetics, the oxidation current increases sharply at small overpotentials and quickly reaches a plateau. The limiting current densities, as functions of rotation rate and solution temperature, are plotted in Figure 3-5. It is seen that the limiting current density increases with increasing rotation rate, as well as with increasing temperature, since the mass transfer rate increases with decreasing Nernst double layer thickness and increasing diffusivity of hydrogen, respectively.
Table 3-1: Properties of the Annual Flow Channel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner radius ( r_i )</td>
<td>0.635cm</td>
</tr>
<tr>
<td>Outer radius ( r_o )</td>
<td>1.025cm</td>
</tr>
<tr>
<td>Radius ratio ( a = r_i/r_o )</td>
<td>0.6195</td>
</tr>
<tr>
<td>Equivalent diameter ( d_e = 2r_o - 2r_i )</td>
<td>0.78cm</td>
</tr>
<tr>
<td>Entrance length ( x_0 )</td>
<td>2.77cm</td>
</tr>
<tr>
<td>Entrance length/annular gap</td>
<td>7.1</td>
</tr>
<tr>
<td>Electrode length ( L )</td>
<td>0.5cm</td>
</tr>
<tr>
<td>Electrode area</td>
<td>1.994cm$^2$</td>
</tr>
<tr>
<td>( \phi \left( = \frac{1-a}{a} \left[ 0.5 - \left( \frac{r_i}{r_o} \right) \ln \left( \frac{r_o}{r_i} \right) \right] \right) )</td>
<td>1.6463</td>
</tr>
<tr>
<td>( r_{max} = \left[ \frac{r_{eq}^2 - r_i^2}{2 \ln \left( \frac{r_o}{r_i} \right)} \right]^{0.5} )</td>
<td>0.8222cm</td>
</tr>
<tr>
<td>( \lambda = \frac{r_{max}}{r_o} )</td>
<td>0.8022</td>
</tr>
<tr>
<td>( f_1 = 0.046 \text{Re}^{-0.20} \left( \frac{1-a}{1-a^2} \right)^{0.20} \frac{a^2-r_o^2}{a(1-a^2)} )</td>
<td>0.05481Re$^{-0.2}$</td>
</tr>
<tr>
<td>( f_1' = 0.079 \text{Re}^{-0.25} \left( \frac{1-a}{1-a^2} \right)^{0.25} \frac{a^2-r_i^2}{a(1-a^2)} )</td>
<td>0.09445Re$^{-0.25}$</td>
</tr>
</tbody>
</table>

The limiting current density, \( i_L \), is a result of complete mass transfer control of the reaction

\[
H_2 \rightarrow 2H^+ + 2e^-
\]  
(Eq. 3.4)
Figure 3-4: Anodic polarization curves for the HOR on platinized Ni electrode in 0.1M KOH solution at 25°C.

Figure 3-5: Limiting current density of the HOR as functions of rotation speed and temperature.
and is related with the bulk concentration (solubility), $C_{H_2}$, and the diffusivity, $D_{H_2}$, of hydrogen in solution by

$$i_c = \frac{nFD_{H_2}C_{H_2}}{\delta} \quad (\text{Eq. 3.5})$$

where $n$ is the number of electrons transferred ($n = 2$ for the HOR), $F$ is Faraday’s constant, and $\delta$ is the effective (Nernstian) diffusion layer thickness. The established hydrogen pressure in the solution tank was 2.68 atm, equivalent to a concentration of $1.9 \times 10^{-3}$ m. Because the solution tank is always maintained at ambient temperature no matter what temperature it is in the reactor autoclave, and the solution is circulating, so the concentration of dissolved hydrogen in the reaction autoclave is the same as that in the solution tank.

Similar to a treatment in a previous study[3], values for the density ($\rho$) and kinematic viscosity ($\nu$) for pure water were used to estimate the mass transfer properties of the system, and they are listed in Table 2 of reference [3] (the values for $\rho$ and $\nu$ at 25°C are 0.9971 g/cm$^3$ and 8.98 x 10$^{-3}$ cm$^2$/s, respectively). Because of the neutral property of the H$_2$ gas, the most probable diffusion coefficient for H$_2$ in 0.1MKOH solution at 25°C is 4.8 x 10$^{-5}$ cm$^2$/s[5]. The diffusion coefficient at elevated temperatures can then be calculated using Einstein’s equation

$$\frac{D_1\nu_1}{T_1} = \frac{D_2\nu_2}{T_2} = const. \quad (\text{Eq. 3.6})$$

where $D_1$ and $\nu_1$ are the known values of diffusivity and kinematic viscosity at temperature $T_1$, and $D_2$ and $\nu_2$ are the corresponding values at temperature $T_2$. The mass transfer coefficients, $K_L = \left( \frac{D_{H_2}}{\delta} \right)$, can be calculated from the obtained limiting current density and the bulk hydrogen concentration as
Using this correlation, the equivalent linear velocity of the fluid can be determined for the fluid flow over wide ranges of temperature and rotation rate. The calculated values of the mass transfer coefficients at each temperature and rotation rate are listed in Table 3-2.

Table 3-2: Mass transfer coefficients, $K_L$ (cm/s), as functions of rotation speed and temperature

<table>
<thead>
<tr>
<th>Rotation Speed (rpm)</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>196</td>
<td>2.805e-03</td>
<td>4.260e-03</td>
<td>8.078e-03</td>
<td>2.143e-02</td>
<td>3.260e-02</td>
</tr>
<tr>
<td>289</td>
<td>3.779e-03</td>
<td>5.208e-03</td>
<td>7.702e-03</td>
<td>1.896e-02</td>
<td>3.169e-02</td>
</tr>
<tr>
<td>400</td>
<td>4.572e-03</td>
<td>6.377e-03</td>
<td>9.611e-03</td>
<td>1.442e-02</td>
<td>1.766e-02</td>
</tr>
<tr>
<td>529</td>
<td>5.338e-03</td>
<td>7.429e-03</td>
<td>1.255e-02</td>
<td>1.766e-02</td>
<td>2.156e-02</td>
</tr>
<tr>
<td>650</td>
<td>5.948e-03</td>
<td>8.403e-03</td>
<td>1.455e-02</td>
<td>1.974e-02</td>
<td>2.377e-02</td>
</tr>
</tbody>
</table>

Flow through the annulus can be either laminar or turbulent, depending on the impeller rotation rate, fluid temperature and pressure. The full calculation of the equivalent linear velocity and the Reynolds numbers under both flow regimes will not be expanded in detail here, if interested, the readers can refer to reference [3]. But it is noted that for any given Reynolds number, the prevailing flow character is that which yields the lower linear velocity. The result of the dimensionless mass transfer correlations is shown in Figure 3-6, which are the plots of log(Sh) and log(St) against log(Re) for various temperatures, where Sh, St, and Re are the dimensionless Sherwood numbers, Stanton numbers, and Reynolds numbers, respectively. These plots illustrate the conditions over which turbulent flow is observed. This range is greatly expanded as the temperature
increases, due to the decreased viscosity of the solution. Turbulent flow is generally desirable for solution mixing, so that the incoming fresh solution could be quickly mixed with the already existing solution in the autoclave, and a homogeneous electrolyte is obtained at all time.

Figure 3-6: Dimensionless mass transfer correlations for the fluid flow in the annular flow channel at various temperatures.

References


Chapter 4
Platinum and Platinum Oxide

As the best electrocatalyst for fuel cells, especially for the oxygen reduction reaction (ORR), platinum has continuously attracted research interest over the past several decades. Lots of research endeavors have been made to increase the reaction rate of the ORR on platinum, but the reaction rate still remains sluggish. The most probable reason for that is the formation of a thin oxide layer on platinum at low overpotentials of the ORR, so that the charge carriers have to tunnel across this thin layer to reach the acceptors adsorbed on the electrode surface or in the solution. Therefore, the surface structure of the electrode and electronic properties of this thin oxide layer are extremely important in understanding the kinetics and mechanism of the ORR, so as to the kinetics and mechanism of the hydrogen oxidation reaction (HOR). This chapter explores some general properties of the platinum electrode, kinetics of the anodic oxide film growth under transient conditions, and discusses the growth mechanism as well as the possible structure for the oxide film.

4.1 Surface Morphology

Electrochemistry is a subject of interfacial processes; therefore, surface structures and electronic properties of the electrode materials are vital to the mechanism and kinetics of redox reactions at the interface. In this dissertation work, three forms of platinum electrode have been employed, e.g. bulk platinum disk, platinized nickel electrode (platinum electroplated on nickel), and sputtered platinum disk electrode. Surface morphologies of the platinized nickel and bulk platinum electrodes were characterized using a variety of surface analysis techniques. Figure 4-1 shows SEM micrographs of two surfaces. It is seen that the platinized nickel electrode has a granular surface morphology, with an average grain size of around 300nm, while the polished
surface of the bulk platinum electrode appears to be very smooth at the selected magnification of the microscope. Therefore, the platinized nickel electrode surface has much higher real surface area than the polished bulk Pt electrode, resulting in a much higher rate (current density) for the hydrogen electrode reaction (HER), if the measured current is divided by the geometrical surface area, as reported in a previous paper[1].

Figure 4-1: SEM micrographs of the surface of a: (a) Platinized nickel electrode; and (b) bulk platinum electrode. Note that the labels for the scale of the two micrographs are both 2.0um.
The thickness of the electroplated layer is approximately 5um as calculated via x-ray diffraction (XRD) analysis, and energy dispersive spectroscopy (EDS) indicates that the surface is pure polycrystalline platinum with no traces of nickel or other impurities within the detection limit of this technique (~1%), as shown in Figure 4-2. The quality of the electroplated layer is important to the durability of the electrode, as any defect or weak spot may cause the flaking off of the electroplated layer, thus failure of the electrode, and this is also true to the sputtered platinum electrode. Note, that a clear surface morphology of the sputtered electrode was not obtainable under low magnification. However, it is generally observed that the sputtered platinum tends to form nano-crystals with (111) preferred orientation[2] as (111) surface is the lowest energy surface. The sputtered platinum electrode tended to peel off very easily and was finally discarded, but its general behavior approaches that of a bulk platinum electrode except the details of the hydrogen adsorption/desorption features.

Figure 4-2: Energy dispersive spectroscopy (EDS) of the platinized nickel electrode surface. The surface layer is pure platinum.
4.2 Cyclic Voltammogram of Platinum

An easy and effective way to examine the electrochemical behavior of a platinum electrode is to check the features yielded by cyclic voltammogram (CV) experiments under a nitrogen environment. As platinum has been widely studied, some fingerprint features have been identified on a CV curve. CVs for a rotating ring disk electrode (RRDE) with a platinized nickel disk in 0.1M KOH solution purged with nitrogen gas (pressure = 1.0atm) at ambient temperature (22 ±2°C), as a function of the reversal voltage on the forward sweep, are shown in Figure 4-3. The potential sweep rate used was 30mV/s, and the forward sweep was reversed at progressively more positive values beginning with 0.1V_{SCE} and increasing to 0.6V_{SCE} in 0.1V increments. The disk is rotated at 900rpm.

Figure 4-3: CVs for platinum in 0.1M KOH at ambient temperature (22°C ± 2°C) with progressively positive reversal potentials. Sweep rate = 30mV/s, sweep direction: positive and then reverse, rotation speed = 900rpm. Three vertical broken lines divide the CVs into four typical regions.
The CVs display standard behavior with four distinct regions typical of a platinum electrode. Starting from left to right: (i) Three conjugate pairs of hydrogen adsorption/desorption peaks in the reverse and forward sweeps, which are postulated to arise from adsorption/desorption of hydrogen onto/from different crystallographic orientations of the polycrystalline platinum electrode, (ii) the double layer region where no appreciable current is observed, (iii) platinum oxidation and reduction, and (iv) the oxygen evolution region. The CVs also show that, as the reversal potential increases, the oxide reduction peak shifts to more negative potentials (the reduction reaction becomes more irreversible possibly due to some structure reorganization upon the formation of oxide) and the reduction charge increases. The findings of the present work are consistent with those reported in other literature\[3-7\] for the electrochemical behavior of platinum. Note, the peak current density of the second pair of hydrogen adsorption/desorption peaks in the first region increases as the reversal voltage increases. Because the sweep rate employed was the same, so this phenomenon might be due to the preferable adsorption of some organic contaminants on specific platinum crystal orientations, and that those organic contaminants are only oxidized at high potentials. On this CV graph, it is also observed that the onset of platinum oxidation is around \(-0.25\text{V}_{\text{SCE}}\) in the positive-going sweep, and that of platinum oxide reduction is around \(-0.1\text{V}_{\text{SCE}}\) in the negative-going sweep for this system.

4.3 Kinetics of Platinum Oxide Film Growth under Transient Conditions

Growth of the anodic oxide film on platinum under transient conditions (potential sweep) has been analyzed in this section, with the purpose of extracting the quantitative values of kinetic parameters in terms of the point defect model (PDM)\[8-10\]. The CVs of the platinum oxidation and reduction with various sweep rates in 0.1M KOH solution are shown in Figure 4-4. As the reduction of the oxide film is relatively irreversible, possibly due to some structure arrangement at high potentials, so the potential from which to start the sweep is set at a slightly higher potential than the onset potential of the platinum oxide reduction (\(-0.1\text{V}_{\text{SCE}}\)), and only the growth kinetics are analyzed here.
As outlined in chapter 2, the PDM describes the anodic oxide film that forms electrochemically on platinum in the oxygen reduction region in terms of interfacial reactions that generate and annihilate point defects (Figure 2-2). Note that, because the passive film (barrier layer) has been found to be n-type in electronic character[11], so only cation interstitials and/or oxygen vacancies can be considered to be the main point defects in the film. Accordingly, Reactions (1) and (4) in Figure 2-2 can be ignored to yield a reduced reaction scheme for the barrier layer on platinum comprising Reactions (2), (3), (5), (6), and (7), as rearranged in Figure 4-5 for convenience.

To simulate the current-voltage ($i$-$V$) curves on platinum during the potential sweep, it is realized that there are two components contributing to the overall measured current of the $i$-$V$ curves: the passive current of platinum oxidation and the current due to the charging of the oxide film and the double layer during potential sweep process. The passive current is discussed first here. It is known that the PDM quantitatively predicts that the rate of thickening of the barrier layer of the passive film on a metal is given by
where C is a simple form of the dissolution rate in Eq. (2.16), and is assumed to be potential independent here (i.e., no change occurs in the oxidation state of the cation upon dissolution), and A is a constant includes the other terms in Eq. (2.16) except the exponential V and L terms. All the other parameters in Eq. (4.1) and below bear the same meaning as those in chapter 2. A is related with the growth rate of the oxide film at equilibrium potential. Now that the potential \( V \) is swept at a constant sweep rate \( v \)

\[
\Delta V = V - V^0 = vt \quad \text{(Eq. 4.2)}
\]
where $V^0$ is the equilibrium potential for platinum oxide formation (or zero film thickness potential) and $t$ is time. By mathematical manipulation, and substituting $t$ using Eq. (4.2), it is derived that the thickness of the oxide film grown during the positive potential sweep is

$$L = -\frac{a_3}{b_3} \Delta V + \frac{1}{b_3} \ln \left\{ \frac{r/A}{1 + (T/A - 1)e^{b_3V_3/e - a_3\Delta V}} \right\}$$  

(Eq. 4.3)

where $r = C - \frac{a_3}{b_3}$. Mathematical derivation of the film thickness is provided in Appendix A. In the limit that the sweep rate approaches zero ($v \rightarrow 0$), Eq. (4.3) reduces to the familiar form

$$L = \frac{1 - \alpha}{e} \Delta V$$  

(Eq. 4.4)

which is the potential dependent steady state film thickness predicted by the PDM. Now, the passive current density can be calculated from the PDM

$$I_{ss} = \Gamma F \left[ k_0^0 e^{a_0V} e^{b_0L} e^{c_0pH} + k_4 e^{a_4V} e^{c_4pH} + k_5 e^{a_5V} e^{c_5pH} \left( C_{H^+} / C_{H^+}^0 \right)^n \right]$$  

(Eq. 4.5)

In this specific case, no change in oxidation state occurs upon dissolution of the film ($\Gamma = \chi$), and the film grows via the oxygen vacancy generation and annihilation mechanism, we get

$$I_{pass} = \Gamma \chi k_4 e^{a_4V} e^{b_4L} e^{c_4pH}$$  

(Eq. 4.6)
Recalling Eq. (4.3) for $L$, we get

$$I_{\text{pass}} = FZk_3^0 \epsilon_c \rho_{PH} e^{\frac{1}{A/r} + (1 - \frac{A}{r})e^{b,c\Delta V} e^{-a,\Delta V}}$$  \hspace{1cm} (Eq. 4.7)

When $v \to 0$, the steady state passive current density is yielded

$$I_{\text{pass}} = FZk_3^0 \epsilon_c \rho_{PH} \frac{C}{A}$$  \hspace{1cm} (Eq. 4.8)

The steady state passive current of a metal is independent of the applied potential when the metal oxide film is n-type in electronic character, according to the diagnostic criteria of the PDM. It can also be seen that the passive current increases by over an order of magnitude when the pH increases from 1 to 14 ($c_3$ is approximately 0.35), which is in accordance with what was observed in literature that the passive current of platinum increases from the nA/cm² scale in acid solution to the uA/cm² scale in alkaline solution[12].

Since the measured current density also includes the charging of the oxide film layer capacitance ($C_{ox}$, per unit area) and the double layer capacitance ($C_{dl}$, per unit area) it is also necessary to derive the mathematical form of the charging current. The charging current density is usually a function of the sweep rate

$$I_{\text{charging}} = C_T \frac{dV}{dt} = C_T V$$  \hspace{1cm} (Eq. 4.9)

where $C_T$ is the total unit area capacitance of the series combination of the double layer capacitance and the oxide film capacitance. $C_T$ can be calculated as
The double layer capacitance usually ranges from $20 \, \mu F/cm^2$ to $100 \, \mu F/cm^2$, and is weakly potential dependent at potentials away from the potential of zero charge (PZC). However, in some special conditions, e.g. adsorption/desorption at the interface, the overall double layer capacitance might be much smaller. The oxide film capacitance per unit area is determined as

$$C_{ox} = \frac{\varepsilon \varepsilon_0}{L}$$  \hspace{1cm} (Eq. 4.11)

Recall film thickness $L$, and substitute Eq. (4.10) and Eq. (4.11) into Eq. (4.9), we get

$$I_{charging} = \frac{\varepsilon \varepsilon_0 V}{-\frac{a_3}{b_3} \Delta V + \frac{1}{b_3} \ln \left[ \frac{r/A}{1+(r/A-1)e^{b_5 \Delta V/\varepsilon \varepsilon_0}} \right] + \frac{\varepsilon \varepsilon_0}{C_{dl}}} \hspace{1cm} (Eq. 4.12)$$

Now, we are at the stage to obtain the total current density as a function of the sweep rate

$$I_{total} = F \frac{u_0 e^{\varepsilon_{pH}}}{k_5} R + \frac{\varepsilon \varepsilon_0}{-\frac{a_3}{b_3} \Delta V + \frac{1}{b_3} \ln R + \frac{\varepsilon \varepsilon_0}{C_{dl}}} \hspace{1cm} (Eq. 4.13)$$
where \( R = \frac{r/A}{1 + (r/A)} e^{c_{3}MV} e^{-a_{3}MV}. \) Optimizing Eq. (4.13) on the experimental \( I-V \) data would yield the kinetic parameters introduced by the PDM. The optimization used the least square algorithm, with some parameters under constraints. The solution pH, cation valence state and the sweep rate are known parameters, the double layer capacitance, electric field strength and the dielectric constant of the film are set to certain values based on previous studies, and parameters \( a_{3}, b_{3} \) and \( c_{3} \) are functions of the most fundamental parameters: \( \alpha, \beta, \) and \( \alpha_{3}, \) which are all under constraints of being within 0 and 1. By optimizing the fundamental parameters and adjusting the rate constant, growth rate and dissolution rate, all the kinetic parameters could be exacted, and they are very valuable in determining the growth rate and thickness of the oxide film.

Figure 4-6: \( I-V \) curves calculated from Eq. (4.13) and obtained experimentally as a function of the sweep rate.

The optimized \( I-V \) curves at various sweep rates are compared with the experimental data in Figure 4-6. It can be seen that good agreements are reached,
especially at low sweep rates, where the passive currents of platinum dominate. At high sweep rate, the capacitance value may cause some variation of the current. This verifies that the PDM describes very well the anodic film growth, not only at steady state, but also under transient conditions. The extracted kinetic parameters are listed in Table 4-1.

Table 4-1: PDM parameter values for platinum extracted by optimizing on $i$-$V$ curves at various sweep rates

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$v$ (mV/s)</th>
<th>5</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>100</th>
<th>Avg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td></td>
<td>0.423</td>
<td>0.523</td>
<td>0.664</td>
<td>0.704</td>
<td>0.694</td>
<td>0.602</td>
</tr>
<tr>
<td>$\beta$ (V)</td>
<td></td>
<td>-0.0332</td>
<td>-0.0364</td>
<td>-0.0422</td>
<td>-0.0424</td>
<td>-0.0438</td>
<td>-0.0396</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td></td>
<td>0.122</td>
<td>0.119</td>
<td>0.117</td>
<td>0.124</td>
<td>0.125</td>
<td>0.119</td>
</tr>
<tr>
<td>$a_3$ (V$^{-1}$)</td>
<td></td>
<td>5.55</td>
<td>4.49</td>
<td>3.11</td>
<td>2.9</td>
<td>3.03</td>
<td>3.82</td>
</tr>
<tr>
<td>$10^7 b_3$ (cm$^{-1}$)</td>
<td></td>
<td>-1.64</td>
<td>-1.88</td>
<td>-1.67</td>
<td>-1.96</td>
<td>-1.98</td>
<td>-1.83</td>
</tr>
<tr>
<td>$c_3$</td>
<td></td>
<td>0.332</td>
<td>0.343</td>
<td>0.390</td>
<td>0.416</td>
<td>0.433</td>
<td>0.383</td>
</tr>
<tr>
<td>$10^{10} A$ (cm/s)</td>
<td></td>
<td>3.4</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>3.9</td>
</tr>
<tr>
<td>$10^{10} C$ (cm/s)</td>
<td></td>
<td>2.6</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.1</td>
</tr>
<tr>
<td>$10^{13} k_3$ (mol/cm$^3$s)</td>
<td></td>
<td>4.44</td>
<td>4.50</td>
<td>4.60</td>
<td>4.60</td>
<td>4.50</td>
<td>4.53</td>
</tr>
<tr>
<td>$C_{dl}$ (uF)</td>
<td></td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$10^{-6} \hat{e}$ (V/cm)</td>
<td></td>
<td>1.7</td>
<td>2.0</td>
<td>1.8</td>
<td>2.0</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>$V^0$ (V SCE)</td>
<td></td>
<td>-0.06</td>
<td>-0.10</td>
<td>-0.10</td>
<td>-0.10</td>
<td>-0.10</td>
<td>-0.09</td>
</tr>
</tbody>
</table>

Note, the dielectric constant for platinum is assumed to be 42.5[11], and the oxidation state for platinum is Pt(II), so that $\chi =2$.

Compared with those parameter values obtained by optimizing the PDM on the electrochemical impedance spectroscopy (EIS) results of platinum growth[11], it is seen that most parameter values are tantamount or comparable to each other, except the standard rate constant for reaction (3) (labeled as reaction (2) in reference [11] as the 5-reaction PDM scheme was used). The standard rate constant reported in reference [10] is
4 orders of magnitude lower than the value this work provides. In this work, when considering the pH effect and the mole volume per cation of the barrier layer, $\Omega$ ($\Omega=$molecular weight/density, for Cr$_2$O$_3$, $\Omega=14.59[10]$), the growth rate and the dissolution rate are in the order of $10^{-10}\text{cm/s}$, equivalent to 1nm per 1000s, which is a very reasonable value. Whereas the growth rate in reference [11] is at most around $10^{-13}\text{cm/s}$, which then would take over several hundreds of hours ($1\times10^6\text{s}$) to grow 1nm thick oxide film at low to medium overpotentials. In other words, measurable film thickness is only obtained at very high overpotentials. In fact, we can see the formation of the oxide layer at moderate sweep rates, which indicates that the growth rate is not that sluggish. Moreover, the oxide films grown at each potential for only 15mins were visible to an ellipsometer even at low overpotential region, as reported by Bockris et al.[13] Thus, the values provided in this work might be closer to the reality. The dissolution rate on the order of $10^{-10}\text{cm/s}$ is also in very good agreement with the experimental findings.

From the table, it is also seen that the electric field strength within the oxide film is extremely high at $2\times10^6\text{V/cm}$, and is sweep rate independent. Other fundamental kinetic parameters, i.e. $\alpha$, $\beta$, $\alpha_3$, including $k_3^0$, are also sweep rate independent or weakly dependent, which are true in terms of the theoretical basis of the PDM. These parameters are intrinsic for a reaction at a certain interface, not functions of other controllable external variables.

The calculated potential dependent film thicknesses under transient conditions are plotted in Figure 4-7. Because the potential is swept at various sweep rates, a steady state could not be reached at each potential, so that a linear relationship between the film thickness and the applied voltage can not be obtained. Instead, the slope increases as the potential is swept to higher values. This could be explained from Eq. (4.1), as the growth rate is inversely proportional to the exponential of film thickness and proportional to the exponential of the applied voltage, and that films are thinner than those obtained under steady state condition at each potential, therefore, higher growth rate at each potential is resulted under transient conditions.

Due to the slow growth rate and limited potential range, the film thickness is highly sweep rate dependent. The lower the sweep rate, the thicker the film at each
potential, because the film could grow at each potential for a relatively longer time. Film thickness drops greatly when sweep rate increases. With a sweep rate of 100mV/s, the whole positive scan takes only 4-5 seconds, within such a limited growth time, and that the growth rate is approximately $10^{-10}$-$10^{-9}$ cm/s, the film is very thin even at high overpotentials. The measured current at high sweep rate is then mainly contributed from the charging effect.

![Figure 4-7: Potential dependent platinum oxide film thicknesses as a function of the sweep rate.](image)

Controversies on the growth mechanism of the anodic oxide film on platinum still remain, as introduced in chapter 2. The place exchange model (PEM) of Sato and Cohen[14] has been extensively advocated by Conway[15,16] and his followers[17,18] to describe the formation of the first two monolayers of PtO. The PEM states that the interfacial place exchange between chemically adsorbed O atom and the top-most Pt atom, driven by dipole rotation under high field (on the order of $10^6$ V/cm as well), results in the formation and growth of the first 1-2 monolayers. The PEM and PDM both yield the logarithmic growth law with time, but the PEM fails to predict the existence of
steady states in the film thickness and current. Moreover, it lacks microscopic vision of the growth kinetics, and provides no further information on the electronic properties of the oxide film. Whereas the PDM provides microscopic vision of film growth and dissolution in terms of defect generation and annihilation reactions, and the kinetic parameters associated with those reactions, once extracted from optimization methods, can then be used to predict other measurable properties or quantities.

4.4 Structure of the Platinum Oxide

Controversy exists regarding the degree of crystallinity of an anodic oxide film on platinum formed at potentials prior to oxygen evolution. According to the discussions in references[11,19], it is concluded from the X-ray photoelectron spectroscopy (XPS) results and other researcher’s work, that the anodic oxide film on platinum has a typical bi-layer structure comprising a highly defective oxide barrier layer, and an outer porous precipitated hydroxide layer. Furthermore, scanning tunneling microscopy (STM) work coupled with CV results by Itaya et al.[20] indicate that if a thin oxide film is formed on an electrochemically inactivated single crystal platinum surface, the structural order of the single crystal surface remains unaltered. The amorphous nature of the oxide film reported by Wagner and Ross[21,22] using low energy electron diffraction (LEED) surface technique is probably due to the existence of a thick hydroxide layer which is structurally amorphous and incorporates water molecules, or due to the extremely thin thickness of the inner oxide layer (that the oxide may consist of only a few monolayers of PtO). Therefore, the anodic oxide film formed on platinum may still have nanoscale crystallinity, with the main composition being PtO\(_{1-x}\) (x is introduced as a consequence of the oxygen vacancies within the oxide film).

The barrier anodic oxide layer on platinum is postulated to be a columnar, nano crystalline structure probably comprising tetragonal unit cells oriented with the c-axis perpendicular to the metal surface[11]. A unit cell of the bimolecular tetragonal PtO is shown in Figure 4-8 (drawn by Crystal Designer PPC 7.0.1), with the lattice parameters of \(a=0.305\text{nm}\) and \(c=0.535\text{nm}\)[23,24]. Since bulk platinum has face centered cubic (fcc)
structure with lattice parameter $a=0.392\text{nm}$[23,24], the distance between the closest neighboring platinum atoms on (111) plane is $0.277\text{nm}$, this matches closely with the platinum atoms on the (001) plane of PtO. Moreover, it is also concluded by Conway et al.[25] that the crystal faces at the polycrystalline platinum surface are mainly oriented in [111] direction according to the similarity of the under potential deposited (UPD) hydrogen atoms in the profile of hydrogen adsorption-desorption cyclic voltammograms of a polycrystalline platinum and a (111) single crystal platinum. Therefore, the proposed orientation is likely to result in the lowest interfacial energy with various crystallographic planes of platinum metal. However, it is only a hypothesis here as no direct experimental evidence is currently available. There might be other orientations that would yield less strain and interfacial energy, and the oxide film may well be a polycrystal. Also note that, the anodically grown film on a metal electrode is generally under very high strain since the oxide layer grows directly on top of the metal substrate.

Figure 4-8: Tetragonal unit cell of PtO with lattice parameters $a=0.305\text{nm}$ and $c=0.535\text{nm}$.
4.5 Conclusions

To better understand the electrocatalysis of platinum for redox reactions in fuel cells, it is important to examine the surface structure and electronic properties of the platinum electrode and the anodic oxide film formed on platinum. In this chapter, the surface morphologies characterized by SEM indicate that the platinized nickel electrode has a granular surface with much more active reaction sites than that of a bulk platinum electrode. EDS analysis verifies that the electroplated layer is pure platinum, and XRD analysis yields a film thickness of approximately 5um. Cyclic voltammograms of the platinized nickel electrode in 0.1M KOH in nitrogen environment shows four regions typical of a bulk platinum electrode. Growth kinetics of the oxide film on platinum is studied using the potential sweep method. By optimizing the current-potential relation derived based on the framework of the PDM, on the transient $i-V$ data, kinetic parameter values for anodic oxide film growth are extracted. The structure of the oxide layer is also portrayed. The anodic oxide film on platinum comprises of bi-layer structure, with a defective inner barrier layer having bimolecular tetragonal PtO structure.

References


Chapter 5
Platinum as an Electrocatalyst for Fuel Cells

Nano-scale platinum particles and platinum based alloys are widely used as the electrocatalyst for the hydrogen oxidation reaction (HOR) in fuel cells operated at low to medium temperature, and pure platinum nano-particles still serve as the best electrocatalyst for the oxygen reduction reaction (ORR). To design better and cheaper electrocatalysts other than platinum, it is necessary to know the kinetics and mechanism of both reactions. In this chapter, the kinetics and mechanism of the hydrogen electrode reaction over a wide temperature range from ambient temperature up to 220°C are thoroughly explored, the ORR is also briefly discussed and the possible reason for its sluggish nature is indicated.

5.1 Kinetics and Mechanism of the Hydrogen Electrode Reaction

As introduced in chapter 2, the hydrogen electrode reaction is the most intensively investigated electrochemical process, and served as a model to establish the so called “volcano plot”[1-3] for electrocatalysis. The “volcano plot” correlates the exchange current density with the standard Gibbs energy of hydrogen adsorption, and platinum sits on top of this volcano. However, regardless of the position where platinum is located in the volcano plot, this plot does not indicate any mechanistic information of the reactions, nor of the temperature effect. Whereas, depending on the nature of the electrode/electrolyte interface, the reaction mechanism may vary from one to another. Currently, the operating temperature for commercially available proton exchange membrane fuel cells (PEMFC) is limited to 80-100°C due to the membrane requires humidification for good proton conduction, but it is envisioned to operate at higher temperatures, as higher temperatures yield higher exchange current densities for the ORR, lower activation overpotentials, and lower susceptibility of the anode catalyst to
poisoning by trace amounts of CO in the hydrogen fuel[7,8]. However, to date, most of the work reported on the HOR and ORR has been carried out at temperatures below 70°C due to equipment limitations. Therefore, it is of great interest and importance to characterize the kinetics and mechanism(s) of the hydrogen electrode reaction and oxygen electrode reaction at elevated temperatures.

With the specially designed equipment having controllable hydrodynamic properties, the hydrogen electrode reaction is investigated over a wide temperature range in this thesis work, but the oxygen electrode reaction is only studied at ambient temperature due to time limitation. Only a few mechanistic studies of the hydrogen electrode reaction have been carried out at elevated temperatures: e.g. that on mercury in HCl solutions at temperatures of up to 300°C by Tsionsky et al[9]. The HOR was previously studied in our laboratory at elevated temperatures (25°C – 300°C) by Biswas[10], but the mechanism was not identified, since only the HOR was explored. Whereas this work covers a wide temperature range (22°C-220°C), and because that both hydrogen oxidation and hydrogen evolution reactions are explored in the same experiment, the measured data are expected to unveil the temperature dependencies of the kinetics parameters (exchange current density and the anodic and cathodic transfer coefficients) and to indicate the mechanism of the hydrogen electrode reaction. Most of the previous work analyzing the mechanism of the hydrogen electrode reaction was carried out in acidic solutions and only recently have several studies in alkaline solutions been reported[11-14]. It is found that fuel cells using alkaline solution (especially KOH) show considerably better performance than do other types of fuel cells when operating below 200°C[11] (though there are drawbacks for alkaline fuel cells, e.g. durability problem due to the formation of carbonate in the electrolyte). For this reason, KOH solutions of different concentrations were used in the present study to investigate the kinetics and mechanism of the hydrogen electrode reaction, with the main focus on the elevated temperature behavior. The working electrode employed in the elevated temperature experiments is a platinized nickel cylinder, and that for ambient temperature experiments on the hydrogen electrode reaction is a bulk platinum disk electrode.
5.1.1 Room Temperature Analysis

Before going to high temperatures, a study of the HOR on a bulk platinum disk electrode at ambient temperature was first carried out using a rotating ring disk electrode (RRDE) in 0.1M KOH with constant hydrogen gas purging. The pressure of the hydrogen is controlled at 1bar and the concentration of dissolved hydrogen in solution is therefore $0.71 \times 10^{-3} \text{mole per 1000g of water}$. The potential sweep rate dependence of the current density at a rotation rate of 400rpm and the rotation rate dependence of the current density at a sweep rate of 10mV/s are shown in Figure 5-1 (a) and (b), respectively. At all sweep rates, there is a sharp increase in the oxidation current with voltage at small overpotentials before reaching a plateau region. At even higher overpotentials, the current gradually drops to another plateau followed by the evolution of oxygen. The drop of current over a certain potential is due to the formation of an oxide layer on platinum whose thickness increases as the potential increases, and that charge carriers can only quantum mechanically tunnel through this oxide layer for the reaction to occur. This is discussed thoroughly in chapter 6.

When the sweep rate is slow (below 30mV/s), three pairs of peaks arise from hydrogen desorption/adsorption away from/on to the different orientations of platinum crystal planes are almost invisible with a rotation rate of 400rpm. As the sweep rate increases (to above 30mV/s), the mass transport rate gradually can not follow the fast kinetics of the hydrogen adsorption/desorption processes, and hence, the peaks become more and more distinct. If the rotation rate increases, then this shift occurs at a higher sweep rate and vice versa. The limiting current at the plateau region, where there is no peak, is only slightly affected by the potential sweep rate, as the reaction is controlled not by the kinetics but by the mass transfer rate of hydrogen from the bulk to the electrode surface, and that the double layer charging current (in the uA magnitude) is not comparable with that of the hydrogen oxidation.

There is some hysteresis with the current upon the reversal of the potential sweep. The platinum oxide is not completely reduced until a very negative potential. But after that, the reverse sweep current almost overlaps the forward sweep current. Note, when
the apparatus was not cleaned thoroughly by acetone, methanol and distilled water, the hysteresis existed till the hydrogen evolution reaction took place, most probably due to the adsorption of the electrode surface by the organic contaminants at low potentials.

Figure 5-1: Sweep rate and rotation rate dependencies of the hydrogen oxidation current on platinum in 0.1M KOH at ambient temperature with \([\text{H}_2]\) = 0.7x10^{-3}M. (a): 400rpm; (b): 10mV/s.
Figure 5-1 (b) shows that when the rotation rate increases, the limiting current of hydrogen oxidation increases, which is a direct result of the increased mass transport rate induced by the rotation of the electrode. If we plot the limiting current density as a function of the square root of the rotation rate, the Levich plot is then yielded. The Levich equation correlates the limiting current of a reaction, $i_L$, with the rotation rate and other hydrodynamic properties of the solution as[15]

$$i_L = 0.62nFAD^{2/3}v^{-1/6}\omega^{1/2}C$$  \hfill (Eq. 5.1)

where $n$ is the number of electrons transferred, $F$ is the Faraday’s constant, $A$ is the electrode area, $D$ is the diffusivity of the reaction species, $v$ is the kinematic viscosity, $\omega$ is the angular rotation rate (rad/s, $\omega=2\pi f$, where $f$ is the frequency and is usually expressed in rpm), and $C$ is the concentration of the reaction species in the electrolyte. The linearity between the limiting current and square root of the rotation rate is demonstrated in Figure 5-2. The slope of this plot yields some information on the diffusivity and kinematic viscosity of the hydrogen and solution.

For this system, $n=2$, $A=0.283\text{cm}^2$, $C_{H_2}^{b}=0.71 \times 10^{-3}\text{M}=0.71 \times 10^{-6}\text{mol/cm}^3$, and the slope is $1.99 \times 10^{-4}\text{A/cm}^2/\text{s}^{1/2}$. If we assume the kinematic viscosity of 0.1M KOH solution approximates that of the water (which is $8.98 \times 10^{-3}\text{cm}^2/\text{s}$), then the diffusivity of the H$_2$ in solution is calculated to be $2.32 \times 10^{-4}\text{cm}^2/\text{s}$, which is about 5 times higher than that reported in literature[16]. The reason for the discrepancy is partly due to the geometrical surface area being smaller than the real surface area of the electrode and partly due to the potential sweep technique employed in this experiment. If the surface area was corrected by the roughness factor and the potential static polarization experiments were carried out, then the steady state limiting current would be much lower, and therefore the slope would be smaller.
From Figure 5-1 (b), it is also seen that, as the rotation rate increases, the sharp increase in the oxidation current at small overpotentials becomes more prominent. However, the difference between the current densities at rotation rates of 900rpm and 1600rpm is rather small in the small overpotential region, which means that above 900rpm, the reaction is solely controlled by the kinetics of the surface reactions not by mixed control of kinetics and mass transfer, thus, mechanistic analysis is feasible without involving mass transport in the analysis.

Figure 5-2: The limiting current of the hydrogen oxidation reaction in 0.1M KOH at ambient temperature as a function of the rotation rate.

Figure 5-3(a) shows the micropolarization plots for the HOR at rotation rates of 900rpm and 1600rpm with a sweep rate of 10mV/s. In this micropolarization region (also called the linear polarization region), because the mass transfer rate is quick enough for the kinetics to be the controlling factor, the Butler-Volmer equation simplifies to

\[ i = i_0 \frac{\eta F}{RT} \]  

(Eq. 5.2)
where $i_0$ is the exchange current density, and $\eta$ is the overpotential for the HOR (the open circuit potential can either be measured by Gamry Instrument/Solatron equipment, or calculated from Nernst equation).

![Graph](image_url)

**Figure 5-3**: (a) Micropolarization plot and (b) Tafel plot for the HOR in 0.1M KOH at rotation rates of 900rpm and 1600rpm.
From the slope of the current vs. overpotential, exchange current densities of 0.29mA/cm² and 0.39mA/cm² at rotation rate of 900rpm and 1600rpm were obtained, respectively, which are very close to those reported in literature for alkaline solutions (a close look at the micropolarization region indicates that, at 900rpm, the reaction is still partially under mass transport control, thus the slope of \( i \) vs. \( \eta \) and the exchange current density are lower than that at 1600rpm): Couturier reported an exchange current density of 0.342mA/cm² on bulk Pt and 0.087mA/cm² on sputtered Pt[11], Conway[17] reported 0.398mA/cm², and other studies[13,14,18] reported similar values. The exchange current density for the HER is generally one or two orders of magnitude lower in alkaline solution than in acid solution. Figure 5-3(b) shows Tafel plot for the HOR at rotation rates of 900rpm and 1600 rpm. The Tafel slopes obtained are around 120mV/dec, which are also very close to the values observed by others[11,13,17,19] with the transfer coefficient being approximately 0.5.

5.1.2 High Temperature Analysis

5.1.2.1 Potential Conversion

For the ambient temperature experiments, the potential can be readily converted to the standard hydrogen electrode (SHE) scale simply by adding the potential of the saturated calomel electrode (SCE, which at 298K is 0.241V \(_{\text{SHE}}\)) to the measured value. However, for the high temperature experiments, thermochemical calculation is required to estimate the temperature-dependent conversion factor since the potential of the Ag/AgCl, KCl (sat) reference electrode itself varies with temperature. The conversion is made using the Chemical Reaction and Equilibrium Software with Extensive Thermochemical Database (Version 5.1) by Outokumpu HSC® Chemistry. The potential of the Ag/AgCl, KCl (sat) reference electrode at each temperature is first converted into the SHE scale, and is then used to convert the measured potential to the SHE scale.

The half-cell reaction of the Ag/AgCl, KCl(sat) reference electrode is
The equilibrium potential of this reference electrode can then be calculated from the Nernst equation

\[ E_{\text{Ag/AgCl}} = E_{\text{Ag/AgCl}}^0 - \left(\frac{2.303RT}{F}\right) \log a_{\text{Cl}^-} \]  

(Eq. 5.4)

where the parameter \( a_{\text{Cl}^-} \) is the activity of chloride ion in the solution, and the standard electrode potential, \( E_{\text{Ag/AgCl}}^0 \), can be calculated by the HSC® chemistry software from the change in standard Gibbs energy for the full cell reaction: \( \text{AgCl} + \frac{1}{2} \text{H}_2 \leftrightarrow \text{Ag} + \text{HCl} \), as \( \Delta G^0 = -nF E^0 \). Since the Ag/AgCl reference element is immersed in saturated KCl solution, the activity of chloride ion is readily calculated from the solubility product of the KCl solution, \( K_{sp} \)

\[ K_{sp} = a_{\text{Ag}^+} a_{\text{Cl}^-} = a_{\text{Cl}^-}^2 \]  

(Eq. 5.5)

where \( a_{\text{Ag}^+} \) is the activity of the potassium ion. Noting that the activity coefficients of the two ions are related to the mean molal activity coefficient by \( \gamma_{\text{Ag}^+} \gamma_{\text{Cl}^-} = (\gamma_\pm)^2 \) and also noting that the molal concentrations of these two ions are the same, the equilibrium potential of the Ag/AgCl, KCl (sat) reference electrode on the SHE scale can then be determined from the equation

\[ E_{\text{Ag/AgCl}} = E_{\text{Ag/AgCl}}^0 - \left(\frac{2.303RT}{2F}\right) \log K_{sp} \]  

(Eq. 5.6)
The change in standard Gibbs energy for the equilibrium \( KCl(s) \rightleftharpoons K^+ + Cl^- \) can be readily calculated using the HSC\textsuperscript{®} chemistry software as well. Once the equilibrium potential of the reference electrode at any temperature is known, the measured potential \( (E_{meas}) \) can be converted to the SHE scale at the temperature of operation

\[
E_{SHE} = E_{meas} + E_{ref}
\]  
(Eq. 5.7)

where \( E_{ref} \) is a general expression for the potential of the reference electrode. The solubility product of KCl, standard electrode potential of the reference electrode, as well as the calculated potential of the Ag/AgCl, KCl(sat) reference electrode at each experimented temperature are listed in Table 5-1.

Table 5-1: Thermodynamic database for the Ag/AgCl, KCl(sat) reference electrode

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>18</th>
<th>70</th>
<th>100</th>
<th>130</th>
<th>160</th>
<th>185</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log(K_{sp}) )</td>
<td>0.777</td>
<td>1.1879</td>
<td>1.2957</td>
<td>1.3334</td>
<td>1.3155</td>
<td>1.2631</td>
<td>1.2160</td>
</tr>
<tr>
<td>( E^0_{Ag/AgCl} (\text{V}_{SHE}) )</td>
<td>0.227</td>
<td>0.1879</td>
<td>0.1605</td>
<td>0.1288</td>
<td>0.0922</td>
<td>0.0576</td>
<td>0.0349</td>
</tr>
<tr>
<td>( E_{Ag/AgCl} (\text{V}_{SHE}) )</td>
<td>0.2041</td>
<td>0.1475</td>
<td>0.1126</td>
<td>0.0755</td>
<td>0.0356</td>
<td>0.0002</td>
<td>-0.0222</td>
</tr>
</tbody>
</table>

To check the stability of the Ag/AgCl, KCl(sat) reference electrode, the measured open circuit potential is compared with the theoretical equilibrium potential of the hydrogen electrode reaction for this system. The theoretical open circuit potential for the hydrogen electrode reaction \( H^+ + e^- \rightleftharpoons \frac{1}{2} H_2, E^\circ \), can be calculated using the Nernst equation:
where \( f_{H_2}^T \) is the temperature dependent fugacity of the hydrogen gas. Since the solution tank with hydrogen saturated electrolyte is maintained at ambient temperature throughout the experiments, and the electrolyte is pumped into the reactor from the solution tank, the amount of hydrogen dissolved in the electrolyte, \( m_{H_2}^T \), is always the same at any temperature. Therefore, the fugacity of the hydrogen can be calculated from Henry’s law

\[
m_{H_2}^T = K_{H_2}^T f_{H_2}^T = K_{H_2}^{T_0} f_{H_2}^{T_0}
\]  

(Eq. 5.9)

where \( T_0 \) is the ambient temperature (294 ± 2K) in this study, \( K_{H_2}^T \) is the temperature dependent Henry’s constant and is given as[20]

\[
\log(K_{H_2}^T) = \frac{1321}{T} - 10.703 + 0.010468T
\]  

(Eq. 5.10)

Therefore, the fugacity of hydrogen at any temperature is calculated as

\[
f_{H_2}^T = \frac{K_{H_2}^{T_0}}{K_{H_2}^T} f_{H_2}^{T_0} \approx \frac{K_{H_2}^{T_0}}{K_{H_2}^T} p_{H_2}
\]  

(Eq. 5.11)

The pressure of hydrogen is controlled at 2.61bar and 2.86bar for experiments in 0.1M KOH (equivalent to 0.1006m at any temperature) and 0.01M KOH (equivalent to 0.01001m at any temperature) + 0.03M K₂SO₄ solutions (equivalent to 0.03016m at any temperature).
temperature, K$_2$SO$_4$ is added to equalize the ionic strength of the solution), respectively. The solution pH can be known from the water ion product, pK$_w$, at any temperature, the latter is provided by the HSC® chemistry software as well. The parameter values and open circuit potential of the hydrogen electrode reaction at each temperature are tabulated in Table 5-2.

Table 5-2: Equilibrium potential (open circuit potential) of the hydrogen electrode reaction and the corresponding parameter values at each studied temperature.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>19</th>
<th>70</th>
<th>100</th>
<th>130</th>
<th>160</th>
<th>185</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^3 K_{H^+}^+$</td>
<td>0.76</td>
<td>0.55</td>
<td>0.55</td>
<td>0.62</td>
<td>0.76</td>
<td>0.95</td>
<td>0.110</td>
</tr>
<tr>
<td>$f_{H_2}^+$ (atm)</td>
<td>2.606</td>
<td>3.624</td>
<td>3.587</td>
<td>3.192</td>
<td>2.612</td>
<td>2.097</td>
<td>1.803</td>
</tr>
<tr>
<td>$E^e$</td>
<td>-0.7764</td>
<td>-0.8243</td>
<td>-0.8545</td>
<td>-0.8888</td>
<td>-0.9261</td>
<td>-0.9599</td>
<td>-0.9817</td>
</tr>
</tbody>
</table>

Figure 5-4 shows the temperature dependence of the theoretically calculated equilibrium potential of the hydrogen electrode reaction and the measured open circuit potential in both 0.1006m KOH solution and 0.01001m KOH + 0.03016m K$_2$SO$_4$ solution, which is measured against the Ag/AgCl, KCl(sat) reference electrode. The difference is shown together with the axis on the right. The open circuit potential decreases almost linearly with increasing temperature. The differences between the calculated and measured open circuit potentials for both systems are within 10mV, which indicates that the stability of the prepared Ag/AgCl, KCl(sat) reference electrode is quite satisfactory for experimental use for the studied temperature range.
Figure 5-4: Theoretically calculated and experimentally measured open circuit potential for the hydrogen electrode reaction in (a) 0.1M KOH solution and (b) 0.01M KOH +0.03M K$_2$SO$_4$ solution.
5.1.2.2 Temperature Dependence

Potential sweep method is used to study the hydrogen electrode reaction on platinum over a wide temperature range, but the sweep rate was set to be very slow (0.5 mV/s), in order to maintain quasi-steady state conditions. The polarization curves in 0.1006m KOH at a series of temperatures with the impeller rotating at 400rpm are shown in Figure 5-5. It is seen that both the limiting current of the HOR and the passive current of platinum increase with the increasing temperature.

Figure 5-5: Temperature dependence of the polarization curves for the hydrogen electrode reaction on platinum in 0.1006m KOH at a H₂ pressure of 2.61bar (equivalent to [H₂] = 1.824x10⁻³m) and at an impeller rotation rate of 400rpm, except at 220°C, where the experiment was carried out in 0.01001m KOH + 0.03016m K₂SO₄ at 200rpm, and at a H₂ pressure of 2.86bar (equivalent to [H₂] = 2x10⁻³m).

It is also noted that the commencements of platinum oxidation (i.e., the down turn in the hydrogen oxidation current from the plateaus) and the oxygen evolution reaction shift toward the open circuit potential of the hydrogen electrode reaction as the temperature is increased, which can be accounted for by the thermodynamics of the
reactions. As mentioned previously, upon further increasing of the overpotential, the reaction rate decreases exponentially with increasing voltage, which can be accounted for by charge carriers tunneling across the passive oxide layers[21-23], and will be discussed in chapter 6.

It can be seen from Figure 5-5 that, at low overpotentials, the polarization curves almost overlap with each other, which indicates that the reaction is under mixed control of mass transport and kinetics. To obtain reliable values for the kinetic parameters, the Butler-Volmer equation is used for the optimization on the experimental polarization data to take into consideration the mass transport effect:

\[
i = \frac{e^{\eta/b_a} - e^{-\eta/b_c}}{1 + e^{\eta/b_a} - e^{-\eta/b_c}} \frac{1}{i_0} \frac{i_{l,a}}{i_{l,c}}
\]

(Eq. 5.12)

where \(2.303b_a\) and \(2.303b_c\) are the Tafel slopes for the HOR and the hydrogen evolution reaction (HER), respectively; and \(i_{l,a}\) and \(i_{l,c}\) are the limiting currents for these same reactions. The Tafel slope is also a function of temperature and the transfer coefficient of the reaction:

\[
b_a = \frac{RT}{\alpha_a nF}
\]

Eq. (5.13)

\[
b_c = \frac{RT}{\alpha_c nF}
\]

Eq. (5.14)

where \(\alpha_a\) and \(\alpha_c\) are the transfer coefficients of the HOR and the HER, respectively, and \(n\) is the number of electrons transferred. By optimizing Eq. (5.12) on the experimental polarization data and noting Eq. (5.13) and Eq. (5.14), the exchange current density and transfer coefficients of the HOR and the HER can then be extracted at each temperature. The activation energy of the hydrogen electrode reaction and the Tafel slopes of the HOR
and the HER can therefore also be determined. In this optimization model, current, overpotential, and limiting current of the HOR are measured values (known parameters), and temperature and number of transferred electrons are known parameters as well. The optimization algorithm is the least square root of the sum of the difference square between the measured current values and calculated current values at each temperature.

Figure 5-6 shows both the experimental data for the hydrogen electrode reaction at several temperatures and the predicted data by the Butler-Volmer equation using the kinetic parameters obtained by optimization. It can be seen that the calculated data matches very well with the experimental data, and the extracted exchange current densities as well as the Tafel slopes are tabulated in Table 5-3.

![Figure 5-6](image-url)

**Figure 5-6:** Experimental (exp) and calculated (eqn) polarization data for the HER and the HOR on platinum in 0.1006m KOH as a function of temperature. The calculated values are estimated using Eq. (5.12) and the parameter values are determined by optimization (Table 5-3).
An Arrhenius plot of the exchange current density is shown in Figure 5-7, from the slope \(-\frac{\Delta H}{RT}\), where \(\Delta H\) is the enthalpy energy of change, an activation energy of 17.3 kJ/mole is calculated, which is in good agreement with those reported in literature for bulk, polycrystalline platinum electrodes with temperatures from ambient up to 70°C[11].

Table 5-3: Kinetic parameters for the HOR and HER on platinized nickel electrode in 0.1M KOH at a series of temperatures

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>(b_a) (mV/dec)</th>
<th>(b_c) (mV/dec)</th>
<th>(i_0) (mA/cm²)</th>
<th>(i'_0) (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>77</td>
<td>106</td>
<td>1.42</td>
<td>0.55</td>
</tr>
<tr>
<td>70</td>
<td>74</td>
<td>105</td>
<td>5.44</td>
<td>2.08</td>
</tr>
<tr>
<td>100</td>
<td>132</td>
<td>115</td>
<td>7.95</td>
<td>3.05</td>
</tr>
<tr>
<td>130</td>
<td>111</td>
<td>109</td>
<td>11.90</td>
<td>4.56</td>
</tr>
<tr>
<td>160</td>
<td>141</td>
<td>115</td>
<td>15.13</td>
<td>5.8</td>
</tr>
<tr>
<td>185</td>
<td>168</td>
<td>120</td>
<td>21.54</td>
<td>8.25</td>
</tr>
<tr>
<td>200</td>
<td>184</td>
<td>107</td>
<td>24.62</td>
<td>9.43</td>
</tr>
</tbody>
</table>

Note: \(i'_0\) is the exchange current density after correcting the hydrogen pressure to 1bar.

Table 5-4 lists the activation energies obtained in this work and that reported in literature. A comparison of these values indicates that the activation energy on the platinized nickel electrode is comparable/within the experimental error with that for a bulk platinum electrode[11], and is lower than that observed on a sputtered platinum electrode[11] and single crystal platinum electrodes in alkaline solutions[24]. The activation energy of a platinum/nickel alloy electrode is slightly lower than both the platinized nickel electrode and the bulk platinum electrode in alkaline solutions. The hydrogen electrode reaction is relatively faster in acid than in alkaline solutions[13,25,26] (The fact that the kinetics of the HOR on Pt is pH dependent[27] poses a problem for the
frequently proposed mechanism: the Tafel-Volmer sequence with the Tafel step as rate determining[13,28]), and a comparison of literature also indicates that the activation energy is lower in acid than in alkaline, which render acid solutions better electrolytes for the kinetics of the hydrogen electrode reaction. However, it also results in the harsh requirements for the electrode materials, e.g. corrosion/dissolution loss of the electrode material and materials that can be used are very limited.

The exchange current density extracted in this work is higher than those measured by other works in alkaline solutions, even after correcting the hydrogen pressure to 1bar (assuming that the current density is proportional to the hydrogen concentration), as shown in Table 5-3. A possible reason is that, although bright platinum is electroplated onto a smooth nickel surface, contrary to a polished bulk platinum electrode, the platinized nickel electrode still possesses a granular surface, as discussed in chapter 4, Figure 4-1, and hence provides more adsorption/reaction sites for the hydrogen atoms. An accurate measurement of the surface area will be carried out using the double layer charging method with an estimation of the double layer capacitance. The 60Pt-40Ni

Figure 5-7: Arrhenius plot of the exchange current density for the hydrogen electrode reaction on platinized nickel electrode in 0.1M KOH with \([H_2] = 1.824 \times 10^{-3} \text{m} \).
alloy[11] has a lower activation energy than does the platinized nickel electrode, but the advantage is greatly diminished by the significantly lower exchange current density ($8.10 \times 10^{-3} \text{mA/cm}^2$ at $25^\circ\text{C}$). It therefore suggests that the platinized nickel electrode used in the present study is superior in electrocatalytic performance than the alloy and other forms of platinum electrodes.

Table 5-4: Activation energies for the hydrogen electrode reaction on platinum and platinum alloy electrodes

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Temperature range (°C)</th>
<th>Electrolyte</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinized Ni</td>
<td>18-220</td>
<td>0.1M KOH</td>
<td>17.3</td>
</tr>
<tr>
<td>Bulk Pt</td>
<td>25-70</td>
<td>1M KOH</td>
<td>19.7[^11]</td>
</tr>
<tr>
<td>60Pt-40Ni</td>
<td>25-70</td>
<td>1M KOH</td>
<td>14[^11]</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>1-60</td>
<td>0.05M H$_2$SO$_4$</td>
<td>9.5[^24]</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>1-60</td>
<td>0.05M H$_2$SO$_4$</td>
<td>12[^24]</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>1-60</td>
<td>0.05M H$_2$SO$_4$</td>
<td>18[^24]</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>2-60</td>
<td>0.1M KOH</td>
<td>46[^14]</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>2-60</td>
<td>0.1M KOH</td>
<td>23[^14]</td>
</tr>
</tbody>
</table>

The ambient temperature Tafel slope of the HER, as shown in Table 5-3, is the generally observed value of approximately 120mV/dec (note the ambient temperature in this study is 18°C, not 25°C). The Tafel slope for the HOR at ambient temperature is 77mV/dec, which is not widely reported in literature, although this value has been observed previously in alkaline solution[12]. A possible mechanism for the HOR is a direct discharge identical to the overall reaction in alkaline solution[12] or through the slow hydrogen dissociation and fast ionization sequence (historically referred to as the
Tafel-Volmer sequence). Combining the Tafel slopes of the HOR and the HER, and also following the criteria provided by Bockris[29], the most probable mechanism for the system studied in this work is the fast discharge/slow recombination sequence (Volmer-Tafel mechanism), provided a suitable isotherm is chosen [Temkin activated adsorption[12]]:

\[
M + H_2O + e^- \leftrightarrow MH + OH^- \quad \text{(Eq. 5.15)}
\]
\[
2MH \overset{\text{ads}}{\rightarrow} 2M + H_2 \quad \text{(Eq. 5.16)}
\]

A thorough investigation of using statistical calculations[30-33] or quantum mechanical calculations[34,35] of H₂ adsorption on metal surface indicates that the mechanism of the hydrogen electrode reaction is very likely temperature related. For the HOR, adsorption of the molecular H₂ onto the electrode surface and the following dissociation to adsorbed H atom are very important, but the adsorption isotherm is temperature dependent (proportional to \(\exp(\frac{\Delta G_{\text{ad}}}{RT})\), where \(\Delta G_{\text{ad}}\) is the adsorption energy). While for the HER, the lateral translation or diffusivity of the adsorbed H atoms is also temperature dependent. Low temperature favors the adsorption of hydrogen, but the diffusivity of the adsorbed H atom, \(H_{\text{ad}}\), is relatively lower. Christmann et al.[34] found that the two states of adsorbed H atoms on Ni(111) surface, \(\beta_1\) (adsorption in bridge sites in adjacent of two nearest neighboring atoms) and \(\beta_2\) (adsorption in hollow sites in the middle of three nearest neighboring atoms), with the \(\beta_1\) state formed after filling most of \(\beta_2\) state, started desorption around 330K and 370K. Quantum mechanical calculations by Kresse[35] concluded that small energy barriers for the lateral translation of the adsorbed H atom from one site to another exist. This is verified by low energy electron diffraction (LEED) study[34] which reported that the surface diffusion/lateral translation of the \(H_{\text{ad}}\) on Ni(100) starts around 250K. This may imply that at ambient conditions, the adsorbed H atoms can be considered as partially localized and partially mobile. This further implies that depending on the relative rate of Tafel step
(2MH ↔ 2M + H₂), Volmer step (M + H₂O + e⁻ ↔ MH + OH⁻), and Heyrovsky step (MH + H₂O + e⁻ ↔ H₂ + M + OH⁻), temperature variation may cause the change of the mechanism from one to another, including the transition region. The temperature dependent mechanism analysis therefore awaits further investigation.

An anomalous phenomenon is observed for the Tafel slope of the HER (hydrogen evolution reaction); that it is independent of temperature. In addition, the Tafel slope of the HOR is also not proportional to the temperature. From Eq. (5.13) and Eq. (5.14), it is seen that the Tafel slopes are expected to increase as the temperature increases. A direct consequence of the temperature invariant Tafel slope is that the transfer coefficients are temperature dependent, as seen in Figure 5-8.

![Figure 5-8](image)

**Figure 5-8:** Temperature dependencies of the transfer coefficients of the HOR and the HER on platinized nickel electrode.

The most plausible explanation found in literature is that there is a compensating effect caused by the temperature-dependent entropy of activation[36]. However, this contradicts the quantum mechanical tunneling theory for charge carriers tunneling across a reaction interface[23,37-40]. We postulate that the temperature dependencies of the apparent transfer coefficients of the hydrogen electrode reaction can be attributed to other
factors. Thus, Kriksunov[41] derived the temperature dependence of the apparent Tafel slope for two parallel electrochemical reactions with different reaction rates and activation energies, and he was able to account for temperature-independent Tafel slopes. For a multi-path electrochemical process, two independent, multi-step parallel reactions may have the same product. Thus, the total current, $i_{tot}$, is a sum of reaction 1 and 2

$$
i_{tot} = i_1 + i_2 = K_1 \exp(-A_1 / RT) \exp(\alpha_1 FE / RT) + K_2 \exp(-A_2 / RT) \exp(\alpha_2 FE / RT)$$

(Eq. 5.17)

where $K_i$ is pre-exponential constant, $A_i$ is the activation energy of reaction, and $\alpha_i$ is the effective transfer coefficient for the corresponding reaction, which is assumed to be temperature independent. Now, the temperature dependence of the apparent Tafel slope, $b$, of the overall reaction can be obtained by the differentiation of the potential with logarithmic current:

$$
\frac{1}{b} = \frac{dE}{d \log i_{tot}} = \frac{i_1}{i_{tot} b_1} + \frac{i_2}{i_{tot} b_2} = \frac{F}{2.3RT} \frac{(\alpha_1 i_1 + \alpha_2 i_2)}{i_{tot}}
$$

(Eq. 5.18)

Therefore, because of the difference in the activation energy of each path, though the Tafel slope of each reaction ($b_1$ and $b_2$) varies proportionally with temperature, the apparent Tafel slope behaves almost invariant with temperature. In this study, it is possible that the two parallel processes might be the two different mechanisms for the hydrogen electrode reaction and that they are occurring on different crystal facets of the electrode surface. Electrochemical impedance spectroscopy (EIS) analysis may resolve this, but due to time and space limitation, this work is not discussed here.
5.2 Oxygen Electrode Reaction

PEMFCs promise to revolutionize transportation systems by eliminating emissions of CO₂ from the combustion of carbonaceous fuels. However, there are still two Achilles’ Heels in PEMFC technology: the sluggish nature of the ORR and the lack of a viable high temperature proton exchange membrane. The rate of the oxygen electrode reaction, even on platinum, is 6 orders of magnitude lower than that of the hydrogen electrode reaction[29], resulting in high overpotentials that limit the fuel cell efficiency, and the reaction does not always occur via the desired four-electron pathway. Hydroxyl radicals/hydrogen peroxide generated during the undesired two-electron pathway result in severe degradation of the current membranes, thereby limiting the membrane electrode assembly (MEA) life. This section explores some general features of the ORR, and proposed a possible reason for the sluggish nature of the reaction, this then leads to the topic in the following chapter.

![Figure 5-9: Linear potential sweep voltammograms for the ORR on a platinized nickel disk electrode in 0.1M KOH solution at 22°C as a function of potential sweep rate. The potential of the ring was maintained at 0.54V_SHE to oxidize any peroxide produced at the disk. Rotation rate: 900rpm. Initial potential sweep direction is negative.](image-url)
Linear polarization curves for the ORR on the platinum disk electrode (platinized nickel electrode) of the RRDE in 0.1M KOH solution as a function of the potential sweep rate are shown in Figure 5-9. Potential is swept in the negative direction and the pressure of oxygen is controlled at the atmospheric value, so the concentration of the dissolved oxygen is approximately 0.26x10^{-3}M. The electrolysis current on the ring electrode, the potential on which was held constantly at 0.54V_{SHE} to oxidize any peroxide produced as an intermediate, is also shown in the figure (the standard electrode potential for \(O_2 + H_2O + 2e^- \rightarrow HOO^- + OH^-\) is -0.065V[42]). From the figure, it is clearly seen that oxygen could not be reduced on platinum at an appreciable rate until a very negative overpotential is attained. At low sweep rates, the current above 0.2V_{SHE} is even positive, though a negative potential sweep was applied. At high overpotentials, the current reaches a plateau indicating mass transport control of the reaction. At even higher overpotentials, the hydrogen evolution reaction begins to take place so that the current increases sharply.

Hydrogen peroxide is only produced in the medium overpotential region where the oxide film on platinum is not completely reduced. The vertical broken line indicates the lower limit of existence of the oxide film as detected by tunneling experiments, and it can also be seen from Figure 5-1 that the hydrogen oxidation current goes back to the plateau value when the oxide film on platinum is reduced at potentials around -0.4V_{SCE}. This lower limit is more negative than that generally recognized platinum oxidation potential and demonstrates that the ORR occurs on an oxide-covered surface over most of the range of technological interest. However, hysteresis between the forward and reverse sweeps in Figure 5-1 persists to potentials as low as -0.5V_{SCE}, indicating that surface species still exist at very negative overpotentials. The tail with the ring current at very negative potentials is due to the oxidation of hydrogen produced at the disk electrode.

Two Tafel regions are observed in Figure 5-10 for the ORR at several sweep rates, one with an unusually high Tafel slope at small overpotentials and the other one with a Tafel slope at approximately 120mV/dec at high overpotentials. Two Tafel regions were also found by Damjanovic et al. in both acid[43] and alkaline solutions[44].
When extrapolated to the equilibrium potential of the oxygen electrode reaction \( (E_e = 0.46 \text{V}_{\text{SHE}} \text{ in 0.1M KOH solution}) \), indicated by the dotted lines in the figure), the Tafel relationship at low overpotentials yields an exchange current density that is two orders of magnitude higher than that calculated from the relationship at high overpotentials, while the generally reported exchange current density for the oxygen electrode reaction on platinum is on the order of \( 10^{-9} \text{A/cm}^2 \)[29]. The Tafel region at low overpotentials reflects the reduction of oxygen on an oxide covered platinum surface, with the thickness of the oxide layer varying with potential. Therefore, it is a pseudo Tafel region and no useful mechanistic information could be extracted in the present analysis. Note, in figure (c), when the sweep rate is very slow, the noise becomes very appreciable at high potentials since the current level is very low, so the current in the high potential region is deleted, and only one Tafel slope is seen. The exchange current density obtained in figure (c) is very close to the values reported for the oxygen electrode reaction[29] since the sweep rate is very slow.

![Diagram showing Tafel relationship](image-url)
The pseudo Tafel relation is further verified by potentiostatic polarization of the ORR on platinum, as illustrated in Figure 5-11. Extrapolation of the Tafel relationship to the equilibrium potential of the oxygen electrode reaction yields an exchange current density of $0.72 \times 10^{-9} \text{ A/cm}^2$, which is close to the values reported in literature\[29\. Interestingly, the current for $E > E_{corr}$ ($E_{corr} = 0.27 \text{V}_{\text{SHE}}$) is positive and almost constant.

Figure 5-10: Tafel plots for the ORR on platinized nickel disk electrode: (a) 100mV/s, (b) 30mV/s, (c) 0.1mV/s. The equilibrium potential for the oxygen electrode reaction (0.46 \text{V}_{\text{SHE}}) is shown by the dotted line in each figure, and the apparent exchange current densities are indicated. The Tafel slopes, $b$, are also shown.
and the magnitude matches well with the passive current density for platinum in alkaline solutions[45], which is in the uA/cm² range, as can also be seen in the following chapter.

The constant passive current density agrees well with the diagnostic criteria of the PDM for an n-type oxide film, provided that the oxidation state of the cation does not change when ejected from the barrier layer[46-48]. Thus, the picture that emerges from the steady state data (Figure 5-11) is that the platinum in oxygenated solution displays the classical corrosion behavior of a passive metal comprising electrochemical reactions of both oxygen reduction and passive metal dissolution. This model dictates that the reduction of oxygen may be inhibited by the oxide layer on the electrode surface, due to the need for the electrons in the metal to tunnel through the oxide film to the oxygen species in the solution or adsorbed on the surface. Accordingly, it is very important to know the thickness and electronic properties of this thin oxide layer on the platinum electrode surface in order to develop an understanding of the kinetics of the ORR. This then leads to the topics covered in the following chapter—chapter 6.

![Tafel plot for the potentiostatic reduction of oxygen on platinum. The equilibrium potential for the oxygen electrode reaction is given by the dotted line. Note that the current values indicated by the inverted triangles for $E > E_{corr}$ are positive whereas the current for oxygen reduction (filled circles) are negative.](image-url)
Most metals are covered with an oxide layer at potentials in the desired range for the ORR, it is for this reason that the kinetics of the ORR are over six orders of magnitude lower than that of the HOR, and that because platinum, as a noble metal, has a relatively higher oxidation potential, it is currently the best electrocatalyst for the ORR. Practically in fuel cell operation, it might be very beneficial to apply cathodic pulses at a constant time interval, e.g. every 1000s as the film growth rate is on the order of $10^{-3}$ nm/s discussed in chapter 4, to reduce the oxide film on the surface.

5.3 Conclusions

This chapter explores the electrocatalysis aspect of platinum in fuel cell electrode reactions at both ambient temperature and elevated temperatures. The principles findings are:

- The measured potentials against a Ag/AgCl, KCl(sat) reference electrode at any temperature are converted into SHE scale via thermodynamic calculations with HSC® chemistry software. The measured open circuit potential of the hydrogen electrode reaction at any temperature is within 10mV difference with the value calculated theoretically for the studied system.

- The kinetics and mechanism of the hydrogen electrode reaction are investigated. Kinetic parameters are extracted by micropolarization analysis and by optimizing the Butler-Volmer equation on the polarization curves. Ambient temperature behavior agrees well with those reported in literature with the exchange current density on the order of mA/cm², and the temperature dependence is also revealed. The exchange current density of the hydrogen electrode reaction on the platinized nickel electrode is higher than the values reported in literature on other forms of platinum electrodes, probably due to the platinized nickel electrode has a granular surface morphology which increases the real surface area or adsorption/desorption sites for the reaction.
• Activation energy of 17.3kJ/mol, obtained from the Arrhenius plot, is also comparable with that of a bulk platinum electrode, and is lower than sputtered platinum and single crystal platinum electrodes in alkaline solutions. The apparent Tafel slope of the hydrogen evolution reaction is found to be temperature independent, of which, the most probable cause is that two parallel reactions with different activation energy and transfer coefficient are occurring at the electrode surface.

• The oxygen electrode reaction on platinum is also studied by potential sweep method and potentiostatic polarization method. The sluggish nature of this reaction is postulated to be due to the existence of a thin oxide layer on the platinum electrode surface. This thin oxide layer inhibits the oxygen reduction in a way that the electrons residing in the metal have to quantum mechanically tunnel through this layer in order to reach the oxygen species in the solution/adsorbed on the surface. Therefore, the thickness of this layer and its electronic properties are very important to the understanding of the kinetics and mechanism of the oxygen reduction reaction, which then leads to the content in the following chapter.

References


Chapter 6

Charge Carrier Tunneling Across a Passive Film on Platinum

Platinum, like many other metals, is covered by an oxide layer when a certain potential is reached. Experimental evidence[1-10] shows that when platinum is anodically polarized to potentials over 0.7V_{RHE}, an oxide film forms. Formation of this oxide layer substantially impact the rates of many redox reactions[6,7,10,11], since charge carriers have to quantum mechanically tunnel through this layer in order for the reaction to proceed. While the theoretical aspects of quantum electrode kinetics and the electronic structures of oxide films formed on metal surfaces demonstrate that a comprehensive understanding of these issues is still poorly developed, significant advances have nevertheless been made in characterizing electron transfer across thin oxide films with the promise to introduce a powerful tool for probing the thickness and properties of thin oxide films. The theoretical background of charge carriers tunneling through a barrier layer (oxide film) at metal/barrier layer/solution interphase is already illustrated in chapter 2, and the method for film thickness measurement combining quantum mechanical tunneling (QMT) theory and the point defect model (PDM) is also developed in chapter 2. This chapter demonstrates the convenience and power of this new method, and provides some fundamental explanations.

6.1 Ambient Temperature Analysis

As introduced in chapter 2, QMT theory[12-14] predicts that the rate of a redox reaction at an oxide film covered interface is inversely proportional to the exponential of the thickness of the film, \( L \)

\[
i = \hat{i}_0 e^{-\frac{\beta}{L}} \quad \text{(Eq. 6.1)}
\]
where $\hat{\beta}$ is the tunneling constant, which defines the blocking character of the film to charge carriers[15-17], and $\hat{i}_0$ is the “film-free” redox reaction current density. When combining QMT with the PDM[18-20] for film growth and dissolution, the QMT-PDM method for film thickness measurement is developed[21-24]

$$L = \frac{1}{\beta} \ln \left( \frac{\hat{i}_0}{\hat{i}} \right)$$  \hspace{1cm} \text{(Eq. 6.2)}

Since the tunneling constant can be obtained from the slope of $\ln(i)$ vs. $E$ (see Eq. (2.22)) by knowing that the anodizing constant $(1 - \alpha)/\hat{\beta}$ is about 2.5nm/V for a wide variety of metal oxides, and the film free current density can be read from the experiments directly, the film thickness can be determined unequivocally. To experimentally implement this method, current of the hydrogen oxidation reaction (HOR) on bare platinum and oxide covered platinum is employed as a probe to obtain the film free current and the tunneling current. The plateau current density (mass transfer control of the HOR), as shown in Figure 5-1(a) and (b) for the linear polarization of the HOR on platinum, is taken as the film free current density, $\hat{i}_0$.

The experiments are first carried out at ambient temperature using the disk electrode of a rotating ring disk electrode (RRDE). While the exponential decay of the tunneling current with applied voltage upon formation and further growth of the film is already demonstrated in the previous chapter with the cyclic voltammograms of the hydrogen electrode reaction (Figure 5-1), to extract reliable values for the electronic property parameters, it is necessary to carry out the experiments under potentiostatic conditions. Figure 6-1 shows potentiostatic polarization curves for the HOR on bare and oxide covered platinum at various rotation rates. The pressure of hydrogen is controlled at atmospheric pressure so that the dissolved hydrogen concentration is approximately $0.7 \times 10^{-3}$m as calculated from the Henry’s law. It is seen that at every rotation rate, the
hydrogen oxidation current density first remains a plateau (film free current density \( i_0 \)), and then after reaching a certain potential above which oxide film is formed, the logarithm of the current density begins to decrease linearly with increasing potential, until a point is reached where the tunneling hydrogen oxidation current is comparable to the platinum oxidation current (the steady state passive current). The recorded current densities at potentials above 0.3V_{SHE} can therefore be deemed as the passive current of platinum, and its value, as mentioned in chapter 5, is of the magnitude of uA/cm\(^2\) range in alkaline solutions. Note that the passive current density in alkaline solutions has been reported by Damjanovic et al.[10,25] to be about one thousand times higher than that in acid solutions, indicating that the dissolution rate of the platinum oxide barrier layer is faster in high pH solutions than in low pH solutions (check Eq. (2.16); however, the steady state film thickness is not necessary thinner than that in acid solutions). The passive current of platinum, though increases when the rotation rate increases, remains almost constant with potential at a constant rotation rate. This again agrees with the diagnostic criteria of the PDM for an n-type oxide film, provided that a change in oxidation state does not occur upon ejection of a cation from the barrier layer. Note, the passive current of a metal electrode increases with potential when the anodic film on that metal is p-type in electronic character.

Now, from the slope of the ln(\( i \)) versus \( E \) correlations, and utilizing the parameter values \( \alpha \) (polarizability of the barrier layer/solution interface) = 0.5 and \( \varepsilon \) (electric field strength within the barrier layer) = 2x10\(^6\) V/cm, obtained by optimizing the PDM on electrochemical impedance spectroscopy (EIS) data[26] and on the linear potential polarization (sweep) of platinum in chapter 4, the tunneling constant can be calculated. An average value of about 0.43x10\(^8\) cm\(^{-1}\) is yielded for the tunneling constant at the platinum/oxide film/solution interphase, which is close to the tunneling constant acquired by Moffat et al.[15] for a passive chromium film (\( \hat{\beta} \) ranged from 0.215x10\(^8\) cm\(^{-1}\) to 0.164x10\(^8\) cm\(^{-1}\)). Decrease of the tunneling constant with increase of the rotation rate is actually an artifact, arising from the passive current of platinum being superimposed on the measured tunneling current of the hydrogen oxidation, such that, as the rotation rate
increases, the passive current increases. From the following experimental results, it is found that the tunneling constant is essentially constant and only determined by the properties of the interphase.

Figure 6-1: Potentiostatic polarization of the HOR on bare and oxidized platinum at ambient temperature as a function of the rotation rate. The corresponding thickness of the oxide film calculated via the QMT-PDM method is also shown.

Once the tunneling constant is known, the oxide film thickness can then be calculated utilizing Eq. (6.2) and substituting the extracted tunneling constants, and the resulting thickness versus the corresponding voltage is also shown in Figure 6-1 with the axis located on the right. As can be seen from the figure, the film thickness increases linearly with applied potential and the slopes all approach 2.5nm/V. Moreover, this QMT-PDM method is sensitive to film thicknesses down to angstrom level, while a film of this thickness is practically invisible to an ellipsometer[3]. Surprisingly, thickness of the oxide film is found to be independent of the rotation rate by and large, although, from the PDM, it was initially expected that a higher rotation rate would result in a lower thickness, since the dissolution rate of the oxide film is expected to be higher at a higher flow velocity. However, we should also note that this is probably correct only if the
dissolution rate is wholly or partially mass transport controlled. Resolution of this issue must therefore await further calibration of the hydrodynamic and mass transfer characteristics of the flow channel used.

The accuracy of the film thickness determined by the QMT-PDM method is compared with thickness data measured using other *in situ* techniques, e.g. by Ellipsometry (with a monochromatic Hg arc source, and the polarizer being set at 45° to the place of incidence) in 0.1N H₂SO₄[3] and as extracted by optimization of the PDM on EIS data in 0.5M H₂SO₄[26]. As shown in Figure 6-2, for all three methods, the film thickness increases linearly with increasing potential and the slope yields the anodizing constant. In the case of the Ellipsometry method, because the measurement was taken shortly after growing the film at each potential for only 15 minutes, the film was very probably not fully developed (as discussed in chapter 4, the growth rate at equilibrium potential and the dissolution rate is on the order of 10⁻³ nm/s, and the growth rate decreases with film thickness) and a steady state was not attained. Therefore, the film is

Figure 6-2: Comparison of the platinum oxide film thickness obtained via three methods: Ellipsometry, EIS-PDM, and QMT-PDM.
expected to be thinner than that obtained by the other two methods, with the extent to which the steady state is approached depending upon the applied voltage. Accordingly, the ellipsometric study is expected to yield a substantially smaller anodizing constant. It is also seen that the film grown in the alkaline solution is thicker than that grown in acid solutions, as was also observed in our laboratory with the thickness of the film grown in acid and alkaline solutions determined by optimization of the PDM on EIS data. Note, because the anodic oxide film usually comprises an inner barrier layer and an outer hydroxide layer, so other thickness measurement techniques that require vacuum environment are generally not accurate in detecting the thickness of the hydroxide layer.

6.2 Temperature Dependence Analysis

Because the proton exchange membrane fuel cells (PEMFCs) are envisioned to operate at temperatures above 100°C, the electronic and structural properties of the oxide film on platinum at elevated temperatures are of great interest and importance, especially the thickness of the film which is postulated to inhibit the reaction rate of the ORR. Accordingly, an intensive investigation of the properties of the oxide layer on platinum over an extended temperature range (from ambient to 220°C) was carried out in our laboratory with a specially constructed controlled, hydrodynamic apparatus. Again, the HOR was employed as a probe, and the anodic polarization curves on bare and oxide covered platinum electrode (platinized nickel cylinder) at a series of temperatures in 0.1M KOH solution (equivalent to 0.1006m at any temperature) and 0.01M KOH (equivalent to 0.01001m at any temperature) + 0.03M K₂SO₄ solution (equivalent to 0.03016m at any temperature, K₂SO₄ is added to equalize the ionic strength of the solution) were recorded. The polarization curves in 0.1006m KOH solution over a wide range of potential are already shown in Figure 5-4, chapter 5, so here only the polarization curves in 0.01001m KOH + 0.03016m K₂SO₄ solution are shown in Figure 6-3. The current-voltage behavior is similar to that discussed in the previous chapter. Again, a slow sweep rate of 0.5mV/s was used in order to obtain a quasi-steady state.
In this chapter, we are only interested in the charge carrier tunneling across the passive platinum, so only the current density data within the potential range of 0.5-1.5V (potential is against the open circuit potential of the hydrogen electrode reaction) are analyzed.

Since the passive current of platinum increases appreciably when the temperature increases, it is necessary to subtract the passive current from the total measured tunneling current of the HOR, in order to better determine the tunneling constant and the oxide thickness. Logarithm of the corrected tunneling current as a function of the potential is shown in Figure 6-4. The curved lines are the experimental polarization data and the straight lines are regressions on the tunneling current data (symbolized) at each temperature based on Eq. (2.22). Again, it is seen that the logarithm of the tunneling current decreases linearly with the polarization potential, demonstrating the rationality of the QMT-PDM theory. The sudden drop of the current at high potentials is originated

Figure 6-3: Temperature dependence of the polarization curves for the hydrogen electrode reaction on platinum in 0.01001m KOH + 0.03016m K2SO4 solution at a H2 pressure of 2.86bar (equivalent to [H2] = 2x10^-3m).and at an impeller rotation rate of 400rpm (except the one at 220°C, the rotation rate is 200rpm).
from the correction of the passive current. The potential dependence of the logarithmic current is exactly the same and independent of the temperature, indicating the tunneling nature of the charge transfer at the oxide covered interface. The tunneling constant at each temperature can then be extracted from the slope of ln(i) vs. E and is also listed in the figure legend.

Figure 6-4: Anodic polarization of the HOR on platinum in 0.1006m KOH at a series of temperatures. Symbols and straight lines are tunneling currents of the HOR and the corresponding regressions.

Again, from Eq. (6.2), and knowing the tunneling constant, the film thickness at each corresponding potential can be calculated, and it is plotted in Figure 6-5 as a function of temperature. The symbols used correspond to those in Figure 6-4, and the straight lines are regressions on the calculated thickness data. Again, the linear relationship between the film thickness and applied potential is observed at all temperatures, and the slopes, the anodizing constant, all approach the generally observed value: 2.5nm/V (the average and standard deviation are 2.492 ± 0.055nm/V, respectively).
Figure 6-5: Temperature and potential dependencies of the platinum oxide barrier layer thickness in 0.1006m KOH solution, calculated from Eq. (6.2) and using the tunneling constant derived in Figure 6-4. The symbols are the same with Figure 6-4.

Figure 6-6: Temperature dependence of the tunneling constant for the platinum/oxide barrier layer/solution interphase.
Figure 6-6 is a plot of the temperature dependence of the derived tunneling constant. Within the estimated uncertainty of the data, the tunneling constant is independent of temperature over the temperature range studied, with the average value being $(0.57 \pm 0.035) \times 10^8 \text{cm}^{-1}$. As previously noted, the tunneling constant defines the blocking character of the oxide film and is mainly determined by the square root of the barrier height, $\Delta E$, at the film/solution interface, which is determined by the conduction band edge of the oxide film and the Fermi level of the redox species at the electrode surface/in the solution. Assuming that the band-gap of the heavily doped platinum oxide (the passive film is a heavily doped, n-type defect semiconductor[26]) does not change significantly with temperature, it is expected that the variation of the barrier height with temperature should be very small, so that the tunneling constant would remain invariant, this is further explained in the following section. However, when compared with the ambient temperature result, the tunneling constant is relatively higher, which implies a higher barrier height for charge carriers. One possible reason is that the tunneling current obtained from the RRDE at ambient temperature was not corrected for the passive current of platinum whereas that from the high temperature cell was corrected. Alternatively, the difference may arise from the different morphological forms of the platinum electrodes used; thus, the RRDE used a bulk platinum disk electrode with relatively smooth surface finish, while the controlled hydrodynamic cell used a platinized nickel electrode with the thickness of the electroplated platinum layer being approximately 5um and a granular surface. A final reason may be that the electrode surface in the controlled hydrodynamic cell was contaminated with nickel, resulting from the large wetted nickel chamber surface in contact with the solution.

As the tunneling constant is a measure of the blocking character of the barrier layer to charge carriers, it provides some useful information of the interface. From the relationship between the tunneling constant and the barrier height

$$\hat{\beta} = \frac{4\pi}{\hbar} \sqrt{2m_e \Delta E} \quad \text{(Eq. 6.3)}$$
the barrier height of the studied oxide film/solution interface can be calculated from the tunneling constant obtained in this work, assuming the static mass of an electron as the effective mass, \( m_e \), of an electron (\( m_e = 9.11 \times 10^{-31} \text{kg} \)). A barrier height of 0.31 ± 0.038 eV is then yielded, which is a very reasonable value. In the equation, parameter \( h \) is Planck’s constant (\( h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \)). Uncertainty of the barrier height is determined by the uncertainty of the effective mass and uncertainty of the anodizing constant for the specific electrode material.

In Figure 6-5, the linear relationship between the film thickness and applied potential is extrapolated to zero film thickness in order to obtain the potential at which the oxide film initially forms on platinum surface. This obtained potential can then be compared with the theoretically calculated equilibrium potential for platinum oxide formation. Figure 6-7 shows the temperature dependence of the extrapolated “film free” potential on platinum, \( E^\circ_{\text{PtO}} \), in comparison with the theoretically calculated equilibrium potential for Pt/PtO reaction obtained from the HSC® thermochemical database:

\[
\text{PtO} + H_2(g) = \text{Pt} + H_2O(l)
\]  
(Eq. 6.4)

From the figure, it appears that platinum is less stable at higher temperatures, and prefers to be covered with an oxide layer at less positive potentials than that predicted theoretically. This finding implies that an oxide will exist on the metal surface at potentials that are more negative than those calculated from the thermodynamic properties of bulk PtO. This is not a surprising finding, as adsorbed oxygen species, with greatly different thermodynamic properties than bulk PtO, may be present on the surface at potentials that would have resulted in the reduction of the bulk oxide. In this regard, it is important to note that even an adsorbed layer on the surface will significantly inhibit charge transfer, as predicted by Eq. (6.1).

It is evident that the QMT-PDM method employing the HOR as a probe can (and does) very conveniently detect an oxide layer on platinum as thin as a monolayer (<
0.1nm) is formed. In chapter 4, the barrier anodic oxide film on platinum is postulated to be a columnar, nano crystalline structure comprising tetragonal unit cells. If the oxide film is oriented with the c-axis perpendicular to the metal surface (Figure 4-8), then the dimension of the thickness that this technique can detect corresponds to the first monolayer of adsorbed oxygen, depicted by “monolayer 1” in Figure 4-8. Whereas with many other techniques, only when the properties of the oxide layer are distinctly different from those of the substrate, or when the surface roughness is very small, can the film thickness be accurately measured. However, currently, the upper limit of the thickness that can be measured with the QMT-PDM method is 1-2nm (corresponding to 3 to 6 unit cells), since the passive current of platinum imposes a lower limit on the HOR tunneling current that can be differentiated from the measured total current. This limitation is promised to be less severe when the electrolyte is an acid solution, as the passive current density for platinum in acid solution is almost three orders of magnitude lower than that in alkaline solution, allowing the HOR tunneling current to be differentiated down to the nano-ampere level.

Figure 6-7: Temperature dependence of the measured “film free” potential on platinum and the theoretically calculated equilibrium potential for platinum oxidation.
The developed QMT-PDM method is also a very sensitive technique. With a tunneling constant of $0.5 \times 10^8 \text{cm}^{-1}$, the current drops by almost three orders of magnitude upon the formation of a 1 nm thick oxide film. In fact, it is the existence of this thin oxide film on platinum surface that is responsible for the low exchange current density and the “sluggish” kinetics of the ORR on platinum (shown in Figure 5-11), not even to mention other metals, which are more readily to be covered by thicker oxide films at potentials for the ORR. However, at low overpotentials (above $0.95 V_{\text{RHE}}$), the observed current density is especially low (Figure 5-9), the reduction current is even positive, because not only are the kinetics of the ORR inhibited by the passive film, but the negative oxygen reduction current is partially compensated for by the positive passive current (completely so at $E_{\text{corr}}$, Figure 5-11).

6.3 H$_2$ Concentration and Solution pH Dependencies

In chapter 2, it is introduced that the tunneling probability is mainly determined by the barrier layer (oxide film) thickness and the square root of the barrier height of the studied interface across which the charge carriers have to tunnel through for the reaction to occur (Eq. (2.12)). Therefore, the concentration of the redox species in the solution and/or the pH of the solution should not alter the tunneling constant, but should only affect the overall current density, unless the electronic properties of the oxide film formed are altered appreciably or if the thickness of the barrier layer is a significant function of the solution pH. The following two figures address these possibilities.

The impact of three hydrogen partial pressures in the solution tank maintained at ambient temperature is examined at 130°C in Figure 6-8: 1.90 bar and 2.61 bar in 0.1006 m KOH (equivalent to $[\text{H}_2] = 1.33 \times 10^{-3} \text{m}$ and $1.824 \times 10^{-3} \text{m}$, respectively), and 2.86 bar ($[\text{H}_2] = 2.002 \times 10^{-3} \text{m}$) in 0.01001 m KOH + 0.03016 m K$_2$SO$_4$. The limiting current of the HOR on bare platinum is only determined by the concentration of the dissolved hydrogen not by pH of the solution. Similar dependencies of the tunneling current on hydrogen concentration are observed, and the extracted tunneling constants are
very close to one another, as shown in the figure legend. Film thicknesses all vary linearly with potential at any pH or hydrogen concentration, with the same slope (anodizing constant). The extrapolated film free potentials (the platinum oxidation potential) for the two hydrogen concentrations in the same 0.1006m KOH solution are almost coincident, and that in 0.01001m KOH solution differs with the previous one by about 80mV in the positive direction, in good agreement with the theoretical value at 130°C of \(\frac{2.303RT}{F}=80\text{mV}\) (for a unit change in solution pH).

Figure 6-8: H₂ concentration and solution pH dependencies of the tunneling hydrogen oxidation current at 130°C. The impeller is rotated at 400rpm. Thickness data are shown with the axis on the right.

Figure 6-9 gives another example of the pH-invariance of the tunneling constant on oxidized platinum/solution interface at 160°C. In this case, the hydrogen concentrations are 1.824x10⁻³m in the 0.1006m KOH solution and 2.002 x 10⁻³m in the 0.01001m KOH + 0.03016m K₂SO₄ solution, respectively, with the result that the limiting current of the latter is relatively higher than that of the former. The values
shown in the figure legend for the tunneling constant demonstrate that the tunneling constant of the studied interface is essentially pH-independent. Because of the dissolution issue for the nickel chamber and flow loops in low pH solutions at high temperatures, only two pH solutions were examined.

Figure 6-9: pH dependence of the tunneling hydrogen oxidation current on platinum at 160°C. The impeller is rotated at 400rpm.

### 6.4 Theoretical Aspects

An atomic-scale view of the growth and dissolution of an oxide film on metal electrode has been well developed by the PDM[18-20], which describes the oxide barrier layer as being a highly (point) defective oxide phase, whose thickness is determined by a competition between the rate of growth from the metal at the metal/barrier layer interface and the rate of dissolution at the barrier layer/solution interface. Importantly, the PDM yields a growth law in terms of interfacial defect generation and annihilation reactions that is readily tested by experiments. The veracity of this model has been extensively
investigated by potential polarization then film thickness measurements, transient techniques[27], Mott-Schottky analyses[28], and EIS studies[26,29,30]. The parameters extracted by optimization of the PDM on EIS data of platinum[26] predict the steady state passive current density and barrier layer thickness versus voltage data that are in good agreement with the experimentally determined correlations. It is, nevertheless, necessary to emphasize here one poorly understood aspect of the PDM: the postulate that, for thin barrier layer films at steady state, the electric field strength is independent of position within the film and is independent of the applied voltage (and hence of the barrier layer thickness).

As introduced in chapter 2, the PDM describes the potential drop at the film/solution interface, $\phi_{f/s}$, as a linear function of the applied potential, $V$, and the solution pH

$$\phi_{f/s} = aV + \beta pH + \phi^0_{f/s} \quad (\text{Eq. 6.5})$$

All the parameters are consistent with those in chapter 2 (check Tables 2-2 and 2-3) and the explanations are skipped here. Therefore, if the electric field strength, $\varepsilon$, within the oxide film is a constant, the potential drop at the metal/film interface, $\phi_{m/f}$, can then be written as a function of the applied voltage

$$\phi_{m/f} = (1 - \alpha)V - \beta pH - \phi^0_{f/s} - \varepsilon L \quad (\text{Eq. 6.6})$$

Therefore, because of the existence of an oxide layer, the potential drops at the two interfaces are both only a fraction of the applied voltage, and that because the electric field strength is so high, a significant portion of voltage drop happens at the film. The postulate that the electric field strength under steady-state conditions is independent of applied voltage receives strong support from the almost ubiquitous finding in anodic oxide film formation studies that the barrier layer thickness varies linearly with applied
voltage. The physics behind this postulate is that the electric field strength is sufficiently high (greater than $10^6$V/cm, which is close to the dielectric strength) that Esaki (band to band) tunneling\cite{31-33} or tunneling between the bands and inter-bandgap states, or even between inter-bandgap states themselves, occurs and effectively buffers the field against any process that would tend to increase the potential gradient.

The postulated potential distribution across the metal/barrier layer/solution interphase is shown in Figure 6-10, with the applied potential being referred to the SHE scale by convention for the electrode potentials. Employing the parameter values extracted from previous EIS studies\cite{26} and the linear potential polarization result in chapter 4 ($\alpha = 0.5$, $\beta = -0.01$, $\phi_f^0 = -0.01$V, and $\epsilon = 2 \times 10^6$ V/cm), it is possible to construct potential distribution diagrams as functions of temperature and applied voltage. These are illustrated in Figure 6-10 and Figure 6-12. Furthermore, previous Mott-Schottky analysis, which gives the dopant concentration from the slope of the inverse square of the measured capacitance vs. applied voltage, indicates that the donor density is over $10^{20}$cm$^{-3}$\cite{26}. Therefore, because of such a high concentration of donors, and that the donors (oxygen vacancies for n-type films here) are generated at the metal/barrier layer interface by reaction (3) of the 7-reaction PDM scheme: $Pt \rightarrow Pt_{Pt} + V_O^{**} + 2e^-$, and are annihilated at the barrier layer/solution interface by reaction (6): $V_O^{**} + H_2O \rightarrow O_O + 2H^+$, the region of the barrier layer close to the metal/barrier layer interface is expected to be degenerate and hence the Fermi level is expected to exist above the conduction band edge. This is embodied in Figure 6-10 and Figure 6-12. Note that because the assumptions of the classical Mott-Schottky theory fail to conform in this extreme condition, e.g. the Debye length$^2$ of the anodic oxide film on platinum is of the same order as the thickness of the film and the donors are not uniformly distributed, so

$$L_{Deb} \geq \sqrt{\frac{\epsilon \epsilon_0 k T q^2 N_D}{\epsilon}},$$

where $\epsilon_0$ is the permittivity of the vacuum, $\epsilon$ is the dielectric constant of the oxide, $k$ is the Boltzmann’s constant, $q$ is the electronic charge, $T$ is the temperature, and $N_D$ is the donor concentration. If we take the dielectric constant to be 42 (from the optimization result), and the donor concentration to be $2 \times 10^{20}$ cm$^{-3}$, then the ambient temperature Debye length is 0.54nm, which is of the same dimension as the thickness of the oxide film.

\footnote{The Debye length, $L_{Deb}$, of an n-type semiconductor can be estimated as\cite{26,38}: $L_{Deb} = \sqrt{\epsilon \epsilon_0 k T q^2 N_D}$.}
the defect concentration calculated via the Mott-Schottky analysis is regarded as being only semiquantitative and presumably corresponds to the concentration close to the metal/film interface[26].

Figure 6-10: Schematic of potential distribution and electronic structure at the metal/barrier layer/solution interphase, in the case that the barrier layer is heavily doped, so that degeneracy occurs in the barrier layer at the region close to the metal/barrier layer interface.

The concentration profile of the oxygen vacancies (or cation vacancies) through the oxide film on platinum can be simulated by solving the steady state Nernst-Plank equation and Poisson’s equation, and the result is shown in Figure 6-11[24]. The concentration of the point defect is exponentially graded, and varies quickly only within the first few angstroms near the film/solution interface.

In this QMT-PDM model, the following features prevail: (1) Because the thickness of the barrier layer is of the same order as the Debye length, the film is completely depleted under such a high electric field strength, and the band bending that is invoked in the Gerischer-type models[14,17] for passive films is inconsistent with the
measured donor density and hence must be discarded; (2) The “flat band potential” corresponds to the potential at which the barrier layer thickness becomes zero; (3) Direct band-to-band (Esaki) tunneling probably does not occur unless the bandgap is very small (bandgap $< 0.2$eV versus the $3.1$eV value for bulk PtO$[34]$), but, as noted above, band-to-inter-bandgap state, and inter-bandgap state to inter-bandgap state tunneling may occur; and (4) The electronic structure can only be described accurately if the impact of the applied voltage on the barrier layer thickness and on the potential drops at the metal/barrier layer and at the barrier layer/solution interfaces are recognized. We should note that we have ignored bandgap narrowing, due to the high donor density, in this analysis.

Quantum electrochemistry concerns with both the properties of metal/solution interfaces and kinetics of charge transfer reactions at interfaces by means of QMT. Gurney$[13]$ was the founder of quantum electrochemistry, and the rate equation provided by him became the starting point for all quantum mechanics and molecular theories for the kinetics of charge carriers transfer at interfaces$[35]$. The development of quantum electrode kinetics for charge carriers tunneling across an interface has been narrated in

Figure 6-11: Point defect concentration profiles through the platinum oxide film based on the PDM: (a) oxygen vacancy; (b) cation vacancy. $x = 0$ is the film/solution interface.
chapter 2, below is the theoretical explanation of the above experimental results based on QMT theory at the interfaces.

QMT deals with transfer of charge carriers (in most cases, electrons) between two equal energy states through a potential barrier which they do not have the energy to overcome in classical physics. In the present study, regardless of the mechanism of the hydrogen electrode reaction, it is assumed that the rate determining step for the HOR on oxide covered platinum electrode is the radiationless (“resonant”) quantum mechanical transfer of an electron from a surface state (Had), or from the reduced species (H2) in the solution, to an empty state in the metal (as the rate of the HOR is greatly lowered by the existence of the oxide film, it is more likely that the charge transfer step Had + OH− → H2O + e− is the rate determining step, so the barrier is the oxide film). It is also assumed that the energy levels of the redox species in the solution, i.e., the vibrational and rotational states of the ion-solvent bonds above ground states, are distributed according to the Boltzmann’s law[35-37], as to recognize the fact that in solution phase, quantized energy levels are subject to collisions with surrounding solvent molecules, and these interactions blur the difference between distinct energy levels of vibrational-rotational states of the ion-solvent bonds. The Boltzmann’s law states that the probability of a state with energy U above the ground level of the solvent fluctuation is inversely proportional to the exponential of its energy level[37]

\[ N(U) = N(U_0)\exp\left(-\frac{U - U_0}{kT}\right) \]  

(Eq. 6.7)

where \( U_0 \) is the ground state energy level, \( U \) is any other higher energy level, and \( k \) is the Boltzmann’s constant. But when the electron energy associated with the ion-solvent bond is considered, the Boltzmann’s law for the distribution of the electrons becomes

\[ N(E) = N(E_0)\exp\left(-\frac{\delta E - E_0}{kT}\right) \]  

(Eq. 6.8)
where $E_\theta$ is the electron energy when ion-solvent bond (e.g. H$^+$-H$_2$O bond) is in the ground vibrational-rotational level, $E$ is the electron energy when the bond is in any other higher vibrational-rotational state, and $\delta$ is a measure of the efficiency of electrical energy used to increase the available energy states of the bond, or in other words, the efficiency of the electrical energy to accelerate the rate of reactions. The electron energy level $E$ is contributed from solvation energy and ionization energy of the proton, and repulsion energy and attraction energy between the H atom and water molecules[13,37]. Details of these energies will not be discussed here since no quantitative or qualitative information can be extracted in this study.

Based on the above discussion, a schematic diagram of the electronic structure at the metal electrode/n-type oxide film/solution interphase can be constructed and is shown in Figure 6-12, in terms of the vacuum scale for energy (so the potential for the SHE is 4.5 ± 0.2V). Together shown is the potential distribution (on the SHE scale) across the interphase according to the PDM and utilizing the experimental data in Figure 6-1 (applied potential and the corresponding film thickness at ambient temperature). The potential drop at each interface is calculated via Eq. (6.5) and Eq. (6.6) with the parameter values extracted from EIS analysis[26] and the linear potential polarization result from chapter 4. The electrons in the metal are distributed according to the Fermi-Dirac distribution

$$F(E) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1} \quad \text{(Eq. 6.9)}$$

where $E_F$ is the Fermi energy of the electron in metal. While the energy levels in the solution side are distributed according to the Boltzmann’s Law. Note, unlike the electrons at the Fermi level in a metal which are mobile and free to go in the metal, electrons in solution are in the bound levels of ion-solvent bonds, and they do not obey the same distribution law as the electrons in the metal which they are in equilibrium with[36].
As seen in the figure, the barrier height, $\Delta E$, at the film/solution interface, is determined by the conduction band edge of the oxide film and the Fermi level of the redox species adsorbed on the electrode surface or in the solution at the inner Helmholtz plane (IHP) or, perhaps, at the outer Helmholtz plane (OHP). Only the electrons at the topmost energy levels are involved in the reaction since they experience the lowest energy barriers to proceed toward the reaction direction, just as chemical reactions are associated with rarely occurring, highly energetic states[36]. From the previous results with the tunneling constant, the barrier height at the film/solution interface is calculated to be 0.31eV.

Figure 6-12 (a) and (b) are energy structure diagrams for the interphase at the same ambient temperature, but with different applied voltages, and Figure 6-12 (c) is...
constructed for a higher temperature. To discuss the tunneling current, the following equation is inevitably brought up

\[ i \propto \int n(E,V)N(E,x)P_T(E,x)dEdx \]  
(Eq. 6.10)

For the specific hydrogen oxidation reaction studied here, then \( n(E,V) \) is the density of empty electron states having energy \( E \) in platinum electrode at the applied voltage \( V \), \( N(E,x) \) is the density of hydrogen species having energy \( E \) at a distance \( x \) from the metal surface in the solution phase or density of \( H_{ad} \) adsorbed at the oxide film surface (which obeys a specific adsorption isotherm under a certain condition), and \( P_T(E,x) \) is the probability of tunneling of an electron from the hydrogen species in the solution/at the surface to an acceptor state in the platinum at the same energy. When the applied voltage increases, the number of the donor species in the solution phase \( N(E,x) \), which contain electrons that are able to tunnel through the barrier, increases slightly, this would increase the tunneling current. However, compared with the significant impact of the film thickness on the tunneling probability, the increase of \( N(E,x) \cdot n(E,V) \) is almost negligible compared with the inhibition factor of the film thickness as the increase of the potential also increases the film thickness, and tunneling probability is inversely proportional to the exponential of the film thickness as expressed in Eq. (2.12). An exact estimation of the product is difficult, as the HOR is under mass transfer control before the formation of the oxide, and then under the tunneling rate control with the formation of the oxide. Furthermore, even though the applied voltage increases, there is the efficiency factor, \( \delta \), associated with the applied potential being effectively used to increase the energy level of the species in the solution, and the PDM also indicates that there is a potential drop within the barrier layer which significantly decreases the potential drop at the film/solution interface, as illustrated in the figure. Therefore, because of the existence and further growth of the film, the energy states in the solution are not significantly altered by the applied potential, so the tunneling current decreases with increasing film thickness even though the overpotential for the reaction increases.
In the presently studied tunneling current region, the accessible potential range extends only over 0.4V, and beyond this range, the tunneling current is not differentiable with the passive current of platinum. The fractions of any additional applied voltage $\Delta V$ that appear across the metal/barrier layer interface and across the barrier layer/solution interface under steady state conditions are $\Delta \phi_{m/f} / \Delta V = (1 - \alpha) - \hat{\epsilon}(\Delta L / \Delta V)$ and $\Delta \phi_{f,s} / \Delta V = \alpha$, respectively, while that which appears across the film is $\Delta \phi_{f} / \Delta V = \hat{\epsilon}(\Delta L / \Delta V)$. Selecting the polarizability of the barrier layer/solution interface $\alpha = 0.5$ and electric field strength within the barrier layer $\hat{\epsilon} = 2.0 \times 10^6$ V/cm, we find that the fractions of the additional imposed voltage that appear across the metal/film (barrier layer) interface, the film/solution interface, and across the film are 0, 0.5, and 0.5, respectively. Thus, for the particular parameter values chosen for this calculation, the metal/film interface is quite insensitive to the imposed voltage and it appears that the principal contribution of the voltage to the reaction system is the growth of the barrier layer thickness, which results in the observed linear decrease of $\ln(i)$ versus $L(V)$.

When the temperature increases, the distribution of the energy states in the solution spreads out (a direct result of Boltzmann’s law), as the higher rotational and vibrational modes of the bonds become occupied. Also, more electrons occupy the energy states above the Fermi level in the metal and leave more available states to accept the electrons from the solution. Thus, not only does the limiting current of the HOR increase, but the tunneling current also increases at the same barrier layer thickness. However, the barrier height, and therefore the tunneling constant, is not determined by the distribution functions, but by the Fermi level of the redox species in the solution and the conduction band edge at the film/solution interface. Assuming that the bandgap of the heavily-doped platinum oxide film does not change with temperature (bandgaps of 2.4eV[39] and 3.1eV[34] have been reported from photo-electrochemical studies), then the change of the barrier height with temperature within the temperature range studied in this work is relatively small (so as to the square root of it), and the tunneling mechanism
remains the same. It is for this reason that the tunneling constant is almost temperature independent.

The fact that the rate of the ORR in the small overpotential range is inhibited by a thin oxide layer on metal electrode, and that the barrier height and barrier layer thickness that the electrons have to tunneling through determine the reaction rate, may serve as some guidance for the design of better electrocatalyst for the ORR. If we could find a platinum based alloy having an appreciably higher oxidation potential, or an anodizing constant much lower than 2.5nm/V, then a film with much thinner thickness would cover the electrode, so that the probability for the tunneling is greatly enhanced. It may also be possible to design an electrode material which forms an oxide film with a small bandgap, so that direct band to band tunneling and inter-bandgap states will also contribute to the tunneling probability, as the oxide layer is heavily doped with defects. Alternatively, it is suggested that periodic, cathodic charging be exploited to the cathode to peel off the oxide film on the electrode so as to expose the fresh bare metal surface during the fuel cell operation.

6.5 Comparison with Other Works

A significant volume of work has been reported on the study of the growth mechanism of the electrochemically formed oxide film on platinum and its thickness measurement. Conway and Jerkiewicz et al.[40-43] have extensively studied the growth of platinum oxide and describes the film growth by the place exchange model. However, that model could not account for the substantial dissolution of platinum in fuel cells. Reddy et al.[3] found that oxide films grown at potentials more negative than 0.95V_{RHE} in 0.1N H$_2$SO$_4$ are invisible to an ellipsometer, and that when the voltage is greater than 0.95V_{RHE}, the film thickness increases linearly with potential. Other workers[25,44-46], however, found appreciable amounts of oxide produced in the potential region from 0.7V_{RHE} to 0.95V_{RHE}, which is consistent with our findings on the HOR on platinum. Furthermore, the kinetics of the oxidation of hydrogen[47], ethylene[48], and other
hydrocarbons[49] on platinum also decreases greatly at about 0.9V_{RHE}. Schuldiner[4]
attributed the decrease in the reaction rate to anion (sulfate) adsorption on the metal
surface at potentials below 1.2V_{SHE}, and above 1.2V_{SHE} those adsorbed anions are
replaced by oxygen species. However, in the present work, experiments in both pure
alkaline solution (0.1M KOH) and a mixture of OH\(^-\) with SO\(_4^{2-}\) (0.01M KOH + 0.03M
K\(_2\)SO\(_4\)) show exactly the same linear potential dependence of the logarithmic current
density, and the extracted tunneling constants are also the same within experimental
error. Either the inhibition of the reaction rate is not due to the anion adsorption (but,
instead, is due to the growth of the oxide layer), or otherwise, the hydroxide ion and the
sulfate ion are adsorbed in the exactly same potential range and have the same effect of
blocking the hydrogen oxidation on platinum. In this work, the decrease in the reaction
current is attributed to the formation and further growth of an oxide layer, and the linear
decrease of the logarithm of current with increasing potential is quantitatively accounted
for by QMT of the charge carriers across the barrier layer with the thickness of the barrier
layer being accurately described by the PDM.

It is also worth noting that the results obtained in the present work are more
consistent with the decrease of the current in the tunneling region being caused by the
thickening of the film than by the progressive covering of the surface by an oxide (i.e. the
nucleation and “patch growth” model[50-52]). In the latter model, the bare platinum
area, upon which the HOR is postulated to occur, progressively decreases with time
under potentiostatic conditions due to the nucleation and spread of the oxide islands. Had
the decrease in the current been due to the progressive covering of the electrode surface
by oxide patches, it might be expected that the surface would become fully covered by
oxide under potentiostatic conditions at potentials above the formation potential and
hence that the current would eventually decay to that of the passive state. This response
should be observed upon stepping the potential from a film-free value to any potential in
the oxide formation region. In other words, there should not have the existence of a
steady state other than the passive state. This is contrary to experimental observation.
Had the decrease in the current been due to the progressive adsorbing of oxygen
atoms/molecules at surface with increasing potential, i.e. different lattice sites have
different adsorption energies, then there would be sudden drops and flat regions of the current instead of continuous decrease. Hence, the patch growth model must be discarded.

6.6 Conclusions

The present work was carried out to explore the impact of oxide films formed electrochemically on platinum on the kinetics of redox reactions at the interface. The principal findings of the study are summarized as follows:

- Formation of an oxide film on platinum considerably affects the kinetics of charge transfer reactions, and the linear decrease of the logarithm of current density with increasing potential is postulated to reflect direct quantum mechanical tunneling (QMT) of charge carriers across the thin oxide film.

- By combining QMT theory with the point defect model (PDM) for the growth and dissolution of oxide films on metal electrodes (which describes the potential dependence of the film thickness), a new method has been developed for probing the thickness of thin oxide films on metals, such as platinum, *in situ*, by employing a fast reaction (hydrogen oxidation) as an experimental probe.

- Experimental results show that the tunneling constant, which describes the blocking factor of the oxide film, is independent of temperature, pH of the solution, and the concentration of the redox species within the ranges of these independent variables studied in this work.

- The average tunneling constant determined by a RRDE at ambient temperature is \((0.43 \pm 0.034) \times 10^9\text{cm}^{-1}\) and that determined by the controlled hydrodynamic cell at a series of temperatures is slightly higher at \((0.57 \pm 0.035) \times 10^9\text{cm}^{-1}\). The difference arises from the different sources of platinum electrode and/or contamination of the platinum surface by nickel (from the material for construction of the hydrodynamic cell and parts of the flow loop) within the high temperature, high pressure controlled hydrodynamic cell. A barrier height of
0.31eV is calculated from the tunneling constant at the barrier layer/solution interface.

- Theoretical interpretation of the tunneling result is implemented by developing a model for the electronic structure of the metal/barrier layer/solution interphase utilizing the Boltzmann’s law for the distribution of the energy states of the redox species in the solution phase and by noting that the barrier layer is a highly doped (and probably degenerate) defect (oxygen vacancy) semiconductor, having a Debye length that is the same order as the thickness of the film.

- The combined QMT-PDM method developed in this work for film thickness measurement is demonstrated to be a very convenient and sensitive, in situ technique. However, since the superimposed passive current and the charging current (when potentiodynamic polarization is used) delimit the lower value of the tunneling current that can be measured, an upper limit exists for the film thickness that can be determined by this technique (about 1 - 2nm). This limit has the potential to be extended in acid solutions.

References


Chapter 7
Conclusions and Suggestions for Future Work

7.1 Conclusions

This dissertation work is carried out to explore the kinetics and mechanism of both the hydrogen electrode reaction and the oxygen reduction reaction on platinum over a wide temperature range from ambient temperature up to 220°C. Because of the significant impact of the anodic oxide film on the kinetics of redox reactions, the structural and electronic properties of the platinum oxide film are also studied. The principle findings of this work are summarized as follows:

1. The surface morphology of the platinized nickel electrode examined by SEM shows granular features. Energy dispersive spectroscopy (EDS) analysis indicates that the electroplated layer is pure platinum with no traces of nickel within the detection limit. The thickness of the electroplated layer is about 5um, so that its cyclic voltammograms under nitrogen environment display the same four regions typical of a bulk platinum electrode.

2. The dynamic growth law for the anodic oxide film electrochemically grown on platinum has been derived for the first time, based on the framework of the point defect model (PDM), and the passive current for the platinum as well as the charging current during the potential sweep process have been developed, which are fitted to the experimental linear polarization data to extract the kinetic parameter values of the platinum oxide growth. The growth rate at the equilibrium potential and the dissolution rate are on the order of $10^{-3}$nm/s, which are in good agreement with experimental findings.

3. The anodic oxide film is concluded to have a bi-layer structure comprising a highly defective oxide barrier layer, and an outer porous precipitated hydroxide
layer. The inner barrier layer is postulated to have a columnar, nano crystalline structure comprising tetragonal unit cells.

4. Kinetics and mechanism of the hydrogen electrode reaction at a series of temperature are studied using a specially designed, controlled hydrodynamic cell for the first time. Kinetic parameters of the reaction are extracted by micropolarization analysis and by optimizing the Butler-Volmer equation on the polarization curves. Ambient temperature behavior on a bulk platinum disk electrode of a rotating ring disk electrode (RRDE) agrees well with those reported in literature. The ambient temperature exchange current density of the reaction on the platinized nickel electrode is higher than the values reported in literature on other forms of platinum electrodes, probably due to the platinized nickel electrode has a granular surface morphology which increases the real surface area or adsorption/desorption sites for the reaction. Activation energy of 17.3kJ/mol, obtained from the Arrhenius plot, is also comparable with that of a bulk platinum electrode, and is lower than sputtered platinum and single crystal platinum electrodes in alkaline solutions.

5. The apparent Tafel slope of the hydrogen evolution reaction is found to be temperature independent, and the transfer coefficients for both the hydrogen oxidation and evolution reactions are temperature dependent. The most probable cause is that two parallel reactions with different activation energies and transfer coefficients are occurring at the electrode surface in a way that the overall apparent Tafel slope is almost temperature invariant. This needs to be resolved by electrochemical impedance spectroscopy analysis. The mechanism of the hydrogen electrode reaction is very likely temperature dependent according to quantum mechanical calculations.

6. The oxygen reduction reaction is also studied on platinum at ambient temperature. The cathodic current above a certain potential ($E_{corr}$) is found to be positive, which turns out to be the passive current of platinum. Therefore, the sluggish nature of this reaction is postulated to be due to the existence of a thin oxide layer at the surface. This thin oxide layer inhibits the oxygen reduction reaction in a
way that the electrons resides in the metal have to quantum mechanically tunnel (QMT) through this layer in order to reach the oxygen species in the solution/adsorbed on the surface. Therefore, the thickness of this layer and its electronic properties are very important to the understanding of the kinetics and mechanism of this reaction.

7. Formation of an oxide film on platinum considerably affects the kinetics of charge transfer reactions, and the linear decrease of the logarithm of current density with increasing potential is postulated to reflect direct QMT of charge carriers across the thin oxide film. Combining QMT theory with the PDM for the growth and dissolution of oxide films on metal electrodes at any applied potential, a new method has been developed for probing the thickness of extremely thin oxide films on metals, such as platinum, in situ, employing a fast reaction (hydrogen oxidation) as an experimental probe.

8. Experimental results show that the tunneling constant, which describes the blocking factor of the oxide film to the charge transfer probability, is independent of temperature, pH of the solution, and the concentration of the redox species within the ranges of these independent variables studied in this work. The average tunneling constant determined by a RRDE with bulk platinum disk at ambient temperature is \((0.43 \pm 0.034) \times 10^8 \text{cm}^{-1}\) and that determined by the controlled hydrodynamic cell with a platinized nickel at a series of temperature is slightly higher at \((0.57 \pm 0.035) \times 10^8 \text{cm}^{-1}\). The difference arises from the different sources of platinum electrode and/or contamination of the platinum surface by nickel (from the material for construction of the hydrodynamic cell and parts of the flow loop) within the high temperature, high pressure controlled hydrodynamic cell. A barrier height of \(0.31 \pm 0.038 \text{eV}\) is calculated from the tunneling constant for the tunneling barrier height at the barrier layer/solution interface.

9. Appreciable amount of oxide film is formed at potentials much negative to the equilibrium potential of platinum oxidation. The film thickness increases linearly
with potential, with the slope, anodizing constant, being approximately $2.492 \pm 0.055$nm/V.

10. Theoretical interpretation of the tunneling result is implemented by developing a model for the electronic structure of the metal/barrier layer/solution interphase utilizing the Boltzmann’s law for the distribution of the vibrational-rotational energy states of the ion-solvent bonds of the redox species in solution phase and the Fermi-Dirac distribution for the electrons in metal, and by noting that the barrier layer is a highly doped (and probably degenerate) defect (oxygen vacancy) semiconductor, having a Debye length that is the same order as the thickness of the film. For the hydrogen oxidation reaction, the tunneling current is determined by the available numbers of donor states in the solution, acceptor states in the metal, and the tunneling probability through the barrier layer which is a function of the barrier layer thickness and barrier height at the film/solution interface.

11. The combined QMT-PDM method developed in this work for film thickness measurement is demonstrated to be a very convenient and sensitive, in situ technique. However, since the superimposed passive current and the charging current (when potentiodynamic polarization is used) delimit the lower value of the tunneling current that can be measured, an upper limit exists for the film thickness that can be determined by this technique (about 1 - 2nm). This limit has the potential to be extended in acid solutions.

7.2 Suggestions for Future Work

Temperature evolution of the mechanism of the hydrogen electrode reaction has not been resolved yet, though quantum mechanical calculations indicate that mobility of the adsorbed H atoms are temperature dependent. Electrochemical impedance spectroscopy (EIS) is the most promising technique to help elucidate this issue. EIS experiments have already been carried out at several temperatures at potentials near the open circuit potential of the hydrogen electrode reaction, due to the time limitation and
complexity of impedance derivation, analysis of the data will be accomplished in the future.

EIS analysis may also help resolve the paradox that the Tafel slope of the hydrogen evolution reaction is temperature independent. EIS analysis can yield both mechanistic and kinetic information of the reaction. After knowing the activation energy and transfer coefficient of each step from the EIS results, the apparent Tafel slope of the overall reaction can be calculated.

Currently, the upper limit of the film thickness that can be measured with the developed QMT-PDM method is 1-2nm due to the passive current of platinum imposes a lower limit of the tunneling hydrogen oxidation current. This technique will be further explored in acid solutions to extend the limit of the film thickness that can be measured, since the passive current in acid solution is about 2-3 orders of magnitude smaller, so that the tunneling current can be easily differentiated from the total measured current down to the nA/cm² range at ambient temperature, and the upper limit of the film thickness can be extended to over 3nm.

In this work, it is proposed that the anodic oxide film on platinum is formed layer by layer. Upon the growth of the oxide film on a single crystal platinum electrode, the quantization phenomenon is predicted for the tunneling current, i.e., the tunneling current drops in steps when more and more oxide film layers are formed. This will be examined in the future work.

Figure 6-5 indicates that at a certain potential, the anodic film thickness increases when the temperature increases. However, it is known that the kinetics of the oxygen reduction reaction (ORR) increases significantly at high temperatures. Clearly, the film thickness is not the only determining factor for the kinetics of the ORR. Instead, previous work by Roh[1] in our lab has demonstrated that the rate of the ORR is related with the concentration of the oxygen vacancies in the anodic oxide film of titanium: the rate increases when the oxygen vacancy concentration increases. This finding will be investigated on platinum as well.

The result obtained in this dissertation work also provides some guidance to the design of electrocatalysts for the ORR. Since the reaction rate at low overpotentials is
inhibited by a thin oxide layer, and the thickness of this oxide layer increases with potential, it is desirable to design a platinum based alloy with higher equilibrium potential for oxide film formation or lower anodizing constant, so that a thinner film forms at a certain potential. The reaction rate of the ORR would then increase exponentially. Preliminary findings indicate that the Pt/Cr alloy has a relatively better performance for the ORR than pure platinum, possibly due to the fast dissolution rate of the chromium oxide film so that the overall thickness of the oxide film on the alloy electrode is thinner. This needs to be further investigated.

Reference

Appendix A

Potential Dynamic Current Behavior on Passive Platinum

This appendix outlines the mathematical derivation of the linear polarization curve for platinum oxidation under various potential sweep rates. To simulate the current vs. voltage curve during the potential sweep, two contributions of current need to be considered first:

\[ i_{\text{total}} = i_{\text{passive}} + i_{\text{charging}} \]  

(Eq. 1.1)

where \( i_{\text{total}} \) is the measured current, \( i_{\text{passive}} \) is the passive current of platinum (oxidation current), and \( i_{\text{charging}} \) is the current due to the charging of the double layer and the oxide film capacitor. Both of them are dependent on the film thickness, therefore, it is necessary to derive the film growth law under the transient conditions based on the point defect model (PDM)[1-3].

![Diagram showing interfacial defect generation-annihilation reactions that are postulated to occur in the growth of anodic barrier oxide films according to the PDM, when the oxide film is n-type in electronic character.](image)

Figure A1-1: Interfacial defect generation-annihilation reactions that are postulated to occur in the growth of anodic barrier oxide films according to the PDM, when the oxide film is n-type in electronic character.
As introduced in chapter 2 of this dissertation, the PDM describes the growth of anodic oxide film in terms of interfacial defect generation and annihilation reactions. In case of platinum, the following 5-reaction scheme is provided in Figure AA1-1. Since the oxide film of platinum is found to be n-type in electronic character.

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

\[ k_i = k_i^0 e^{i \Delta V} e^{b_i} e^{c_i \rho H} \]  
\[ \text{(Eq. 1.2)} \]

where \( k_i \) is the rate constant for the \( i \)-th reaction, \( k_i^0 \) is the standard rate constant, expressions for \( a_i \), \( b_i \), and \( c_i \) can be found in Table 2-2 and the corresponding meaning for each symbols are listed in Table 2-3. All the symbols used in the appendix bear the same meaning as they do in chapter 2.

The PDM qualitatively predicts that the growth of the barrier layer under any condition is determined by the rate of growth (reaction (3)) and rate of dissolution (reaction (7)) as they are the only two lattice non-conservative reactions: proceeding of reaction (3) moves the metal/barrier interface toward metal, and reaction (7) also moves the film boundary toward the metal/barrier layer interface

\[ \frac{dL}{dt} = \frac{dL^+}{dt} - \frac{dL^-}{dt} = \Omega k_3^0 e^{a_3 V} e^{b_3 L} e^{c_3 \rho H} - \Omega k_7^0 \left( \frac{C_{H^+}}{C_{H^+}^0} \right) e^{a_7 V} e^{c_7 \rho H} \]  
\[ \text{(Eq. 1.3)} \]

A simpler form of the rate law is available when no change occurs in the oxidation state of the cation upon dissolution, so that the dissolution rate can be simplified to a potential independent constant \( C \). Now by noting the voltage is swept at a constant rate \( v \)
where $V^0$ is the equilibrium potential for platinum oxide formation. Then the grow law simplifies to

$$\frac{dL}{dt} = Ae^{aV}e^{bL} - C$$  \hspace{1cm} (Eq. 1.5)

where $\Delta V = V - V^0$. Solving this differential equation, we can get the film growth law under transient conditions. By variable substitution

$$Z = e^{aV}e^{bL}$$  \hspace{1cm} (Eq. 1.6)

We get

$$dZ = a_3ve^{aV}e^{bL}dt + b_3e^{aV}e^{bL}dL$$  \hspace{1cm} (Eq. 1.7)

then

$$\frac{dZ}{dt} = a_3vZ + b_3Z \frac{dL}{dt}$$  \hspace{1cm} (Eq. 1.8)

$$\frac{dL}{dt} = (\frac{dZ}{dt} - a_3vZ) / b_3Z$$

Accordingly, from Eq. (1.5), we get
And hence

\[
\frac{1}{b_3 Z} \frac{dZ}{dt} = AZ - C + \frac{a_3 v}{b_3} \quad \text{(Eq. 1.10)}
\]

Defining \( r = C - \frac{a_3 v}{b_3} \), then Eq. (1.10) becomes

\[
\frac{dZ}{dt} = b_3 Z(AZ - r) \quad \text{(Eq. 1.11)}
\]

Or the equivalent

\[
\int_{Z_o}^{Z} \frac{dZ}{Z(AZ - r)} = b_3 \int_{0}^{t} dt \quad \text{(Eq. 1.12)}
\]

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

\[
\frac{1}{Z(AZ - r)} = -\frac{1}{rZ} + \frac{1}{r(Z - r / A)} \quad \text{(Eq. 1.13)}
\]

and integrating yields
Also integrating the right side, we get

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

(Eq. 1.14)

Also integrating the right side, we get

\[
-\frac{1}{r} \ln\left(\frac{Z}{Z_0}\right) + \frac{1}{r} \ln\left(\frac{Z - r / A}{Z_0 - r / A}\right) = b(t - t_0)
\]

(Eq. 1.15)

Rearrange Eq. (1.15) yields

\[
\frac{Z_0(Z - \frac{r}{A})}{Z(Z_0 - \frac{r}{A})} = e^{b(t - t_0)} = \theta
\]

(Eq. 1.16)

then solve Z

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

(Eq. 1.17)

Recalling Eq. (1.6), we therefore get

\[
Z_0 = e^{a_{2} \nu_{0}} e^{b_{1} \nu_{0}}
\]

(Eq. 1.18)
where $L_0$ is the thickness of the anodic film at $t_0$, since $t_0$ corresponds to the time at the equilibrium potential of platinum oxidation, then $L_0 = 0$, therefore $Z_0 = e^{a_0 t_0} = e^{a_0 v_0}$.

Further recalling that $\theta = e^{b r (t_0 - t)}$ we then get the description for the film growth rate law under transient conditions

\[
L = -\frac{a_3}{b_3} \Delta V + \frac{1}{b_3} \ln \left( \frac{r/A}{1 + (r/A - 1)e^{-b_3 e^{\Delta V/r} e^{-a_3 \Delta V}}} \right) \quad \text{(Eq. 1.19)}
\]

In the limit that the sweep rate approaches zero ($v \to 0$), and noting the expressions for the parameters $a_3 = \alpha_3 (1 - \alpha) \chi \theta$ and $b_3 = -\alpha \chi \hat{e} \gamma$, where $\gamma = F/RT$, Eq. (1.19) then reduces to the familiar form

\[
L = \frac{1 - \alpha}{\hat{e}} \Delta V \quad \text{(Eq. 1.20)}
\]

which is the potential dependent steady state film thickness predicted by the PDM (check Eq.(2.19)). Now we are at the stage to derive the passive current density of platinum, which can also be derived by considering that the fluxes of a given defect at the two interfaces are equal under steady state conditions

\[
I_{ss} = \Gamma F \left[ k_0 e^{a_V} e^{b_L} e^{c_z p_H} + k_0 e^{a_V} e^{c_z p_H} (C_{H^+} / C_{H^0})^{\gamma} \right] \quad \text{(Eq. 1.21)}
\]

where the first and second terms represent the generation and transport of cation interstitials and oxygen vacancies, respectively, with the latter being expressed in terms of the equivalent rate of dissolution of the barrier layer. Note, since platinum oxide film has n-type electronic character, so the identified point defects are platinum interstitials and oxygen vacancies, then the second term in Eq. (2.20) is neglected.
For the specific case where no change in oxidation state occurs upon dissolution of the film we get

\[ I_{pass} = F \chi k^0_{f} e^{a \gamma L} e^{b_{f} \gamma_{L}} e^{c_{f} \gamma_{H}} \]  
\[ \text{(Eq. 1.22)} \]

Recall Eq. (1.19) get

\[ I_{pass} = F \chi k^0_{f} e^{c_{f} \gamma_{H}} \frac{1}{A/r + (1 - A/r)e^{b_{f} \gamma_{L}/r} e^{c_{f} \gamma_{H}/r}} \]  
\[ \text{(Eq. 1.23)} \]

When \( v \to 0 \), the steady state passive current density is yielded

\[ I_{pass} = F \chi k^0_{f} e^{c_{f} \gamma_{H}} \frac{C_{A}}{A} \]  
\[ \text{(Eq. 1.24)} \]

Since the measured current density also includes the charging of the oxide film layer capacitance (\( C_{ox}, \) per unit area) and the double layer capacitance (\( C_{dl}, \) per unit area), it is also necessary to derive the mathematical form of the charging current. The charging current density is usually a function of the sweep rate

\[ I_{charging} = C_{T} \frac{dV}{dt} = C_{T} v \]  
\[ \text{(Eq. 1.25)} \]

where \( C_{T} \) is the total unit area capacitance of the series combination of the double layer capacitance and the oxide film capacitance. \( C_{T} \) can be calculated as

\[ \frac{1}{C_{T}} = \frac{1}{C_{ox}} + \frac{1}{C_{dl}} \]  
\[ \text{(Eq. 1.26)} \]
The double layer capacitance usually ranges from $20 \mu F/cm^2$ to $100 \mu F/cm^2$, and is weakly potential dependent at potential away from the potential of zero charge (PZC). However, in some special conditions, e.g. adsorption/desorption at the interface, the overall double layer capacitance might be much smaller. The oxide film capacitance per unit area can be determined by taking the film as a parallel-plate capacitor with the dielectric constant of the medium being that of the film

$$C_{ox} = \frac{\varepsilon \varepsilon_0}{L} \quad \text{(Eq. 1.27)}$$

Recall Eq. (1.19) for film thickness $L$, and substitute Eq. (1.26) and Eq. (1.27) into Eq. (1.25), the overall charging current density is yielded

$$I_{charging} = \frac{\varepsilon \varepsilon_0 V}{-\frac{a_3}{b_3} \Delta V + \frac{1}{b_3} \ln \left( \frac{r/A}{1 + (r/A - 1)e^{b_3c\Delta V}/e^{-a_3 \Delta V}} \right)} + \frac{\varepsilon \varepsilon_0}{C_{dl}} \quad \text{(Eq. 1.28)}$$

Now, we are at the stage to obtain the total current density as a function of the sweep rate

$$I_{total} = F \chi C_0^0 e^{cvH} R + \frac{\varepsilon \varepsilon_0 V}{-\frac{a_3}{b_3} \Delta V + \frac{1}{b_3} \ln R + \frac{\varepsilon \varepsilon_0}{C_{dl}}} \quad \text{(Eq. 1.29)}$$

where $R = \frac{r/A}{1 + (r/A - 1)e^{b_3c\Delta V}/e^{-a_3 \Delta V}}$. Optimizing Eq. (1.29) on the experimental $I$-$V$ data would yield the kinetic parameters introduced by the PDM. These kinetic parameters
could be very valuable in determining the growth rate and thickness of the oxide film. The results are discussed in chapter 4.

References

VITA

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JianEr Bao (also goes with Valerie since 1997) was born on March 9th, 1978 in FengHua, ZheJiang province, China. She enrolled in Tsinghua University, Beijing, China, in 1996, and got her bachelor’s degree in the department of materials science and engineering in 2000, and her master’s degree in the same department in 2002. She started doing research in the State Key Laboratory of New Ceramics and Fine Processing since 1998, and worked on various types of electronic ceramics. From August 2002 to May 2003, she worked for General Electric in Shanghai, Asia Technology Center, as a ceramic engineer. Since May, 2003, she joined Pennsylvania State University, and worked with Dr. Macdonald in the department of materials science and engineering. Her dissertation topic is “Fundamental Aspects of Electrocatalysis of the Hydrogen and Oxygen Electrode Reactions on Platinum”. She is expecting to get her Ph.D degree in August, 2007.