THEORETICAL PREDICTIONS OF POTENTIALS FOR INTERMEDIATE STEPS IN METHANOL AND ETHANOL ELECTROCHEMICAL OXIDATION ON Pt(111)

by

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Table of Contents

Table of Contentsi
List of Tablesiv
List of Figuresv
Acknowledgementsviii
List of Abbreviationsx
Abstractxii
1. Introduction to Direct Alcohol Fuel Cell and Theoretical Overview 1
1.1 Overview of direct alcohol fuel cell
1.1.1 A brief introduction to the polymer electrolyte fuel cell2
1.1.2 Direct alcohol fuel cell (DAFC)4
1.1.3 Electrochemistry of DAFC5
1.2 Theoretical Overview7
1.2.1 Electrode Surface Structure Modeling7
1.2.2 Electric Double layer Structure Models
1.2.3 Solvation models
1.2.4 Models incorporating electrode potential change

theory10
2. Electrochemical Oxidation of Methanol on Pt(111) Electrode 13
2.1 Background of electrochemical oxidation on the Pt(111) electrode14
2.2 Theoretical methodology
2.3 Adsorption internal energies of methanol and reaction intermediates on the Pt(111)
surface
2.4 Reversible potentials for elementary steps in the methanol oxidation reaction25
2.5 Concluding Remarks
3. Electrochemical Oxidation of Ethanol on Pt(111) Electrode
3.1 Background of electrochemical oxidation on the Pt(111) electrode34
3.2 Theoretical methodology
3.3 Adsorption internal energies of ethanol and Reaction Intermediates on the Pt(111)
surface
3.4 Reversible potentials for elementary steps in the ethanol oxidation reaction45
3.5 Possible reasons for the low efficiency of ethanol oxidation on the Pt(111)
electrode

	3.6 Concluding Remarks	53
4.	Using Gibbs Energies to Calculate the Pt(111) H _{upd} Cyclic Voltammogram	55
	4.1 Introduction	56
	4.2 Theoretical methodology	58
	4.3 Results and discussion	62
	4.4 Concluding Remarks	76
5.	CO formation from oxidation of formyl on Pt(111) surface	78
	5.1 Introduction	79
	5.2 Theoretical methodology	79
	5.3 Adsorption of CO on Pt(111)	82
	5.4 Reversible potentials of CO formation from formyl	86
	5.5 Concluding Remarks	90
Aŗ	opendix	91
Bi	bliography	94

List of Tables

2.1	Most stable adsorption sites and energies of reaction intermediates of methanol
	oxidation over the Pt(111) surface. * stands for the atom bonded to the surface.
	Structures are shown in Figure 1 except for *OH and *OH24
2.2	Reversible potentials for electron-transfer steps and free energy changes for non-
	electron transfer step in solution and on surface
3.1	Most stable adsorption sites, energies of reaction, and bond distances of C-C and
	C-O bonds of intermediates of ethanol oxidation over the Pt(111) surface. *
	stands for the atom bonded to the surface. Structures are shown in Figure (3.1)
	except for *OH and *OH ₂ . H*OCH, O*CH and HO*C have been shown
	previously in Chapter 2, Figure (2.1)
3.2	Calculated reversible potentials using the LGER theory for electron-transfer steps
	and calculated free energy changes for non-electron transfer steps in solution and
	on the surface
4.1	Calculated reversible potentials, U_{rev} , using the method of Figure (4.2). θ_{oxd} and
	$\theta_{\rm red}$ are the initial and final H coverages in the patterns
4.2	Values of H(ads) coverage used in Figures (4.3- 4.5) and corresponding reversible
	potentials energies for reduction from interface calculations and with $T\Delta S_{conf}$
	included73
5.1	Internal energy of adsorption, ΔE_{ads} , and Gibbs free energy of adsorption, ΔG_{ads} ,
	for the CO molecules at different sites of Pt(111) surface

List of Figures

1.1	Schematic diagram of a DEFC from Ref 32
2.1	(a) top view of 1/6 ML HOCH ₃ (ads) showing 3×2 translational cell; and (b) side
	view
2. 2	Top view of optimized structures for methanol and its oxidation reaction
	intermediates on Pt(111) surface. (a) methanol; (b) methoxy; (c) formaldehyde;
	(d) hydroxylmethyl; (e) hydroxylmethylidene; (f) formyl; (g)
	hydroxymethylidyne; (h) carbon monoxide; (i) formic acid; (j) hydrocarboxyl
	radical; (k) formyloxyl radical and formate anion, and (l) carbon
	dioxide23
2.3	Different pathways for the methanol oxidation on the Pt(111) surface and
	predicted reversible potentials, $U_{\rm surf}^{\rm rev}$, and the reaction energy for combining
	OH(ads) and CO(ads)
2.4	Dependency of activation energy on electrode potential
3.1	(a) top view of 1/12 ML HOCH ₂ CH ₃ (ads) showing $2\sqrt{3}\times3$ translational cell; and
	(b) side view
3.2	Off normal view of the optimized structures for ethanol and its oxidation
	intermediates on Pt(111) surface. (a) ethanol;(b) ethoxy; (c) acetaldehyde; (d) 1-
	hydroxylethyl; (e) 1-hydroxylethylidene; (f) acetyl; (g) ketene; (h) ketenyl; (i)
	acetic acid; (j) acetate radical and anion; (k) methyl and (l)
	methane

3.3 Pathways for ethanol oxidation on the Pt(111) surface with reversible potentials, $U_{\text{surf}}^{\text{rev}}$, for electron transfer steps and reaction energies for non-charge transfer

- 4. 6 Predicted cyclic voltammogram at 298.15 K.....74
- 4.7 Superposition of voltammogram copied from Figure (4.2b) in Ref 81 on the predicted result in Figure (4.6) (black curves). The red points are the extended voltammogram obtained from chronoamperometric experiments. The vertical grey line reaches zero current density at the experimental onset potential for hydrogen evolution. The blue dots are a theoretical projection based on a total

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Dedication

To Mom....I wish you endless happiness

To Dad....you are always alive in my heart

To Gahadah....I love you

List of Abbreviations

ML	Monolayer
PEMFC	Proton Exchange Membrane Fuel Cell
SHE	Standard Hydrogen Electrode
e	electron charge, 1.602×10^{-9} Coulombs
LGER	Linear Gibbs Energy Relationship
UPD	Underpotential Deposited
XPS	X-ray Photoelectron Spectroscopy
SEIRAS	Surface-Enhanced Infrared Absorption Spectroscopy
LEED	Low Energy Electron Diffraction
STM	Scanning Tunneling Microscopy
IRAS	Infrared Reflection-Absorption Spectroscopy
DEMS	Differential Electrochemical Mass Spectrometry
HPLC	High Performance Liquid Chromatography
in situ FTIR	in situ Fourier Transform Infrared Spectroscopy
in situ IRRAS	in situ Infra-Red Reflection-Absorption Spectroscopy
SPAIRS	Single Potential Alteration Infrared Spectroscopy
SNIFTIRS	Subtractively Normalized Interfacial Fourier Transform
	Infrared Spectroscopy
CV	Cyclic Voltammogram
Fcc	face-centered cubic
Нср	hexagonal close-packed

DAFC	Direct Alcohol Fuel Cell
DEFC	Direct Ethanol Fuel Cell
DMFC	Direct Methanol Fuel Cell
GGA	Generalized Gradient Approximation
PW91	Perdew and Wang's 1991 functional
RPBE	Revised Perdew-Burke-Ernzerhof Functional
МРВ	Modified Poisson-Boltzmann Theory
PZC	Potential of Zero Charge
VASP	Vienna Ab initio Simulation Package
DFT	Density Functional Theory

Theoretical Predictions of Potentials for Intermediate Steps in Methanol and Ethanol Electrochemical Oxidation on Pt(111)

by

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Abstract

The elementary steps of methanol and ethanol electrochemical oxidation on Pt(111) were investigated using quantum mechanics theory. The reversible potential for each electron-transfer step and the reaction energy for non-electron transfer steps were calculated in bulk solution using Interface 1.0. This density functional theory (DFT) code uses modified Poisson-Boltzmann theory (MPB) and the dielectric continuum model to model the solvent, and allows adding or subtracting electronic charge to the solute or the surface with considering electrolyte response. Adsorption energies for reaction intermediates were calculated and used along with reversible potentials in bulk solution to predict surface reaction reversible potentials using linear Gibbs energy relationship model (LGER). This theory is capable of predicting approximate reversible potentials of redox reactions at solid-liquid interfaces by perturbing reversible potentials in bulk solution by internal energies of adsorption. Results were analyzed and compared with available experimental data and oxidation mechanisms were proposed. The accuracy of LGER was tested by comparing reversible potential of CO reduction to formyl on Pt(111) with the one obtained by a more accurate method, the Gibbs energy curve crossing procedure. The results confirm the reliability of LGER in predicting reversible potentials for surface reactions. The Gibbs energy curve crossing procedure was also applied in predicting the cyclic voltammogram of underpotential deposited hydrogen H_{upd} on Pt (111). The predicted CV showed good agreement with experiment.

Chapter 1

Introduction to Direct Alcohol Fuel Cell

and Theoretical Overview

1.1 Overview of Direct Alcohol Fuel Cell

1.1.1 A brief introduction to the polymer electrolyte fuel cell

A fuel cell is a device that converts the chemical energy in fuels directly into electricity through electrochemical and chemical reactions.¹ The fuel cell considered here consists of a negative anode electrode where fuel is oxidized, a positive cathode electrode where oxygen is reduced, and an electrolyte in between. Both cathode and anode are coated with a catalyst. When fuel comes into contact with the electrode, electrons split off of fuel molecules as a current that travels through an external circuit. The oxidized protons transfer through the electrolyte and combine with oxygen to produce water.^{2,3} Figure (1.1) illustrates these features for the case of ethanol as the fuel.



Figure 1.1 Schematic diagram of the direct ethanol fuel cell (DEFC) from Ref 3.

The hydrogen fuel cell was first invented in 1839 when William Grove was able to generate an electric current by reversing the water electrolysis reaction.⁴ In the beginning of 1960s, the idea of solid electrolyte first came to light at the General Electric Company through using sulfonated polystyrene membranes. However, since 1966 until today, Nafion® has dominated other membranes due to its durability and exceptional performance.⁵

Nowadays polymer electrolyte fuel cell, PEMFC, more than any other type of fuel cell, has attracted the automotive and portable electronics industries.⁶ In addition to their high thermodynamic efficiency, they operate at low temperature, making them suitable for transportation. Compact fuel cells are also being tested for portable applications such as cell phones and laptops.⁷

Hydrogen is the most efficient fuel for PEMFCs as 1 kg of pure hydrogen can deliver (32.8 kWh) of energy.⁸ However, hydrogen produced from hydrocarbons is usually mixed with carbon monoxide, which poisons the anode surface and lowers the efficiency. Storage is also an issue associated with using hydrogen as fuel. Where onboard storage of hydrogen is impractical, alcohol or hydrocarbon steam reforming systems will produce hydrogen but carbon monoxide and carbon dioxide formed in the process are issues.²

1.1.2 Direct alcohol fuel cell (DAFC)

Attention was drawn to small organic molecules such as alcohols as alternative fuels to hydrogen. Methanol is the most promising organic fuel due to several advantages. Methanol is inexpensive and, as a liquid, it is easy to store and transport. It is highly soluble in electrolyte solution and has high energy density (6.1 kWh/kg).⁸ These features put direct methanol fuel cell (DMFC) in the spotlight for fuel cell research. However, the efficiency of DMFC is not as high as for H₂ due to low catalytic activity, catalyst surface poisoning by CO, and methanol cross-over to the cathode through the membrane.⁹ There is also environmental concern about methanol being a relatively toxic material.

The direct ethanol fuel cell (DEFC) is potentially the most attractive ideal green energy technology in today's world. The emitted CO₂ in DEFC, Figure (1.1), can be recycled by plants (biomass) which is the main source of ethanol, it can be safely said that ethanol is a renewable energy source. Ethanol is far less toxic than methanol and it has high energy density (8.0 kWh/kg).⁸ The complete oxidation reaction of one molecule of ethanol delivers 12 electrons, compared to 6 for methanol, which accounts for the higher energy density. However, the commercialization of DEFC to meet the global demand has been held back by a multiple of challenges. Since they run at low temperature, DEFC suffer from the slow oxidation kinetics.¹⁰ Moreover, the catalyst used plays a role in defining the overall efficiency of DMFC. As a pure metal, platinum has shown a high initial activity toward ethanol oxidation. However, its surface is prone to poising by reaction intermediates such as CO.^{11, 12,13}

1.1.3 Electrochemistry of DAFC

In the direct methanol fuel cell, there are two electrode reactions:

At the anode:

$$CH_3OH(aq) + H_2O(l) \rightleftharpoons CO_2(g) + 6H^+(aq) + 6e^ (U^o = 0.032 \text{ V})^{14}$$
 (1.1)

At the cathode:

$$3/2O_2(g) + 6H^+(aq) + 6e^- \rightleftharpoons 3H_2O(l)$$
 (U^o = 1.229 V) (1.2)

The overall reaction:

$$CH_3OH(aq) + 3/2O_2(g) \rightleftharpoons CO_2(aq) + 2H_2O(l)$$
 (U° = 1.197 V) (1.3)

Similarly, in the DEFC, the reactions are:

At the anode:

$$CH_3CH_2OH(aq) + 3H_2O(l) \rightleftharpoons 2CO_2(g) + 12H^+(aq) + 12e^-$$
 (U^o= 0.090 V) (1.4)

At the cathode:

$$3O_2(g) + 12H^+(aq) + 12e^- \rightleftharpoons 6H_2O(l)$$
 (U^o = 1.229 V) (1.5)

The overall reaction:

$$CH_3C_2OH(aq) + 3O_2(g) \rightleftharpoons 2CO_2(aq) + 3H_2O(l)$$
 (U^o = 1.139 V) (1.6)

The alcohol oxidation reactions at the anode, eqs (1.1) and (1.4), are slower than oxygen reduction at the cathode.¹⁵ Poor kinetics of alcohol oxidation is responsible for the low efficiency of the DAFC. If the ideal anode catalyst is found, both methanol and ethanol will oxidize at potentials just above 0.0 V under standard conditions. However, platinum surfaces which are active for deprotonation steps becomes blocked by adsorbed CO molecules at potentials less than about 0.6 V. Thus, it impossible for continuous oxidation to occur except at very high potentials.¹⁶

Understanding the mechanism of alcohol (methanol, ethanol) electrochemical oxidation on Pt anode surfaces a timely endeavor. Electrochemical oxidation of alcohols on Pt involves several intermediate steps. Knowing the potentials at which each step occurs provides information needed for choosing or designing platinum alloys or other materials with higher electrocatalytic efficiency.

1.2 Theoretical overview

Many physical, biological, chemical, and electrochemical phenomena occur at the liquid–solid interface. Interfacial characterization is a major focus in contemporary research, including electrocatalysis in fuel cells. A description of both surface and electric double layer is given in this part of the Chapter.

1.2.1 Electrode surface structure modeling

Surface properties depend on the last few atomic layers of the solid at the vacuum/solution phase. Surfaces made by cleaving a solid crystal into two pieces are classified as low Miller index surface (100), (110) and (111), or a high Miller index surfaces depending on the surface structures.

Surface can be modeled by cluster models or slab models. While the cluster models show success in modeling ionic crystals with localized wave function, the slab model is more realistic for covalent catalyst and metals.

The slab is infinite and created by periodic translational cell of limited thickness repeated in two dimensions parallel to the surface. There are two surfaces of the slab, vacuum and vacuum or vacuum and solution. The two of them are separated by the atomic layers. The more are the intervening atomic layers, the thicker the slab and a better representation of the bulk will be obtained. The structure of bottom layers, close to one vacuum side is fixed, while the remaining layers relaxed and optimized as the surface layers. Vacuum is on the relaxed side in case of modeling reactions under high vacuum conditions, UHV, and a solution model is used in case of electrochemical reactions. Density functional theory, DFT, is currently used for obtaining relatively accurate results for solids to interpret measurements. However, the choice of the functional affects the results to a great extent. Calculations using the Revised Perdew, Burke, and Ernzerhof (RPBE) functional have shown good agreement with experiments for predicting adsorption energies for oxygen, CO, and NO on Ni, Rh, and Pd surfaces¹⁷ and in predicting redox potentials.¹⁸ The RPBE functional is used in the work reported in this thesis.

1.2.2 Electric double layer structure models

The term electric double layer is used to describe the structure of charges and electrolyte in the interfacial region. When potential is applied in a fuel cell environment, the metal surface becomes, for example, positively charged and is compensated by countercharges. The concentration of countercharges will be higher at the double layer region and decreases as a function of distance into the liquid phase. The various models for the double layer such as those of Helmholtz, Gouy, and Chapman and Stern are presented in texts, including the Srinivasan¹⁹ monograph on fuel cells. The Gouy and Chapman Poisson-Boltzmann approach is most related to the electrochemical interface theory used in this thesis.

1.2.3 Solvation models

Solvation is usually described by the change in Gibbs free energy obtained from solute-solvent interactions. Hence, solvation energy can be defined as "the free energy of

transferring the solute from a vacuum to the solvent environment of interest".²⁰ To represent the solvent and account for the electrostatic interaction between solvent and solute in the electrolyte solution, different models have been proposed, explicit solvation, implicit solvation, and hybrid solvation models. A hybrid approach is used in this research for obtaining the Gibbs energy of H⁺(aq) and solvation Gibbs energies of the other molecules are estimated using only implicit solvation model, namely the dielectric continuum approach.²¹

1.2.4 Models incorporating electrode potential change

Modeling the effect of change in electrode potential on properties of molecules adsorbed on electrode surface has been difficult. When the potential is changed, the Fermi level of the electrode surface changes by the same amount. The earliest model was developed in this lab and used semiempirical molecular orbital theory wherein the Fermi level was shifted parametrically and the potential dependencies of adsorbate vibrational frequencies were calculated²² and adsorption sites predicted.²³ More recently, Neurock et al. have used DFT slab band model wherein the potential is changed by adding surface charge, either positive or negative, and the counter charge is handled as a diffuse background charge.²⁴ Lozovoi and Alavi model also included changing the potential by adding or subtracting charge but the countercharge was treated as a plane of countercharge as in the Helmholtz approach.²⁵

1.2.5 Combination of density functional theory and modified Poisson-

Boltzmann theory

The Poisson-Boltzmann equation (PBE) is an essential tool to describe the electrostatic interaction in electrolyte solutions where the Poisson part of the equation treats the electric potential and the Boltzmann part deals with ions distribution. However, the standard equation does not take into account the finite size of the ions, which leads to a very high density of ions at the surface at high potential. The equation has been modified by different approaches with some success to overcome this defect. Borukhov et al. have introduced a modified Poisson–Boltzmann equation that takes into account the finite size of the ions.²⁶

Otani and Sugino suggested combining DFT, to describe the surface, and a modified Poisson-Boltzmann theory, MPB, to describe the electric double layer in one model to obtain a better description for ion distribution at the solid-liquid interface.²⁷

Just five years ago, Borukhov model was modified by using a different continuum model. The new theory was developed in our laboratory.²¹ The theory was coded into computational program, Interface 1.0, which was shown to be capable of predicting accurate reversible potentials at the liquid-solid interface for surface electron transfer reactions and for molecules in bulk solution.

In the theory, ground or local minima of the system structure are calculated by minimizing the total energy using variation theory where the total Gibbs free energy for isolated solvated molecules or a neutral solid-liquid interface is given by:

$$G = E + \Omega_{\rm ss,nonel} + \Omega_{\rm is,nonel} - TS_{\rm e} - TS_{\rm i} + H_{\rm vib} - TS_{\rm vib}$$
(1.7)

E is the internal energy. $\Omega_{ss,nonel}$ and $\Omega_{is,nonel}$ are the free energies due to non-electrostatic solute-solvent and ions-solute interactions, respectively. The term $H_{vib} - TS_{vib}$ is the thermal contribution to the free energy of the solute. The thermal component for adsorbed species was calculated through a frequency analysis using the optimized structures of the neutral systems. *T* is the temperature, and *S*_e and *S*_i, are the entropies of the electrons, and ions, respectively. When charge is added to the surface to change the potential, a mass term, Ω_{mc} , is added to the Gibbs free energy:

$$G = E + \Omega_{\rm ss,nonel} + \Omega_{\rm is,nonel} - TS_{\rm e} - TS_{\rm i} + H_{\rm vib} - TS_{\rm vib} + \Omega_{mc}$$
(1.8)

where
$$\Omega_{mc} = -E_f N_e + \mu_+ N_+ + \mu_- N_-$$
 (1.9)

In eq (1.9), $E_{\rm f}$ is the Fermi energy level, Ne is the number of electrons, N_+ and N_- are the number cations and anions in solution, and μ_+ and μ_- are their respective chemical potentials. For calculations at potential of zero charge (PZC), $\Omega_{mc} = 0$

Electrode potential is calculated by:

$$U = -(E_f + \varphi_{SHE})/e \tag{1.10}$$

The φ_{SHE} is the thermodynamic work function of a standard hydrogen electrode which was predicted to be 4.43 eV.²¹ Predictions of potential dependent properties at the Pt-electrolyte interface are of good accuracy.^{18,28} The theory can also be used for molecules, solids, and surface-vacuum interface.

Two approaches were employed, using Interface 1.0, in the work of this dissertation. First, is an approximate model that was developed in our laboratory in 1999²⁹ called linear Gibbs free energy relationship (LGER) and it is used in Chapters 2 and 3. Details of the method can be found in section 2.2. The second approach is based on potential dependencies of Gibbs free energies of reactants and products of electron transfer reactions and it is used to calculate reversible potentials. This method is called Gibbs energy curve crossing procedure and it was employed in Chapters 4 and 5.

Chapter 2

Electrochemical Oxidation of Methanol

On Pt(111)

2.1 Background of electrochemical oxidation of methanol on Pt(111)

The search for renewable, environment friendly and efficient sources of energy as alternatives to fossil fuel combustion has been going for many years. The direct methanol fuel cell (DMFC) has been one of the top candidates to meet the global demands of energy for portable applications. 6.1 kWh of energy is stored in 1 kilogram of methanol.⁸ This energy is released when molecules are fully oxidized, losing 6 electrons each. The high energy density, theoretically, combined with the other features makes DMFC a superior energy source to hydrogen. However, up to now, DMFC has not reached the expectations.

Methanol electrochemical oxidation has been extensively studied by experimentalists. Cyclic voltammetry studies^{30,31} reveal onset potential > 0.4 V for methanol oxidation, indicating a high overpotential to the standard reversible potential, 0.032 V. Understanding the reaction mechanism by which the oxidation occurs on pure platinum electrode surfaces may play a role in finding a catalyst where methanol can be oxidized at a lower potential.

It is generally assumed that there is "a dual pathway mechanism" for methanol electrooxidation on Pt. The assumption is based on the variation of reaction intermediates that have been detected under different experimental conditions. Examples of such experimental studies are given below.

An excellent review and evaluation of the variety of experimental techniques that are often used in DMFC research was recently published by Abruña el al.³² Differential

electrochemical mass spectrometry (DEMS) has been used to identify the reaction intermediates from methanol oxidation in acidic electrolyte. Using this technique, Vielstich and Xia, proposed that CO₂ is produced only through CO oxidation.³³ However, using the same technique, Wang et al. reported soluble intermediates that have the potential to be oxidized to CO_2 .³⁴ Itwasita et al. have investigated the oxidation of 1 M of methanol in 0.1 M HClO₄ and 0.5 M H₂SO₄ at a potential where CO is stable on the Pt(111) surface.³⁵ During the experiment, the potential was held at 0.6 V for 15 min. of electrolysis. High performance liquid chromatography (HPLC) was used to analyze the products. The most important result was CO₂ composing 6 to 59% of the products. Formaldehyde formed 35 to 81 % with a yield inversely proportional to the CO₂ yield. The presence of formaldehyde and formic acid as soluble products of methanol oxidation on Pt(111) has been reported.^{35,36,37} A monitoring of the electrochemical oxidation of 0.5 M methanol on a Pt thin film electrode in 0.1 M HClO₄ was done by recording in situ surface enhanced infra-red absorption (SEIRA) spectra during measurement of a cyclic voltammogram. It was seen that as the absorption band intensity of CO decreased, another band attributed to formate started to arise at 0.5 V. This band was accompanied by an increase in the faradic current. Based on this observation, the authors concluded that at least some of the CO_2 was produced by the oxidation of formate and not $\text{CO}.^{38}$ In possible support, Wieckowski and Neurock et al. used a combination of chronoamperometry and fast scan cyclic voltammetry and found a secondary pathway became active at potentials > 0.35 V, with increasing contribution at higher potentials.³⁹ Also, early work using in situ Fourier transform infrared spectroscopy (FTIR) and

polycrystalline Pt electrode, identified hydrogenated species such as COH and H_x COH along with CO when potential was held at 0.35 V.⁴⁰

The main conclusion of all these studies is the appearance for two parallel pathways of the electrochemical oxidation of methanol on Pt. One pathway is proposed for potentials where CO formation leads to CO_2 . This is the "CO-pathway" or indirect path. In the parallel pathway, intermediates, such as formaldehyde and formic acid, form at high potential and become oxidized to CO_2 . This pathway is called "non-CO pathway" or direct path. There is some ambiguity in defining the concept of the "dual pathway mechanism" due to the variety of possibilities of pathways that can be suggested. One proposal is the following:³

Early theory papers investigated the mechanism of methanol decomposition over Pt(111) under UHV conditions,⁴¹⁻⁴⁴ and a few took into account the effect of solvent^{45,46} and the surface potential.⁴⁷ Except for Ref 47, all of these studies only explored the homolytic dehydrogenation of methanol to adsorbed dissociation products, not the electrochemical oxidation, which generates $H^+(aq)$. For example, first homolytic dehydrogenation step for methanol to form methoxy could be the following,

$$CH_3OH(ads) \rightarrow CH_3O(ads) + H(ads)$$
 (2.2)

The presumption is that H is oxidized from the surface by:

$$H(ads) \rightarrow H^{+}(aq) + e^{-}$$
(2.3)

The corresponding direct electrochemical reaction would be:

$$CH_3OH(ads) \rightarrow CH_3O(ads) + H^+(aq) + e^-$$
(2.4)

Wieckowski and Neurock³⁹ et al. used DFT calculations within a model for the electrochemical interface to study reaction energies as functions of potential for the electron and proton transfer steps that make up the two routes of the oxidation. A platinum slab model of 3 layers with 9 Pt atoms for a 3×3 unit cell was used in 3 dimensional Vienna Ab initio simulation package (VASP) DFT calculations with the PW91 functional. Adsorbed intermediates were placed on one side of the slab. The solvent was modeled by 24 H₂O molecules filling the space between the layers. Electrochemical potential changes were modeled by adding or subtracting electrons to or from the unit cell while the net charge was maintained at zero by the addition of a homogenous distribution of countercharge across the unit cell. By comparing the relative stabilities of possible oxidation products, they proposed that a parallel pathway becomes active at 1.2 V. This is higher than the experimental ≈ 0.4 V. According to the authors, an absolute error of ± 0.5 V in the calculated potential makes the calculations useful only for qualitative and not quantitative analyses. It is clear that their findings are far from complete.

This Chapter presents results of a comprehensive theoretical exploration of possible pathways for the six electron electrooxidation of methanol over the Pt(111) electrode. A comprehensive self-consistent theory for predicting and describing reaction steps at the electrochemical interface, coded as the program Interface 1.0, is employed for

predicting bulk solutions reversible potentials and adsorption bond strengths for use in the linear Gibbs energy relationship (LGER) model for estimating reversible potentials for redox reactions of the adsorbed intermediates. The reversible potentials are the key parameters to understanding the electrocatalysis, as will be explained below.

2.2 Theoretical methodology

Predictions of the reversible potentials for oxidation of adsorbed intermediates were made using the LGER approach whose development was initiated for solution reactions in Anderson laboratory in 1999 and was subsequently extended to surface reactions.^{48,29} LGER is understood as follow. Reversible potentials for reactions at the electrode surface, U_{surf}^{rev} , can be predicted by using known values of the standard reversible potentials for reactions in bulk solutions, U^o , and perturbing them by adsorption Gibbs energies of products and reactants on the surface:

$$U_{\text{surf}}^{\text{rev}} = U^o + \left[\Delta_{\text{ads}}G(\mathbf{P}) - \Delta_{\text{ads}}G(\mathbf{R})\right]/nF$$
(2.5)

where $\Delta_{ads}G(P)$ and $\Delta_{ads}G(R)$ are Gibbs adsorption energies at U_{surf}^{rev} of the product P and reactant R in the solution phase.²⁹ Whereas eq (2.5) is exact, it is difficult to apply, as shown in Ref 29, but it can be approximated to advantage by replacing $\Delta_{ads}G(P)$ and $\Delta_{ads}G(R)$ by internal adsorption energies of the gas phase species at the potential of zero charge:

$$U_{\text{surf}}^{\text{rev}} \approx U^{o} + [\Delta_{\text{ads}} E(\text{Ox}) - \Delta_{\text{ads}} E(\text{R})]/nF$$
(2.6)

This is the formula used in this work. It is noted that both $\Delta_{ads}G$ and $\Delta_{ads}E$ depend on the potential applied to the electrode, but it has been found that these dependencies are small.

Also, there is approximate cancelation of $T\Delta S$ terms when $\Delta_{ads}G$ is replaced by $\Delta_{ads}E$ so that errors in predicted U^o value are believed to be < 0.2 V.²⁹

As there are no experimental data available for standard reversible potentials for most of the elementary steps that are likely to occur during methanol oxidation on the electrode, calculations of the needed U^o were carried out using the Interface 1.0 code.^{18,21} The electrolyte was modeled as a dielectric continuum with the distribution of charge in the electrolyte determined using a modified Poisson-Boltzmann theory. The electrolyte concentration was 1 M and 3.0 Å radii were assumed for the ions.

For the reaction,

$$Ox(aq) + e^{-}(U^{o}) \stackrel{\leftarrow}{\to} R(aq)$$
(2.7)

The reversible potential U^{o} is given by:

$$U^{o} = \{G(Ox) - G(R)\}/nF - \varphi/F$$
(2.8)

The Gibbs energies, G, were calculated using eq (1.7), which is repeated:

$$G = E + \Omega_{\rm ss,nonel} + \Omega_{\rm is,nonel} - TS_{\rm e} - TS_{\rm i} + H_{\rm vib} - TS_{\rm vib}$$

$$\tag{2.9}$$

where G is the total Gibbs free energy for the solute in bulk solution, E is the internal energy, $\Omega_{ss,nonel}$ and $\Omega_{is,nonel}$ are the respective free energies from non-electrostatic solutesolvent and ion-solute interactions, T is temperature, and S_e and S_i are entropies of the electrons and ions and $H_{vib} - TS_{vib}$ are the atom vibrational contributions to the free energy and Ω_{mc} is a mass correction term. The $H_{vib} - TS_{vib}$ contributions were calculated using the Gaussian 09 program.⁴⁹ Finally, in eq (2.9), F is the faraday constant, φ is the work function of the standard hydrogen electrode, and n is the number of electrons transferred.

Calculations of internal energies for use in eq (2.8) were performed using Interface 1.0 with the RPBE functional.¹⁷ The entropies of translation and rotation of the solvated species were approximated by using the calculated values for the gas phase molecules as obtained from the Gaussian calculations. In case of water, this approximation overestimates the total entropy⁵⁰ by about (0.015kcal/mol.K) because the translational and rotational motions are actually restricted in solution by strong hydrogen bonds. The exact error in case of methanol and O-H containing species is unknown. It is also unknown if there is entropy error in case of intermediates that do not form hydrogen bonds. However, errors are cancelled in most the elementary steps due to the presence of hydrogen bonds in both products and reactants in the oxidation reactions. U^{o} for OH(aq) reduction in bulk solution was taken from experiment. Since thermal contributions were calculated for gas phase molecules, it was necessary to add a term that corresponds to Gibbs energy of condensation or dilution to take into account the change in concentration between the 1 atm gaseous state and the 1 M solution state at 298.15 K. This term is called the concentration term, G_{conc} , and can be calculate as:

$$\Delta G = k_B T \ln \left(C_2 / C_1 \right) \tag{2.10}$$

where k_B is the Boltzmann constant, *T* is the temperature, C_1 is the molar concentration corresponds to 1 atm of any gas and it equals 1/24.46 mol/L, and C_2 is the molar concentration for the liquid phase and it equals 55.3 mol/L for H₂O(l) and 1.0 mol/L for any other species. The activity coefficient was assumed to be unity in these calculations.

Adsorption internal energies for intermediates were calculated as follows:

For the reaction,

$$Ox + Surf \rightarrow Ox(ads)$$
 (2.11)

The change in internal energy upon adsorption of the oxidized intermediates is:

$$\Delta_{ads} E(Ox) = E(Ox(ads)) - E(Surf) - E(Ox)$$
(2.12)

Similarly for the reduction reaction,

$$R + Surf \rightarrow R(ads) \tag{2.13}$$

The change in internal energy of the reduced intermediates is:

$$\Delta_{\text{ads}}E(\mathbf{R}) = E(\mathbf{R}(\text{ads})) - E(\text{Surf}) - E(\mathbf{R})$$
(2.14)

In these equations, E(Ox(ads)) and E(R(ads)) are the internal energies of the surfaces with adsorbates, E(Surf) is the internal energy of the surface, and E(Ox) and E(R) are the internal energies of the isolated molecules. An 18 atom, 3×2 unit cell with 2-dimentional periodic boundary condition was used, Figure (2.1), to generate a three-layer thick slab model of the bulk surface. The 6 atoms in the bottom layer were fixed in the calculated bulk structure with lattice constant 4.03 Å.²¹ A $3 \times 6 \times 1$ grid was used for the Monkhorst-Pack sampling⁵¹ in the Brillouin-zone.


Figure 2.1 (a) top view of 1/6 ML HOCH₃(ads) showing 3×2 translational cell; and (b) side view.

2.3 Adsorption internal energies of methanol and reaction intermediates on Pt(111)

Structures in Figure (2.2) were calculated to be the most stable ones among the tested configurations for 1/6 monolayer (ML) coverage of adsorbates on the Pt(111) surface. The calculated adsorption internal energies are in Table (2.1). Methanol adsorbs weakly by lone-pair donation from oxygen to a Pt atom at a top site. As may be seen in Table (2.1), the adsorption bond strength is close to that of a water molecule. Methoxy bonds to a top site through O, formaldehyde in a di- σ bridging site through C and O, formyl in a top site through C and CO in bridging site through C.

At the electrochemical interface it is thought that the first H removal is from the carbon because the O-H bond is held away from the surface by hydrogen bonds. This forms hydroxylmethyl, that bonds through C to a top site and can go next to hydroxylmethylene which bonds through C in a bridging site, or formaldehyde. A third hydrogen loss from HOCH forms formyl or hydroxylmethylidyne which bonds through C



Figure 2.2 Top view of optimized structures for methanol and its oxidation reaction intermediates on Pt (111) surface. (a) methanol; (b) methoxy; (c) formaldehyde; (d) hydroxylmethyl; (e) hydroxylmethylidene; (f) formyl; (g) hydroxymethylidyne; (h) carbon monoxide; (i) formic acid; (j) hydrocarboxyl radical; (k) formyloxyl radical and formate anion, and (1) carbon dioxide. 23

Table 2.1 Most stable adsorption sites and energies of reaction intermediates of methanol oxidation over the Pt (111) surface. * stands for the atom bonded to the surface. Structures are shown in Figure (2.2) except for *OH and $*OH_2$.

Species	adsorption site	$\Delta_{ads} E / eV$
methanol (H*OCH ₃)	top	-0.277
hydroxylmethyl (HO*CH ₂)	top	-2.131
hydroxymethylene (HO*CH)	bridge	-3.105
formyl (O*CH)	top	-2.392
hydroxymethylidyne (HO*C)	fcc	-4.342
carbon monoxide (*CO)	bridge ^a	-1.640
carbon dioxide (CO ₂)	-	-0.029
methoxy (*OCH ₃)	top	-1.439
formaldehyde (*O*CH ₂)	di-o-bridge	-0.546
*OH ₂	top	-0.229
hydroxyl (*OH)	top	-1.951
formic acid (HOOCH)	-	-0.111
hydrocarboxy radical (HO*CO)	top	-2.320
formyloxy radical (*OCH*O)	di-o-bridge	-2.112
formate anion (OCHO ⁻)	di-o-bridge	-0.345 ^b

^a Site preference depends on potential and coverage.

^b $\Delta_{ads}G$ was used for this anion.

to a fcc site. The third hydrogen loss from formaldehyde forms formyl. Loss of the fourth H gives CO, which bonds through C to a bridge site.

Formation of the CO_2 or other carboxylic intermediates requires reaction with an adsorbed hydroxyl group which is produced by the oxidation of water (see section 2.4). Formic acid was at a distance from the surface while formyloxy radical adsorbed strongly through both oxygen atoms. On the other hand, abstracting hydrogen from C of formic acid forms a trans structure of C-bonded hydrocarboxyl radical.

2.4 Reversible potentials for elementary steps in the methanol oxidation reaction

Several theoretical predictions made in Anderson's lab found low energy barriers of $\approx 0.1 - 0.2$ eV at the reversible potentials for electroreduction of O₂, O, and OH and the reverse reactions on the platinum electrode.⁵²⁻⁵⁵ It is assumed here that the electroreduction of COH(x) intermediates and the reverse reactions will also have low activation energies at the reversible potentials.

As a check of the accuracy of the Gibbs energy calculations, the standard reversible potential, U° , for the oxidation of methanol to CO₂ was calculated from predicted Gibbs energies for comparison with 0.032 V determined using standard thermodynamic data for the reaction:

$$CH_3OH(aq) + H_2O(1) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$$
 (2.15)

The predicted value is -0.095 V which is 0.127 V less.

Reversible potentials were calculated for intermediates that have been identified experimentally as well as for possible intermediates that might participate in the six electron oxidation. The LGER predictions for adsorbed intermediates were determined as perturbations of the bulk solution reversible potentials. The only potential available from experiment is for OH(aq) reduction to H₂O(l), 2.72 V.⁵⁶ The calculated, 2.445 V underestimates this. For OH(ads) formation by H₂O oxidation on the surface, the predicted potential is about 0.07 V higher than the experimental onset potential of ≈ 0.65 V.⁵⁷⁻⁶¹ This is because the surface models used in this study did not include co-adsorbed H₂O molecules. In earlier work adding a co-adsorbed water stabilized OH(ads) by hydrogen bonding decreased the potential to 0.59 V. With a second H₂O(ads), the potential increased to 0.65 V.²⁸ Due to their structures, hydrogen bonding stabilization of other intermediates would be less and were not calculated, but the lack of the stabilizations introduces small errors in the reversible potential predictions. Defect sites are expected to activate OH(ads) formation more than (111) platinum surface sites. An LGER study using Vienna Ab initio simulation package (VASP) produced a 0.10 V decreased for H₂O oxidation to OH(ads) on a step site, supporting the expectation.⁶²

Summing over the ΔG° values for solution in Table (2.2) and dividing by 6F yields -0.095 V, which checks with the result using Gibbs energies for eq (2.14). Summing over ΔG_{surf} gives -0.016 V for $U_{\text{surf}}^{\text{rev}}$. The difference, 0.079 V is traced to the one step not involving electron transfer, the C-O bond forming step. Using approximate reaction internal energies to represent the reaction Gibbs energy is responsible for the difference. In LGER, any errors in energies of adsorption and desorption of the intermediates cancel out when there are no non-electron transfer steps.

Reaction	$\Delta G^{o}_{sol} / \mathrm{eV}$	<i>U°</i> / V	^a ΔG_{surf} / eV	U ^{rev} /V
$HOCH_3 \rightarrow HOCH_2 + H^+_{(aq)} + e^-$	1.388	1.388	-0.466	-0.466
$HOCH_2 \rightarrow HOCH + H^+_{(aq)} + e^-$	1.057	1.057	0.083	0.083
HOCH \rightarrow HCO + H ⁺ _(aq) + e ⁻	-0.843	-0.843	-0.130	-0.130
$HCO \rightarrow CO + H^{+}_{(aq)} + e^{-}$	-1.449	-1.449	-0.697	-0.697
$OH + CO \rightarrow HOCO$	-1.076	-	0.195	-
HOCO \rightarrow CO ₂ + H ⁺ _(aq) + e ⁻	-2.093	-2.093	0.198	0.198
$OCH + OH \rightarrow HOCHO$	-4.042	-	0.190	-
HOCHO \rightarrow OCHO $+ H^+_{(aq)}$	0.231	-	-0.005	-
$OCHO^{-} \rightarrow OCHO + e^{-}$	1.805	1.805	0.038	0.038
HOCHO \rightarrow OCHO + $H^+_{(aq)}$ + e^-	2.035	2.035	0.034	0.034
$OCHO \rightarrow CO_2 + H^+_{(aq)} + e^-$	-2.612	-2.612	-0.529	-0.529
$HOCHO \rightarrow HOCO + H^{+}_{(aq)} + e^{-}$	1.517	1.517	-0.692	-0.692
$HOCH_2 \rightarrow OCH_2 + H^+_{(aq)} + e^-$	-0.943	-0.943	0.644	0.644
$OCH_2 \rightarrow OCH + H^+_{(aq)} + e^-$	1.157	1.157	-0.706	-0.706
$HOCH_3 \rightarrow OCH_3 + H^+_{(aq)} + e^-$	1.862	1.862	0.699	0.699
$OCH_3 \rightarrow OCH_2 + H^+_{(aq)} + e^-$	-1.416	-1.416	-0.523	-0.523
$H_2O \rightarrow OH + H^+_{(aq)} + e^-$	2.445	2.445	0.723	0.723

 Table 2.2 Reversible potentials for electron-transfer steps and free energy changes for

 non-electron transfer step in solution and on surface.

^a $\Delta_{ads}G$ is replaced by $\Delta_{ads}E$ in LGER theory.



 $OH(ads) + H^+(aq) + e^- \rightleftharpoons H_2O(ads) \qquad U^{\circ}_{rev} = 0.723 V$

Figure 2.3 Different pathways for the methanol oxidation on the Pt(111) surface and predicted reversible potentials, U_{surf}^{rev} , and the reaction energies for combining OH(ads) and CO(ads) and OCH(ads).

Several reaction paths and reversible potentials are in Figure (2.2). On the ideal methanol catalyst each step will have a reversible potential at 0.0 V. Several steps have negative reversible potentials and activation barriers for these oxidations are expected to be small << 0.2 eV. This is because the potential dependencies of the activation energies are as shown in Figure (2.3). This is why steps with negative reversible potentials are unlikely be rate limiting in methanol electrooxidation.



Figure 2.4 Dependency of activation energy on electrode potential.

The indirect route (CO-path) is represented by the solid arrows in Figure (2.2). This path starts with a C-H bond oxidation. The possibility of oxidizing the O-H bond around 0.0 V is unlikely because its predicted oxidation reversible potential is very high, 0.699 V. Wieckowski et al. also suggested the first step in methanol oxidation under electrochemical conditions is the C-H scission.⁶³ From their study using cyclic voltammetry, chronoamperometry, and kinetic analysis, they proposed that the O-H bond is held intact by the hydrophilic/hydrophobic interaction and by the local electric field. However, the calculated reversible potentials show that the OH bond will not be oxidized preferentially to the CH bond at anode operative potential and this makes the argument in Ref 65 superfluous. The HOCH₂ is predicted to be oxidized to HOCH with $U_{surf}^{rev} = 0.083$ V, and to formaldehyde with $U_{surf}^{rev} = 0.644$ V, which is very high. This means relatively little formaldehyde should form. The HOCH is oxidized to HOC with $U_{surf}^{rev} = -0.575$ V and to OCH with $U_{surf}^{rev} = -0.130$ V. Both HOC and OCH have favorable reversible potentials, = -0.252 V and -0.697 V, respectively, for oxidation to CO.

CO formation at low potentials is well known^{38,64} and it is confirmed by these results. CO oxidation requires the presence of oxygen containing species. These could be OH(ads) or O(ads), formed by oxidation of water. However, experiments revealed that OH(ads) forms from water oxidation at potential range of about 0.5 to 0.7,⁵⁷⁻⁶¹ while O(ads) forms from OH(ads) oxidation at higher potential of ≈ 0.8 V on the Pt(111) single crystal electrode surface.⁵⁹ This excludes O(ads) as an oxidant in the potential range of interest. Using Interface 1.0, Anderson and Tian studied O(ads) reduction to OH(ads) at different coverages of H₂O(ads) and OH(ads) on Pt(111). Predicted reversible potentials varied depending on the amount of co-adsorbed H₂O and OH but a value of 0.83 V was calculated when one H₂O molecule was placed adjacent to the O and OH.⁶⁵ Thus the experimental and theoretical findings both exclude the possibility of O(ads) being the source of oxygen for CO oxidation.

If CO and OH combine on the surface forming hydrocarboxyl radical (HOCO) bonded to a Pt atom through C, the reaction is slightly endothermic by (0.195 eV).

Subsequent oxidation to CO₂ has the potential value, $U_{surf}^{rev} = 0.198 \text{ V}$. A pre-wave of CO₂ was observed at 0.15 V during the oxidation of H₂/CO mixture on Pt/C in 0.5 M H₂SO₄.⁶⁶ Another study reported a CO₂ pre-wave at 0.3 V on Pt(111) during the oxidation of CO(ads) in 0.5 M H₂SO₄.⁶⁷ The CO(ads) oxidation pre-wave can be explained by the presence of defect sites on Pt surface where water is oxidized to OH(ads) at less than 0.5 V. The potential for HOCO oxidation is higher than potentials for the steps preceding its formation. It is possible that this oxidation step will have larger activation energy at 0.0 V than the earlier steps will have at this potential. Nevertheless, the overpotential should be dominated by the high potential that is necessary for generating OH(ads).

According to results in Figure (2.2), as the potential is increased through the range where CO(ads) is removed by oxidation, formaldehyde forms from HOCH₂ with U_{surf}^{rev} = 0.644 V. At about the same potential, methanol O-H bond oxidation can occur, leading to methoxy followed by its oxidation to formaldehyde. Methoxy has not been reported under electrochemical conditions. The usual explanation is that the OH bond is not the first one oxidized but perhaps it is oxidized and forms a short-lived intermediate since U_{surf}^{rev} for its oxidation to formaldehyde is -0.523 V. The calculated U_{surf}^{rev} for formaldehyde oxidation to formic acid in a 0.190 eV endothermic surface reaction. Formic acid is a weak acid and it is very weakly bonded to the surface, so some molecules may desorb and some may become a hydrocarboxl radical or a formyloxyl radical. Another possibility is that formic acid desorbs into solution and ionizes to form a formate anion which bonds only weakly to the surface, Table (2.1). Using SEIRA measurements, it was observed that formyloxyl radicals form from formic acid during the

electrooxidation of 0.1 M formic acid on Pt nano particles in 0.5 M H_2SO4 .¹² Similar to the indirect path; this path also requires the presence of OH(ads) species to advance. Formation of CO₂ in the non-CO path occurs at potentials around 0.0 V by the formyloxyl radical route compared to 0.198 V by hydrocarboxyl radical route.

As can be seen from Figure (2.2), potentials for methanol oxidation as far as CO(ads), should take place around 0.0 V. The formation of OH(ads) limits the reaction to a higher potential range. In addition, H_{upd} coverage is high at potentials ≥ 0.0 V and will block methanol from adsorbing. This may explain why some oxidation intermediates are not observed at potential < 0.35,⁴⁰ although our results predict their formation around 0.0 V if the surface were not blocked. At potentials ≤ 0.0 V, H₂ evolution interferes with methanol adsorption.

2.5 Concluding remarks

Our calculations indicate that the indirect pathway is the dominant route for methanol electrooxidation at low potentials. None of the elementary steps, for both CO and non-CO path, is rate limiting. The oxidation might be complete if OH(ads) were formed at low potential. However, Pt(111) is not capable of forming OH(ads) by water oxidation at potentials < 0.5 V. Therefore, Pt(111) does not have characteristics of an ideal catalyst toward methanol electooxidation. Research has been going in the direction of alloying Platinum with other metals to enhance catalyst reactivity.^{68,69}

Chapter 3

Electrochemical Oxidation of Ethanol On

Pt(111)

3.1 Background of electrochemical oxidation of ethanol on Pt(111)

Unlike a fossil fuel, ethanol is a renewable and can be produced from biomass. Compared to methanol, ethanol is less toxic. The specific energy density of ethanol is high (8.0 kWh/kg).⁸ It is liquid, which makes it easy to store and transport. All these advantages make the direct ethanol fuel cell (DEFC) a promising green energy source. However, commercialization of DEFC is hindered by the slow inefficient electrooxidation reaction of ethanol on platinum.

The electrochemical oxidation reaction which takes place at the anode surface in DEFC is:

$$CH_3CH_2OH(aq) + 3H_2O(l) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^-$$
 (3.1)

The reversible potential, U° , is 0.090 V in solution under standard conditions, as calculated from standard thermodynamic data.¹⁴ However, cyclic voltammetry studies indicate that oxidation of ethanol does not occur at potentials below 0.4 V.^{16,70} Even at high potentials, ethanol oxidation in a fuel cell environment does not produce 12 electrons. This is due to the formation of partial oxidation products which are not fully oxidized to CO₂. Lamy et al. used several techniques to detect oxidation products for 0.1 M ethanol in 0.1 M HClO₄, over a Pt/C catalyst.⁷¹ Following six hours of electrolysis at constant potentials, they were able to detect acetaldehyde at 0.35 V and acetic acid at 0.45 V by high performance liquid chromatography (HPLC). Using subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) and single potential alteration infrared spectroscopy (SPAIRS), they detected CO at 0.3 V and CO₂

at 0.6 V over the potential range 0.01 to 1 V. Using in situ infrared spectroscopy (FTIR) and electrochemical measurements, Cantane and Gonzalez identified oxidation products during electrooxidation of several concentrations of ethanol (0.05 to 0.1M) over unsupported Pt particles in 0.1 M HClO₄.⁷⁰ For all concentrations, acetaldehyde was detected at 0.55 V. Behm et al. studied ethanol oxidation on Pt thin film electrode, using a technique combining in situ FTIR spectroscopy with attenuated total reflection (ATR) spectroscopy.⁶⁴ They observed adsorbed acetyl starting to form at 0.3 V in the positive going sweep, and detected also CO(ads) and $CH_x(ads)$ at this potential. Using in situ FTIR spectroscopy and differential electrochemical mass spectroscopy, DEMS, Iwasita and Pastor confirmed the formation of methane and ethane in 6:1 ratio at U < 0.25 V during the negative going sweep which reduced adsorbed species produced at higher potentials by the electrooxidation of 0.1 M ethanol on porous Pt in 0.05 M H₂SO₄.¹² Adzic and Shao used surface enhanced infrared absorption spectroscopy (SEIRAS) with ATR, to identify ethanol oxidation products.⁷² Along with acetyl, CO, and acetaldehyde, acetic acid (in the form of adsorbed acetate) was detected at 0.55 V in their study. The Behm group also detected adsorbed acetate in equilibrium with acetic acid in solution at potentials > 0.5 V.⁶⁴ The acetate was accompanied by CO₂ from oxidation of adsorbed CO. Current measurements did not indicate occurrence of acetic acid and acetate oxidation in the potential range of experiment ≤ 1.3 V.

Based on these experimental observations, a dual pathway mechanism can be assumed for the electrooxidation of ethanol on the Pt(111) electrode surface. One representation of the dual pathway mechanism is: ⁷³

$$CH_{3}CH_{2}OH \rightarrow CH_{3}CHO \rightarrow CH_{3}COOH$$

$$\searrow \qquad \qquad \downarrow$$

$$CO + additional fragments \rightarrow 2CO_{2}$$

$$(3.2)$$

The CO forming pathway becomes active at low potentials, which is where CO(ads) is observed, and is followed by its oxidation to CO_2 . The parallel, non-CO pathway takes place at higher potentials with the formation of CO_2 and stable products, such as acetic acid, which are unlikely to be oxidized further.

The variety of reaction intermediates, the formation of unwanted partial oxidation products, the coexistence of different pathways and, moreover, the presence of C-C bond, make understanding the oxidation mechanism challenging.

Theoretical investigations addressing the electrooxidation of ethanol on Pt electrodes are rare. Dumesic et al. used periodic DFT theory to calculate structures and energies for several adsorbed reaction intermediates that might form during ethanol dehydrogenation on Pt (111) at the vacuum interface.⁷⁴ The C-O and C-C bond cleavage energies and activation energies were calculated. For the most stable structures, it was found that breaking the C-C bonds in ketenyl (OC-CH) had a high activation energy of around 0.95 eV and was relatively exothermic compared to C-C bond cleavage of other intermediates adsorbed on Pt(111). Ketene (OC-CH₂) had an even higher activation energy of 1.34 eV. Similar high C-C scission barriers have been reported in more recent DFT studies using model of the electrochemical interface.⁷⁵ The elementary approach of the Norskov group was used where calculations are done at the potential of zero charge (PZC), that is, there was no potential control, and only the electron reduction reaction, the

reactant energy is shifted by -eU to account for the potential dependence.⁷⁶ The model excluded the electrochemically significant solvation interactions, surface charging, and electrolyte response to surface charging. The C-C bond scission activation energies in these DFT calculations are probably significantly overestimated. Vesselli et al. estimated barriers of 0.26 eV and 0.22 eV for ketenyl and ketene, respectively, on the Pt(111) vacuum interface based on theoretical and experimental considerations.⁷⁷ Such barriers are comparable with electrochemical results.

In this Chapter, possible pathways are analyzed for the 12 electron electooxidation of ethanol on the Pt(111) electrode. Conclusions are based on predicted reversible potentials for surface intermediate steps that were calculated using the linear Gibbs energy relationship (LGER) theory. Three reactions pathways are discussed.

3.2 Theoretical methodology

Reversible potential predictions were obtained with the linear Gibbs energy relationship (LGER) theory which was presented in section 2.2.^{29,48} This theory uses the standard reversible potentials for reactions in bulk solution, U^o , and perturbs them with the difference in adsorption Gibbs energies, *G*, of products, P, and oxidized reactants, Ox, on the electrode surface. This yields prediction for the reversible potentials for reactions at the electrode surface, $U_{\text{surf}}^{\text{rev}}$:

$$U_{\text{surf}}^{\text{rev}} = U^o + \left[\Delta_{\text{ads}}G(\text{Ox}) - \Delta_{\text{ads}}G(\text{R})\right]/nF$$
(3.3)

In this work, the $\Delta_{ads}G$, which are dependent on the electrode potential, are replaced by

 $\Delta_{ads}E$ at the PZC as a model. Values for U^o were calculated using the Interface 1.0 code.^{18, 21} The procedure is as follows:

For the reaction in bulk solution,

$$Ox + e(U) \rightleftharpoons R \tag{3.4}$$

where Ox is the reactant, and R is the product. The Gibbs energies of Ox and R are required and calculated as:

$$G = E + \Omega_{\rm ss,nonel} + \Omega_{\rm is,nonel} - TS_{\rm e} - TS_{\rm i} + H_{\rm vib} - TS_{\rm vib} + \Omega_{\rm mc}$$
(3.5)

where G is the total Gibbs energy for the solute in bulk solution; E is the internal energy; $\Omega_{ss,nonel}$ and $\Omega_{is,nonel}$ are the respective Gibbs energies from non-electrostatic solute-solvent and ion-solute interactions; T is temperature; and S_e and S_i are entropies of the electrons and ions and $H_{vib} - TS_{vib}$ are the vibrational contribution to the enthalpy and entropy, calculated with the Gaussian09 program⁴⁹ and Ω_{mc} is the mass correction term.

The standard reversible potential for the reaction in bulk solution is a function of the Gibbs energies:

$$U^{o} = \{G(\mathrm{Ox}) - G(\mathrm{R})\}/nF - \varphi/F$$
(3.6)

where *F* is the faraday constant, φ is the work function of the standard hydrogen electrode and *n* is the number of electrons transferred, which is one for the intermediate steps considered.

Adsorption internal energies of (Ox) and (R) were calculated as internal energy differences, omitting vibrational zero point energy:

$$\Delta_{ads} E(Ox) = E(Ox(ads)) - E(Surf) - E(Ox)$$
(3.7)

$$\Delta_{ads} E(R) = E(R(ads)) - E(Surf) - E(R)$$
(3.8)

The internal energies for these systems were obtained using Interface 1.0.

In cases of intermediates with two carbon atoms, 1/12 ML coverage was used to minimize interactions among the adsorbates. A three-layer-thick slab was created using a $2\sqrt{3}\times3$ unit cell with 2-dimentional periodic boundary condition, Figure (3.1). The unit cell was made of 36 atoms with 12 in the bottom layer kept frozen and position of the remaining 24 was variationally optimized. For C1 species, 1/6 ML coverage was used and a 3 × 2 unit cell was employed. The theoretically predicted lattice constant value of 4.03 Å was used.²¹ A 3×4×1 grid of k-points was used for the $2\sqrt{3}\times3$ unit cell and $3\times6\times1$ grid was used for 3 × 2 unit cell for a uniform Monkhorst-Pack sampling⁵¹ in the Brillouin-zone.



Figure 3.1 (a) top view of 1/12 ML HOCH₂CH₃(ads) showing $2\sqrt{3}\times3$ translational cell; and (b) side view.

3.3 Adsorption internal energies of ethanol and reaction intermediates on Pt(111)

Like methanol and water, ethanol adsorbs by electron lone-pair donation from oxygen to a Pt atom, bonding on the top site with the C-C bond nearly parallel to the surface. The calculated adsorption energy, -0.253 eV, Table (3.1), is close to those of methanol and water, -0.277 and -0.229 eV, respectively. There are three possibilities for the dehydrogenation: loss of H from (i) the hydroxyl group, (ii) the α -C of ethyl group, and (iii) the methyl group; the last was not calculated. Structures for the intermediates considered are in Figure (3.2).

If ethoxy forms, (i), it is bonded through oxygen (-1.431 eV) with a short Pt-O distance, 2.01 Å, compared to 2.41 Å for ethanol. Loss of H from the α -C gives acetaldehyde. Our calculations show that the most stable site for acetaldehyde at 1/12 ML coverage is bridge with oxygen and carbon bonded to adjacent Pt atoms. The O-C bond is nearly parallel to the surface and the methyl group is tilted away from it.

H loss from the α -C in ethanol, (ii), gives 1-hydroxyethyl (HOCHCH₃) which bonds to a Pt atom through the α -C and the OH and CH₃ groups bend away from the surface and the CO bond length is 1.40 Å. When the second H is removed from the α -C, the product 1-hydroxylethylidene (HOCCH₃) remains on the top site and bond length shortens to 1.31 Å. Loss of H from the OH group now generates acetyl which bonds through the α -C standing upright on a Pt atom with both O and CH₃ group pointing away from the surface and now the C-O bond length is shortened to 1.20 Å. The first H loss

Table 3.1 Most stable adsorption sites, energies of reaction, and bond distances of C-C and C-O bonds of intermediates of ethanol oxidation over the Pt (111) surface. * stands for the atom bonded to the surface. Structures are shown in Figure (3.1) except for *OH and $*OH_2$. H*OCH, O*CH and HO*C have been shown previously in Chapter 2, Figure (2.2).

Species	C-C/Å	C-O/Å	adsorption site	$\Delta_{\mathrm{ads}} E / \mathrm{eV}$
ethanol (H*OCH ₂ CH ₃)	1.530	1.471	top	-0.253
1-hydroxylethyl (HO*CHCH ₃)	1.530	1.397	top	-2.030
1-hydroxylethylidene (HO*CCH ₃)	1.504	1.310	top	-3.232
acetyl (O*CCH ₃)	1.537	1.199	top	-2.358
ketene (O*C*CH ₂)	1.523	1.195	di-σ-bridge	-1.797
ketenyl (O*C*CH)	1.477	1.196	µ-bridge	-3.551
carbon monoxide (*CO)	-	1.176	bridge ^a	-1.640
*OH ₂	-	-	top	-0.229
hydroxyl (*OH)	-	-	top	-1.951
hydrocarboxyl radical (HO*CO)	-	1.204,1.351	top	-2.320
carbon dioxide (CO ₂)	-	1.175,1.175	-	-0.029
СН	-	-	fcc	-6.126
hydroxymethylene (HO*CH)	-	1.385	µ-bridge	-3.105
formyl (O*CH)	-	1.198	top	-2.392

continue

Species	C-C/Å	C-O/Å	adsorption site	$\Delta_{\mathrm{ads}} E / \mathrm{eV}$
acetaldehyde (*O*CHCH ₃)	1.525	1.347	di-σ-bridge	-0.351
hydroxymethylidyne(HO*C)	-	1.342	fcc	-4.342
ethoxy (*OCH ₂ CH ₃)	1.542	1.426	top	-1.431
methyl (*CH ₃)	-	-	top	-2.051
methane (CH ₄)	-	-	-	-0.023
acetic acid (HOOCCH ₃)	1.543	1.209,1.378	-	+0.173
acetate radical (*OCCH ₃ *O)	1.534	1.279,1.280	di-o-bridge	-1.972
acetate anion (OCCH ₃ O ⁻)	1.553	1.274,1.274	di-o-bridge	-0.304 ^b

^a site preference depends on potential and coverage.

^b $\Delta_{ads}G$ was used for this anion.

from the β -C gives ketene (OCCH₂) and loss of a second H gives ketenyl (OCCH) both with C-O bond length of 1.20 Å, almost as short as 1.18 Å for CO(ads). Ketene is bridge bonded through the two carbon atoms with C-C bond parallel to the surface. In ketenyl, the α -C is bonded to a single Pt atom on the top site while the β -C is in the bridge site of two neighboring Pt atoms. As Table (3.1) shows, C-C bond lengths for the adsorbed intermediates range from 1.48 Å to 1.54 Å. Products of C-C bond breaking in their adsorbed species are strongly adsorbed, bonding through the carbon atoms with strengths in the order, CO < CH₃ < CH. The last, with adsorption energy of -6.126 eV, might be a poisoning species to reactions on the electrode surface. Methane and CO₂ are weakly adsorbed, -0.023 and -0.029 eV, respectively.

Other intermediates can include hydroxylmethylene, HOCH, possibly formed by combining OH(ads) and CH(ads). Loss of a hydrogen gives HOC or OCH and finally CO when the last H is removed. Hydrocarboxyl radical, HOCO, and acetic acid, HOOCCH₃, are produced by reaction of certain adsorbed oxygen-containing intermediates with OH(ads). The hydrocarboxyl bonds through the carbon with the hydrogen pointing toward the surface. The adsorption energy of acetic acid is positive, meaning it is repelled by the surface. On the other hand, the acetate radical, OOCCH₃, is strongly bonded to the surface through both oxygen atoms and it stands upright over two adjacent Pt atoms with the methyl group pointing away from the surface. In comparison, the acetate anion, OOCCH₃⁻, is weakly adsorbed. Bonding energies of the adsorbed intermediates are all in Table (3.1).









Figure 3.2 Off normal view of the optimized structures for ethanol and its oxidation intermediates on Pt(111) surface. (a) ethanol;(b) ethoxy; (c) acetaldehyde; (d) 1-hydroxylethyl; (e) 1-hydroxylethylidene; (f) acetyl; (g) ketene; (h) ketenyl; (i) acetic acid; (j) acetate radical and anion; (k) methyl and (l) methane.

3.4 Reversible potentials for elementary steps in the ethanol oxidation reaction

In Chapter 2 we made the assumption that the activation energies for adiabatic electron and proton transfers to carbon in methanol and its derivatives are low, a proposal based on previous predictions made in our lab for elementary steps in reduction of oxygen species adsorbed on Pt electrodes. ⁵²⁻⁵³ The same assumption was used here.

A check of the accuracy of the theory for determining reaction Gibbs energies, was made by comparing the predicted potential for the 12 electron oxidation of ethanol to CO_2 , eq (1.1), and that obtained using tabulated standard thermodynamic data, which is 0.090 V. The predicted potential for the reaction is -0.004 V; 0.094 V less than the thermodynamic value, a good agreement.

The DFT study of Dumesic et al. indicated increasingly higher stabilities for species made by dehydrogenations of α -C-H bonds compared to the ones made by β -C-H bond scissions.⁷⁴ The study also showed that the activation energy for C-C bond breaking is lower than for C-O bond breaking in ethanol and its derivatives. As discussed in the introduction, intermediates such as acetyl, methane, acetaldehyde and acetic acid, have been observed in experiments. This supports the consideration of α -C-H bond scission in preference to other reactions in the early oxidation steps. The present study ties together past experimental and theoretical findings into a coherent electrochemical picture.

Experimental standard reversible potentials given in Table (3.2) are unknown for most of the intermediate reactions and so were calculated. By combining them with the adsorption energies in Table (3.1) in the LGER model, the reversible potentials U_{surf}^{rev}

shown also in Table (3.2) were calculated. A determination of the overall 12 electron oxidation potential can be made by summing calculated reaction Gibbs energies for all steps, and the result is, -0.004 V, which equals the value using the calculated Gibbs energy difference for eq (3.1), as it should.

The 1.167 eV energy loss during dissociation of the C-C bond in the adsorbed ketenyl (see below), would increase the 12 electron reversible potential by 0.097 V. This effective reversible potential cannot be considered as the only contribution to the high overpotential. For further discussion of the concept of effective reversible potential, see Ref 29.

Reaction	$\Delta \boldsymbol{G^{o}}_{\mathrm{sol}}$ / eV	<i>U</i> % V	^a $\Delta G_{ m surf}$ / eV	U ^{rev} /V
$HOCH_2CH_3 \rightarrow HOCHCH_3 + H^+(aq) + e^-$	1.677	1.677	0.100	-0.100
$HOCHCH_3 \rightarrow HOCCH_3 + H^+(aq) + e^-$	0.928	0.928	-0.274	-0.274
$HOCCH_3 \rightarrow OCCH_3 + H^+(aq) + e^-$	-0.817	-0.817	0.057	0.057
$OCCH_3 \rightarrow OCCH_2 + H^+(aq) + e^-$	-0.605	-0.605	-0.044	-0.044
$OCCH_2 \rightarrow OCCH+H^+(aq)+e^-$	1.893	1.893	-0.139	-0.139
$OCCH \rightarrow CO + CH$	3.048	-	1.167	-
$\rm CO + OH \rightarrow HOCO$	-1.076	-	0.195	-
$HOCO \rightarrow CO_2 + H^+(aq) + e^-$	-2.093	-2.093	0.198	0.198
$CH + OH \rightarrow HOCH$	- 4.874	-	0.098	-
HOCH \rightarrow OCH + H ⁺ (aq) + e ⁻	-0.843	-0.843	0.130	0.130
OCH \rightarrow CO + H ⁺ (aq) + e ⁻	-1.449	-1.449	0.697	0.697
$OH + CO \rightarrow HOCO$	-1.076	-	0.195	-
HOCO \rightarrow CO ₂ + H ⁺ (aq) + e ⁻	-2.093	-2.093	0.198	0.198
$H_2O \rightarrow OH + H^+(aq) + e^-$	2.445	2.445	0.723	0.723

Table 3.2 Calculated Gibbs reaction energies, ΔG°_{sol} and ΔG_{surf} , and calculated reversible potentials, U° and U_{surf}^{rev} , according to the LGER theory surface.

continue

Reaction	$\Delta G^{o}_{sol} / eV$	<i>U%</i> V	^a ∆G _{surf} / eV	U ^{rev} /V
HOCH \rightarrow HOC + H+(aq) + e-	0.662	0.662	-0.575	-0.575
HOC \rightarrow CO + H ⁺ (aq) + e ⁻	-2.955	-2.955	-0.252	-0.252
$HOCH_2CH_3 \rightarrow OCH_2CH_3 + H^+(aq) + e^-$	2.159	2.159	0.981	0.981
$OCH_2CH_3 \rightarrow OCHCH_3 + H^+(aq) + e^-$	-1.581	-1.581	-0.501	-0.501
$OCHCH_3 \rightarrow OCCH_3 + H^+(aq) + e^-$	1.210	1.210	-0.797	-0.797
$OCCH_3 \rightarrow CO + CH_3$	0.235	-	-1.098	-
$\mathrm{CH}_3 + \mathrm{H}^+(\mathrm{aq}) + \mathrm{e}^- \rightarrow \mathrm{CH}_4$	1.981	1.981	-0.070	-0.070
$OCCH_3 + OH \rightarrow HOOCCH_3$	-3.986	-	0.323	-
$HOOCCH_3 \rightarrow OOCCH_3 + H^+(aq) + e^-$	1.888	1.888	-0.084	-0.084
$HOOCCH_3 \rightarrow OOCCH_3 + H^+(aq)$	0.323	-	-	-
$OOCCH_3 \rightarrow OOCCH_{3+} e^-$	1.565	1.565	-0.103	-0.103

^a $\Delta_{ads}G$ is replaced by $\Delta_{ads}E$ in LGER theory.

A network of the elementary steps is presented in Figure (3.3). As can be seen, some steps take place at potential < 0.0 V. The activation energies for these reactions should extrapolate to very low values at potentials ≥ 0.0 V due to the potential dependencies of redox activation energies discussed earlier.^{52,55}

As can be seen from Figure (3.3), the reversible potential for the α -C in ethanol to lose H by oxidation, forming 1-hydroxylethyl, is much lower than that for oxidizing the O-H bond to form ethoxy. Therefore, in the low potential range, C-H will be oxidized and O-H will not. The next step proceeds by oxidizing the second H from the α -C at a very low potential. H can then be oxidized from –OH with $U_{surf}^{rev} = 0.057$ V to form OCCH₃(ads), acetyl. From here, three reaction routes were considered.

The first route was to dissociate the C-C bond, which was exothermic by -1.098 eV. This produced CO(ads) and $CH_3(ads)$. The latter has a reduction potential of -0.070 V for forming methane.

The second route was oxidation of H from the β -C, which produced OCCH₂(ads), ketene, with $U_{surf}^{rev} = 0.044$ V. Oxidation of the second H formed OCCH(ads), ketenyl, with $U_{surf}^{rev} = 0.139$ V. The C-C bond scission there gives CO(ads) and CH(ads) and is exothermic by -1.167 eV. According to Ref 77, this C-C bond dissociation also has a low activation energy. Hence, at low potential, there are two slow indirect routes can occur in parallel, the first one generating CO₂ and CH₄, and C₂H₆ by dimerization of two CH₃ radicals, and the other leading ultimately to CO₂. The conclusions from the theoretical calculations are in agreement with experiment.^{64,75}



Figure 3.3 Pathways for ethanol oxidation on the Pt(111) surface with reversible potentials, $U_{\text{surf}}^{\text{rev}}$, for electron transfer steps and reaction energies for non-charge transfer bond dissociation and formation steps. * does not adsorb.

The third possible route for acetyl uses OH(ads) which forms at ≈ 0.6 V from H₂O oxidation. Reacting acetyl with OH(ads) to form acetic acid is calculated to be 0.323 eV endothermic, suggesting this pathway is slow. The acetic acid desorbs according to the calculations, entering the bulk solution. A small amount will be ionized, forming solvated acetate anions. These anions bond to the surface by 0.304 eV which will force the equilibrium strongly toward dissociation. The adsorbed anions are oxidized to adsorbed radicals with $U_{surf}^{rev} = -0.103$ V. Another possibility for acetic acid is to be directly oxidized to an adsorbed acetate radical, $U_{surf}^{rev} = -0.084$ V. Acetic acid and adsorbed acetate were detected at potentials > 0.5 V, which confirms the necessity of OH(ads) for their formation.^{70,71} According to the work of Behm et al., acetic acid cannot be oxidized in potential range of 0.06 to 1.3 V and acetate species are adsorbed in equilibrium with acetate anions in solution.⁶⁴ This is consistent with the theoretical findings.

When OH(ads) is present, it reacts with CO(ads) in a 0.195 eV endothermic reaction, forming hydrocarboxyl radical HOCO(ads), which oxidizes to CO₂(g) with $U_{\text{surf}}^{\text{rev}} = 0.198$ V. A CO oxidation pre-wave in acid electrolyte was observed at 0.15 V⁶⁶ and another at 0.3 V⁶⁷ which could be a result of OH(ads) formation at low potential at defect sites on the electrode surface. Strong bonding of OH to defect sites would drive its formation at low potentials.

The combination of CH(ads) with OH(ads) to form HOCH is 0.098 eV endothermic. The C-H bond is oxidized forming HOC with $U_{surf}^{rev} = -0.575$ V and this is oxidized to CO at $U_{surf}^{rev} = -0.252$ V. Alternatively, the OH bond can be oxidized first with $U_{surf}^{rev} = -0.130$ V followed by the C-H bond oxidation, $U_{surf}^{rev} = -0.697$ V. Nothing appears to favor one path over the other. According to the calculated results, as the electrode potential reaches 0.581 V, formation of acetaldehyde becomes possible by the O-H bond scission in 1-hydroxylethyl. Acetaldehyde was detected at 0.55 V and 0.35 V experimentally.^{68,69} Once it forms, acetaldehyde will be oxidized to acetyl which can be oxidized by the three different pathways just discussed earlier. Desorption of acetaldehyde as a soluble intermediate may be possible as it is weakly adsorbed to the surface. Acetaldehyde formation via ethoxy oxidation is unlikely to occur since U_{surf}^{rev} for ethoxy formation is 0.981 V.

3.5 Possible reasons for the low efficiency of ethanol oxidation on Pt(111)

- Initially formed CO(ads) and CH(ads) cannot be oxidized and removed at potentials < 0.5 V due to the absence of OH(ads). At potentials > 0.5 V, the OH(ads) forms and the CO(ads) can be oxidized to CO₂(g), which desorbs leaving free sites available for ethanol adsorption, and unwanted methane, acetic acid and adsorbed acetate which are reaction dead ends. Acetate is also a site blocker.
- C-C bond dissociations in acetyl and the later oxidation intermediate, ketenyl, are exothermic by 1.10 and 1.17 eV, respectively, increasing the 12 electron reversible potential to an effective value of ≈ 0.19 V. At potentials greater than 0.19 V, reactions by either path seem possible. When the C-C bond breaks in ketenyl, adsorbed CO and CH are formed. The CH(ads) combines

with OH(ads) to form HOCH and three more oxidations yield CO_2 but the electrode potential must be high enough for OH(ads) formation. In the second route, breaking the C-C bond in acetyl leads to the formation of CO(ads) and CH₃(ads). The latter can be reduced at low potential to CH₄(g), and CO oxidation requires OH(ads) which forms at higher potential.

Most of the calculated reversible potentials in the present study are negative or slightly positive, i.e., in the underpotential deposited hydrogen (H_{upd}) region. Ethanol oxidation intermediates have never been detected at potentials < 0.3 V.⁶⁴ At such low potentials, H_{upd} is blocking the surface. At 0.3 V less than 10% of surface sites are blocked by H_{upd}.⁷⁸ The role of H_{upd} as surface poison is also discussed in Ref 64.

3.6 Concluding remarks

The results of this study confirm the well-known role of CO(ads) as poisoning species for the Pt(111) electrode at potentials < 0.5 V and the importance of OH(ads) formation at low potentials to oxidize CO to CO₂, leading to more complete oxidation with low overpotential. Calculations also rationalize the formation of carboxylic intermediates, acetic acid and acetate, at high potentials by the need to OH(ads) for their formation, the latter does not form below < 0.5 V.

The ideal catalyst should be capable of oxidizing $H_2O(l)$ at low potentials close to 0 V. Not only that, but it has to have a smaller range for H_{upd} than that on Pt(111), so it would not inhibit ethanol adsorption to the electrode surface in that range.

It has been believed that the C-C bond cleavage in ethanol is the rate limiting step for ethanol electrooxidation. DFT calculations in Refs 74 and 75 seem to support this, but experimental and theoretical results in Ref 77 show this conclusion is incorrect, Further support lies in the experimental observation of CO(ads) at low potentials. We propose the exothermicity results in an effective reversible potential of ≈ 0.19 V, but this is not the cause of the high overpotential even though the ideal catalyst will display less exothermic C-C bond breaking. Clearly, Pt (111), as is suggested by our calculations, is not an ideal catalyst for ethanol oxidation. Efforts on alloying Platinum with other metals have shown some improvment.^{79,80}

Chapter 4

Using Gibbs Energies to Calculate the

Pt(111) H_{upd} Cyclic Voltammogram

4.1. Introduction

Standard reversible potentials, U^0 , are those potentials which apply to reduction reactions where reactants and products are in their standard states. These potentials are related to the standard reaction Gibbs energy, $\Delta_{\text{react}}G^0$:

$$U^{0} = -\Delta_{\text{react}} G^{0} / (nF) \tag{4.1}$$

In this equation *n* is the number of electrons transferred and *F* is the Faraday constant. If U^0 is not easily measured electrochemically, it may be determined using eq (4.1) when $\Delta_{\text{react}}G^0$ is known by means of thermodynamic data found by experiment or theory.

Electrodes in a cell generally are not totally inert when participating in electron transfer reactions. The single crystal Pt(111) electrode in a standard hydrogen half-cell reduces some $H^+(aq)$ as the potential is swept from the 0.6 V - 0.4 V double layer region toward 0.0 V reversible hydrogen half-cell potential. The reduction on the 0.4 V - 0.0 V region deposits H(ads) on the electrode surface, which is usually called underpotential deposited hydrogen, or H_{upd} . When, during the sweep, 0.0 V is reached the reduction forms hydrogen gas:

$$H^{+}(aq) + e^{-} = \frac{1}{2} H_2(g)$$
 (4.2)

Prior to reaching 0.0 V, if the potential is held at some value in the 0.4 V to 0.0 V range there will be an equilibrium surface coverage of H(ads). The coverage starts at 0.0 monolayers (ML) and increases as the potential is decreased toward 0.0V. However, when the platinum electrode is immersed in uniform acid solution and H_2 is not bubbled over it, then, since H_2 in the ambient is at low pressure, the onset potential for H_2 formation is given approximately by the Nernst equation,

$$U = 0.0 - 0.059 \log \{ P(H_2)^{\frac{1}{2}} [H^+] \}$$
(4.3)

and is greater than 0.0 V. Measured onset potentials are around 0.05 V.^{81,82}

Voltammograms show current densities as functions of electrode potential when the scan rate is constant and for the (111), (100) and (110) surfaces, they are reversible at typical scan rates. In the following, the potentials are referred to the reversible equilibrium state and thus might be labeled as U_{rev} , but the subscript will be dropped in most of what follows. By assuming that the total charge passed in a branch of a cyclic voltammogram is linearly proportional to the coverage of upd species, it is easily shown that the current density at potential U is:

$$i(U) = \pm KQ_{\max} \,\mathrm{d}\theta(U)/\mathrm{d}U \tag{4.4}$$

where *K* is the constant scan rate in mV/s, Q_{max} is the maximum coverage achievable, and $d\theta(U)/dU$ is the slope of coverage with electrode potential. The + and – signs correspond to the oxidation and reduction waves, respectively. The challenge to applying eq (4.4) is calculating the dependence of coverage of H(ads) on electrode potential. The purpose of this study is to apply a self-consistent theory for the electrochemical interface, using the code Interface 1.0, to calculate $d\theta(U)/dU$ and predict the *i*(*U*) voltammogram for the Pt(111) electrode. The (111) surface of platinum presents the simplest cyclic voltammogram in the upd potential region, with a broad hump in the oxidation and reduction potential directions, which means that the $d\theta(U)/dU$ factor in eq (4.4) approaches zero at the onset potential for upd hydrogen and as maximum coverage is
reached, but is nearly constant over the broad hump range, and there is no contribution form H₂O(1) oxidation to OH(ads). Voltammograms for the (100) and (110) surfaces are complex, with multiple peaks,^{81,82} which means that there is more coverage-dependent variability in the slopes of $d\theta(U)/dU$ for these surfaces, and there are contributions from water oxidation to form OH(ads) in the H_{upd} potential ranges for the (100) and (110) surfaces.

5.2 Theoretical methodology

The Interface 1.0 code^{18,21} was used. This is a program for density functional calculations that employs atomic orbitals and atomic pseudopotentials. As in past studies with Interface, we used the RPBE functional.¹⁷ In this work the two-dimensional band option was employed with adsorbates and electrolyte on one side of a three-atom thick slab of platinum atoms representing the electrode and vacuum on the other side. In two-dimensional density functional theory, the potential of the model electrode on the standard hydrogen electrode scale is easily evaluated as

$$U = -(E_{\rm f} + \varphi)/e \tag{4.5}$$

where $E_{\rm f}$ is the calculated Fermi level energy and φ is the calculated work function of the standard hydrogen electrode, determined to be 4.43 eV in the interface calculation, and e is the electron charge unit. The potential is changed by adding or subtracting electronic charge on the translational unit cell. The counter charge is in a polarized electrolyte composed of 1.0 M 3.0 Å diameter positive and negative spherical charges and their

density distribution is optimized using a modified Poisson-Boltzmann theory. The electrolyte also contains the dielectric continuum, which is a model for the implicit inclusion of bulk water. Water molecules that bond strongly with adsorbed or solution phase species by hydrogen-bonding or lone-pair donation are added to the calculations and the dielectric continuum is maintained in the model when this is done. Complete details are in Refs 18 and 21.

We used a three-Pt layer slab with the bottom layer (on the vacuum side) atoms held rigidly in the calculated bulk structure with lattice constant 4.03Å.²¹ Positions of the platinum atoms in the central layer and the top layer (on the solution side) were variationally optimized in all calculations. Studied hydrogen atom coverage spanned from 1/12 monolayer (ML) to greater than 1.0 ML.

It is necessary to establish the surface adsorption site for upd H for our theoretical study. From the experimental side, in 1994 Ogasawara and Ito found evidence by in situ infrared reflection adsorption spectroscopy that at the electrochemical interface upd hydrogen is on terminal site, atop a single Pt atom on the (100) and (110) surfaces, but on the (111) surface terminal bonded H was not seen.⁸³ However, shortly thereafter a sum-frequency generation determination of vibrational spectra of H at the electrochemical interface by Tadjeddine and Peremans gave evidence that in the upd potential range H is adsorbed on the atop site.⁸⁴ It is still uncertain which structure for upd H on Pt(111) is correct and for a recent discussion of this and the overall issue of upd hydrogen the reader is referred to the review of Jerkiewicz.⁸⁵

The structure results for upd H on Pt(111) are also mixed from the theoretical side. In the case of the vacuum interface, different computational methods seem to agree that the differences in energies between 3-fold fcc, 3-fold hcp, 2-fold bridging, and 1-fold atop sites are small.⁸⁶ In the literature reported in Ref 86, some DFT slab-band calculations for Pt(111) found the atop site to be most stable, some the fcc site, and one favored the bridge site. Some of these calculations showed stronger adsorption at the higher of two coverage models studied, which implies such models will not be able to account for the smooth cyclic voltammograms in the upd H potential range on Pt(111). This is likely because the interaction parameter of the Frumkin isotherm is positive,⁸¹ and further analysis in Ref 81 yielded the coverage dependence of the adsorption enthalpy, which showed interactions between adsorbed H to be repulsive.

Calculations for the electrochemical interface including the double layer are small in number. Hamada and Morikawa developed a model to calculate the potential dependence of the Pt-H vibrational frequency.⁸⁷ In their DFT slab-band calculations they included variable electric fields, variable degrees of H(ads) coverage, and variable amounts of explicit water molecules. With just the field added, the fcc site was favored for different coverage models. But, with water molecules added, structures were found in which the 1-fold atop site was the most stable adsorption site for H.

An earlier computational approach to predicting the cyclic voltammogram from adsorption energies is that of Norskov and coworkers who added ad hoc contributions to a DFT slab-band vacuum interface model to calculate H adsorption Gibbs energies.⁸⁸ In their model, H(ads) was placed in the fcc site favored by vacuum interface calculations and the thermal and entropy terms added to the calculated adsorption internal energies

were estimated using calculated vibrational energy levels. Adsorption Gibbs energies were obtained for different degrees of coverage, all at the potential of zero charge, meaning the effect of electrode charging on the strength of the Pt-H bonds was nil in the model. No double layer or field were employed and the potential dependence was taken to be linear in the calculated Gibbs adsorption energy of $\frac{1}{2}H_2(g)$, $\Delta G = \Delta G^0 + eU$, with the value of zero when $\Delta G = \Delta G^0 = 0.0$. In their model the adsorption Gibbs energies were calculated to decrease linearly with increasing coverage of H(ads) up to 1.0 ML, showing Frumkin behavior. They added a Langmuir isotherm contribution due configurational entropy to the Gibbs energy:

$$-T\Delta S_{\rm conf}\left(\theta\right) = -Tk_{\rm b}\ln\left[(1-\theta)/\theta\right] \tag{4.6}$$

Using this and the calculated $U(\theta)$ data, they determined $d\theta(U)/dU$ for use in eq (4.4) and thereby obtained qualitative fits to an experimental cyclic voltammogram for upd H on Pt(111).

5.3 Results and discussion

In this study we used Interface to calculate Gibbs adsorption energies for H as functions of its coverage on Pt(111) at 298.15 K. Gibbs and internal energies for H(ads) on the 1-fold atop site were more stable than the fcc site over the potential range studied. We used eleven different coverage models, with ten of the structures shown in Figure (4.1). The translational cells are outlined in the figure and the number of atoms used is shown. For the 1/12 ML coverage shown coverage a 36 Pt atom translation cell was required and for 1/6, 1/3, $\frac{1}{2}$, 2/3, 5/6 and 1 ML a 18 Pt atom cell was used. This sequence was employed to generate coverage-dependent potentials over increments of 1/12 ML and 1/6 ML. For the 1/8 ML coverage shown a 24 Pt atom cell was required and for the $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ and 1 ML sequence a 12 Pt atom cell was used.

We employed the dielectric continuum model and the modified Poisson-Boltzmann theory without explicit water molecules. Water molecules interacted weakly with adsorbed H atoms and surface platinum atoms. This is a case where the dielectric continuum model is adequate and including them and optimizing their structures would have greatly increased computational time.



Figure 4.1 Top view of various structures of H adsorption on Pt (111) surface arranged from low to high coverage (ML) and labeled a through j. Translational cells and number of atoms are shown for all but 1.0 ML coverage.

The reversible potentials for incremental increases in H(ads) coverage were calculated as the crossing points for the Gibbs energies of reactants and products, as shown for example in Figure (4.2) for going from 1/6 to 1/3 ML. The resulting reversible potential was assigned to the average H(ads) coverage used in its determination. Interestingly, the G versus U curves in this and the other figures (not shown) are well fit by second order polynomials and the vertical distances between the curves, $G_{ox}(U)$ - $G_{\rm red}(U)$, are nearly linear in $U - U_{\rm rev}$. This is the consequence of a the functions $[G_{\rm ox}(U) - U_{\rm rev}]$ U] being only a little perturbed in shape when small additional amounts of H(ads) are deposited on the surface. Table (4.1) shows the calculated reversible potentials and the coverage pairs and structure patterns used in calculating them. All of the resulting potentials are plotted as a function of coverage in Figure (4.3), but with U and $\theta(U)$ as the ordinate to make it easy to visualize the slope $d\theta(U)/dU$ for use in eq (4.4). A third order polynomial curve is fit to the data so that the derivative can be determined analytically from the fit. It is seen that over the potential range 0.0V to 0.25 V, the coverage goes from 0.0 ML to an upper limit of about 0.9 ML.



Figure 4.2 At reversible potentials, U_{rev} , reactant and product Gibbs energies are equal.

**	<u>^</u>	2	
$U_{\rm rev}$	$ heta_{ m oxd}$	$ heta_{ m red}$	patterns
0.032	5/6	1	j,1
0.048	2/3	5/6	h, j
0.146	1/2	2/3	f, h
0.139	1/3	1/2	e, f
0.155	1/6	1/3	c, e
0.212	1/12	1/6	a, c
0.015	3/4	1	i, 1
0.088	1/2	3/4	g, i
0.141	1/4	1/2	d, g
0.200	1/8	1/4	b, d
0.209	0	1/8	0, b
0.235	0	1/12	0, a

Table 4.1 Calculated reversible potentials, U_{rev} , using the method of Figure (4.2). θ_{oxd} and θ_{red} are the initial and final H coverages in the patterns.

Some points in Figure (4.3) are further from the third-order fitting than others. At this time no rationalization for these deviations is evident. As examination of Figure (4.1) will show, the adsorption patterns chosen for each coverage are constrained by the sizes of the translational cells used and so are not well randomized. It is expected that by the use of very large translational cells and resulting energies for a given coverage a more random most stable pattern would be found. One step further in accuracy could be to use a Boltzmann distribution at the ambient temperature over many such patterns. In the high and low coverage limits the potentials may be more accurate because the sparse H(ads) and H(ads) vacancies are well separated. Finally, weak interactions of water molecules may exert subtle influences.



Figure 4.3 Calculated H coverage vs. Pt(111) electrode potential excluding Langmuir configurational entropy contribution, based on data in Table (4.1).

The potential span of Figure (4.3) is too narrow to produce the experimental upd H voltammograms in which H appears on the surface at about 0.4 V during a negative voltammetric sweep from the double layer potential region, and the last remnant departs at about 0.4 V during the oxidation sweep. For each point of the θ versus U curve in Figure (4.2) we may write:

$$\Delta G(\theta) = -FU(\theta) \tag{4.7}$$

Adding the configutational entropy contribution to the Gibbs energy, eq (4.6), gives a new equation for potential,

$$U(\theta) = -\Delta G(\theta)/F + [Tk_b/F] \ln[(1 - \theta)/\theta]$$
(4.8)

The Langmurian contribution broadens the coverage versus potential curve so that it takes the new form in Figure (4.4), with the two highest coverage points are shifted to negative potentials. Table (4.2) contains the data plotted in Figures (4.3), (4.4), and (4.5).

In Figure (4.5) the fitted curve extends to the region of zero slope, about -0.1V. This curve is converted into a cyclic voltammogram by evaluating $d\theta(U)/dU$ as the derivative of the analytic third order fitting curve and multiplying by the 50 mVs⁻¹ scan rate, and by $Q_{\text{max}} = 210 \,\mu\text{Ccm}^{-2}$. The predicted voltammogram is in Figure (4.6). For full monolayer coverage of Pt(111), Q_{max} would be 240 μ Ccm⁻², but in their combined cyclic voltammetric and chronoamperometric study Strmcnik et al. measured the lower value.⁸² They were able to do this by measuring the H adsorption isotherm to about -0.1 V. Their reconstructed cyclic voltammogram extended down to -0.1 V and at 0.05 V, where H evolution commences, the surface coverage was only about 2/3 ML. Our calculated coverage at 0.05 V, taken from Figure (4.5), is 0.72 ML, in close agreement. Our



Figure 4.4 Calculated H coverage vs. Pt(111) electrode potential including Langmuir configurational entropy contribution.



Figure 4.5 Calculated H coverage vs. Pt(111) electrode potential including Langmuir configurational entropy contribution and extended to negative potentials. Data points are numbered in connection with Table (4.2).

 U_{rev} - $RT\Delta S_{\text{conf}}/F$ coverage (θ) $U_{\rm rev}$ point 1 0.917 0.032 -0.029 0.750 0.048 2 0.0198 0.583 0.146 3 0.1378 0.417 0.139 4 0.148 5 0.25 0.155 0.183 0.125 0.212 6 0.262 0.875 0.015 -0.035 7 0.625 0.088 8 0.0749 9 0.375 0.141 0.1549 0.188 0.200 10 0.238 0.062 0.209 11 0.2648 0.042 0.235 12 0.316

Table 4.2 Values of H(ads) coverage used in Figures (4.3 - 4.5) and corresponding reversible potentials energies for reduction from interface calculations and with $T\Delta S_{conf}$ included.



Figure 4.6 Predicted cyclic voltammogram at 298.15 K.

calculated maximum coverage is 0.91 ML, taken from Figure (4.5), is in close agreement with 210/240 = 0.875 ML as estimated by Strmcnik et al. The maximum current density we calculate, taken from Figure (4.6), is 32 μ Acm⁻², which is between the values 27 μ Acm⁻² which we estimate from Figure (4.2b) in the paper by Strmcnik et al. and 34 μ Acm⁻² which we estimate from Figure (4.1) in the paper by Gomez et al.⁸¹

To illustrate the agreement between our predicted voltammogram and the one in Figure (4.2 b) by Strmcnik et al., we have superimposed the two in Figure (4.7). The authors did not specify the temperature of the measurements, which was presumably close to 298 K. Gomez et al. illustrated the dependence of voltammogram shape on temperature in their Figure (4.1), where it may be seen that going up to 25 C higher or lower than ambient makes small graphical changes but those changes do allow the determination of thermodynamic adsorption entropy and energies. Therefor it is concluded that the agreement with regard to width and height between the predicted voltammogram and the measured ones in Refs 81 and 82 will not be graphically affected by changes in temperature of this magnitude.



Figure 4.7 Superposition of voltammogram copied from Figure (4.2b) in Ref 82 on the predicted result in Figure (4.6) (black curves). The red points are the extended voltammogram obtained from chronoamperometric experiments. The vertical grey line reaches zero current density at the experimental onset potential for hydrogen evolution. The blue dots are a theoretical projection based on a total coverage corresponding to 240 μ Ccm⁻² total charge or 1.0 ML H(ads) final coverage.

4.4 Concluding Remarks

Calculated reversible potentials for a limited sampling of surface coverage and adsorption patterns for H(ads) in Pt(111) can parameterize eq (4.4) to predict the voltammogram as shown here and also in the somewhat less accurate result reported in Ref 88, where a simpler model for calculating Gibbs energies was used. There is need for improvement in the broad region of high current density where the predicted current density is not constant enough. This disagreement is due to the noticeable inflection in the middle of the calculated coverage versus potential graphs, much of which is a consequence of adding the Langmuirian $-T\Delta S_{conf}$ contribution to the Gibbs energy. For better agreement with experiment, the curves need to be closer to linear in this region, meaning the change in potential should be linear in changes in coverage. At this time we do not know what it is about the experimental system that achieves such linearity, whether the formula for the $-T\Delta S_{conf}$ contribution needs to be modified to apply only at high and low coverage, or if there is another explanation.

The Pt(100) and (110) surfaces present H_{upd} voltammograms with greater complexity. One difference from the (111) case is the interference of OH(ads) formation currents from the oxidation of H₂O(l) with the H(ads) currents.^{81,89} This was not an issue for the Pt(111) surface studied here, but for the other two surfaces the higher potential regions where H(ads) is deposited has enhanced current density in the voltammograms. On the (100) surface there is a dip in current density at around 0.2 V.^{81,82} In this region $d\theta(U)/dU$ must decrease to zero. Around 0.4 V there is a two-peaked hump about 0.2 V wide which is broadened slightly by OH(ads) formation currents. On the Pt(110) surface there are two sharp peaks. Sharp peaks suggest rearrangement of H(ads) to new adsorption patterns when certain coverage is achieved as the potential cycles, that is, they suggest phase transitions. Such transitions would be caused by potential-dependent adsorption internal energies (bond strengths) and reorganizational entropies of the hydrogenated surface and of the double layer water molecules. A complete understanding has not yet been achieved. For further discussion the reader is referred to the cited literature.^{81,82,85,89.}

Chapter 5

CO Formation from oxidation of formyl

on Pt(111) electrode

5.1 Introduction

Carbon monoxide has received special attention in surface electrochemistry research as a poisoning species on anodes in hydrogen fuel cells and as an overpotential inducing intermediate in alcohol fuel cells. Only at potentials more positive than 0.5 V does OH(ads) start to form and participate in oxidation of CO(ads) to CO₂. This causes approximately 0.5 V overpotential for hydrogen anodes and similar overpotentials for methanol and ethanol anodes.

The formation of CO from methanol and ethanol was discussed in Chapters 2 and 3 and reversible potential for its formation was calculated using the linear Gibbs energy relationship (LGER).²⁹ In this Chapter, we calculate the reversible potential for CO formation from formyl using accurate Gibbs energies calculated with the Interface 1.0 code.^{18,21} The reaction is:

$$HCO(ads) \stackrel{\leftarrow}{\rightarrow} H^+(aq) + CO(ads) + e^-(U_{rev})$$
(5.1)

where U_{rev} is the reversible potential for the reaction on the surface. To find U_{rev} reactant and product Gibbs energies are needed.

5.2 Theoretical methodology

Calculations of Gibbs energies were performed using two dimensional density functional band theory option of the Interface 1.0 program. The electrolyte was included and its ion distribution functions were calculated using a modified Poisson-Boltzmann theory (MPB). Solvation effects were calculated by the dielectric-continuum model with water molecules added when needed for modeling strong hydrogen bonds to solute and adsorbed molecules. In interface 1.0, the electrode potential is calculated from Fermi level as follows:

$$U = -(E_f + 4.43 \text{eV})/nF$$
(5.2)

where $E_{\rm f}$ is the Fermi energy calculated for the slab, 4.43 eV is the previously calculated work function of the standard hydrogen electrode²¹ and U is potential on the SHE scale. The surface potential is changed by adding or subtracting charge to the translational unit cell and a counter charge distribution in the double layer is determined self-consistently using a modified Poisson-Boltzmann theory within a dielectric continuum model.

In the theory, the free energy is given by:

$$G = K + E_{\rm xc} + E_{\rm es} + \Omega_{\rm ss,nonel} + \Omega_{\rm is,nonel} - TS_{\rm e} - TS_{\rm i} + H_{\rm vib} - TS_{\rm vib} + \Omega_{\rm mc}$$
(5.3)

where *K*, E_{xc} , and E_{es} are the kinetic, exchange-correlation, and electrostatic energies, respectively; $\Omega_{ss,nonel}$ and $\Omega_{is,nonel}$ are the respective free energies from nonelectrostatic solute-solvent and ion-solute interactions; *T* is temperature; and S_e and S_i are entropies of the electrons and ions, respectively. Thermal contributions, H_{vib} - TS_{vib} , were calculated by vibrational frequency analysis for the optimized structures of the neutral adsorbed systems, using Interface 1.0. These contributions were calculated with Gaussian 09,⁴⁹ for isolated molecules. The Ω_{mc} , is a mass term that accounts for changing the band occupation during charging the surface. It is given by:

$$Q_{\rm mc} = -E_f N_e + \mu_+ N_+ + \mu_- N_- \tag{5.4}$$

where $E_{\rm f}$ is the Fermi level energy, $N_{\rm e}$ is the number of electrons, N_{+} and N_{-} are the number cations and anions in solution, and μ_{+} and μ_{-} are their respective chemical potentials, calculated as shown in Ref 21.

The reaction Gibbs energy, $\Delta_{rxn}G$, as a function of potential is give as following:

$$\Delta_{\rm rxn}G(U) = \{G_{\rm red}(U) - G_{\rm ox}(U)\} + n(\varphi + FU)$$
(5.5)

 $G_{\rm red}$ is Gibbs energy for reduced species and $G_{\rm ox}$ is Gibbs energy for oxidized species.

 $\Delta_{rxn}G(U)$ is zero at equilibrium and the potential in this case is the reversible potential, U_{rev} , given by:

$$U_{\rm rev} = \{ G_{\rm ox} (U) - G_{\rm red}(U) \} / nF - \varphi / F$$
(5.6)

 U_{rev} must be found graphically as the crossing point of $G_{\text{ox}}(U) - \varphi F$ with $G_{\text{red}}(U)$

A 3 × 2 unit cell consists of three layers, 6 atoms each was used to create a twodimensional slab. The bottom layer of the slab was kept frozen in the previously calculated bulk lattice positions with lattice constant 4.03 Å,²¹ while the top two were optimized. The (RPBE) exchange functional¹⁷ was used with the generalized gradient approximation (GGA). Monkhorst-Pack⁵¹ sampling in the Brillouin-zone was done with a grid of $3 \times 6 \times 1$ k-points.

5.3 Adsorption of CO on Pt(111)

Adsorption internal energies for CO at different sites were calculated by the formula:

$$\Delta_{\text{ads}} E(\text{CO}) = E(\text{CO/Pt}) - E(\text{Pt}) - E(\text{CO})$$
(5.7)

where E(CO/Pt) is the total energy of the adsorbed system, E(Pt) is the total internal energy for the Pt surface and E(CO) is the total internal energy for the isolated CO molecule. CO was optimized on four high symmetry adsorption sites, 1-fold coordinated top, 2-fold coordinated bridge and 3-fold coordinated fcc and hcp. Adsorption energies are in Table (5.1) and structures in Figure (5.1).

Table 5.1 Internal energy of adsorption, ^a $\Delta_{ads}E$, and Gibbs free energy of adsorption, $\Delta_{ads}G$, for the CO molecules at different sites of Pt(111) surface.

Site	hcp	fcc	bridge	atop
$\Delta_{\rm ads} E/~{\rm eV}$	-1.612	-1.647	-1.614	-1.432
$\Delta_{\rm ads}G/~{\rm eV}$	-1.566	-1.601	-1.574	-1.383

^a zero-point vibrational energies were not included when calculating $\Delta_{ads}E$.



Figure 5.1 Top view of the optimized structures for four different adsorption sites of CO and formyl on Pt(111): (a) bridge; (b) fcc and hcp; (c) on top; (d) on top formyl. Translational cells are outlined.

Adsorption energies for the bridge, fcc and hcp sites lie in the range -1.61 to -1.65 eV. The top site is calculated to be less stable with $\Delta_{ads}E = -1.43$ eV.

Low-energy electron diffraction (LEED) and electron energy loss vibrational spectra of CO adsorbed on Pt(111) at the vacuum interface indicated adsorption at the atop site.⁹⁰ However, it is well-known that DFT calculations using the GGA generally predict the higher coordinates site to be more stable. Our results in Table (5.1) have the same difficulty.

King et al. have studied the CO heat of adsorption on Pt(111) as a function of coverage using single crystal adsorption calorimetry under UHV conditions.⁹¹ They reported -1.71 eV for 0.17 ML coverage. Kinne et al. made more detailed kinetic measurements and found at low coverage, -1.43 eV for adsorption energy at the bridge site and -1.39 to -1.40 eV for the top site.⁹²

Adsorption site preference for CO under electrochemical conditions is known to depend on coverage, surface structure, and potential. One of the very early analyses of CO bonding to metals, in terms of σ donation from CO to the metal and metal back donation to the CO π^* , was done by Blyholder in 1964.⁹³ This model can be used in exploring the change in CO(ads) vibrational frequency and adsorption site when the potential is changed.

An early work by Anderson and Mehandru, modeled electrode potential changes and calculated the potential dependent adsorption energies of CO on 1, 2 and 3 fold on a small Pt cluster. They found that the 1-fold site is the most stable at high potentials, when back donation to π^* is weakened and the 3-fold becomes the most stable at low potentials when back donation to π^* is strengthened.²³ Chang and Weaver⁹⁴ employed infrared reflection-absorption spectroscopy (IRRAS) to study the effect of the potential and coverage on CO site preference on Pt(111) in 0.1 M HClO₄. They concluded that the majority of CO adsorbed with bridging site at 0.05 V and with increasing the potential; the site preference changed to the top site at 0.2 V. They also found that as coverage increased, at constant potential, the bridging site became occupied more than the on top site.

In a study of methanol oxidation on Pt(111) surface, Iwasita et al.,⁴⁰ found the majority of the CO produced at 0.25 V was adsorbed to top site and small traces bonded at bridge site.

Using in-situ scanning tunneling microscopy (STM) and infrared reflectionabsorption spectroscopy (IRAS), Villegas and Weaver,⁹⁵ reported a higher coverage of the atop site compared to the 3-fold site at 0.17 V. Scanning to high potentials there was a decrease in 3-fold coverage accompanied by an increase for the bridge site coverage while coverage at the top was constant until the potential of CO oxidation was reached.

It is noted that in studies of site preference of CO, the electrolytes were saturated with CO, resulting in high coverages and, hence these experiments may not represent low coverage findings. The island formation due to other adsorbates such as H₂O affects the distribution of CO species and the site preference by pushing CO molecules together forcing them to occupy the multi coordinate sites.⁹⁴ The only electrochemical study, so far, that was able to prepare a dispersed distribution of CO without the island formation did so by exposing a platinum film electrode to a mixture of 1% CO mixed and 99% Ar

in 0.5 M H_2SO_4 for different times to obtain different coverages.⁹⁶ In the potential range 0.3 – 0.6 V, IR spectra showed both 1-fold and high coordinate sites were occupied by CO.

The electrooxidation of methanol on a Pt thin film in $HClO_4$ was monitored by recording in situ surface enhanced infra-red absorption (SEIRA) spectra simultaneously with a cyclic voltammogram. Two bands were detected at 0.05 V correspond to linearly and bridge bonded CO with low intensity for the later.¹²

Chang and Weaver,⁹⁴ rationalized the preference to occupy the high coordinate sites at low potentials to the increasing Pt d to π^* back donation, which favors multiple coordination as shown in the theoretical work by Anderson and Mehandru.²³

Gibbs free energies of adsorption at the potential of zero charge were also calculated for the four sites and are given in Table (5.2). However, those potentials are positive of the potential region where CO is formed during alcohol electrooxidation. Potential-dependent adsorption energy calculations were not performed for this study. As is seen from the above discussion, in the electrochemical environment, 1-fold and high coordinates can be occupied simultaneously by CO.

5.4 Reversible potential of CO formation from formyl

As shown in Figure (5.1), formyl is calculated to adsorb through C at a 1-fold site. The reversible potential for oxidizing it to CO(ads) was calculated for two CO adsorption sites. For the more stable 2-fold CO site, the value -0.880 V is found from the crossing point of the reactants and products Gibbs energies, as shown in Figure (5.2). Since CO bonding to the 1-fold site is weaker, it is expected that the $CO(ads) + H^+(aq) + e^-$ curve will not change shape much and will shift up about 0.2 eV causing the crossing point to decrease to a lower potential. However, the potentials of zero charge are different for the two sites, about 1.25 V for 2-fold and 0.75 V for 1-fold. So, for the same electron energy and potential for each point on the 1-fold and the 2-fold, the 2-fold curve must be moved about 0.5 V left, in addition to the 0.2 eV shift up. The resulting crossing is at lower



Figure 5.2 Change in the total free energy, G_{tot} as a function of electrode potential, U, for both reactant and products with CO adsorbed at the 2-fold site.

potential that comes from just shifting the 2-fold curve up. Figure (5.3) shows the crossing point based on full calculations for the 1-fold site to be -0.421, it is concluded that errors of x eV in calculated adsorption Gibbs energy can cause errors in potentials > x V.



Figure 5.3 Change in the total free energy, G_{tot} as a function of electrode potential, U, for both reactant and products with CO adsorbed at the 1-fold site.

When the LGER method was used to calculate U_{surf}^{ev} for adsorbed formyl oxidation, the values -0.698 and -0.489 V were obtained for the 2-fold and 1-fold CO adsorption site, respectively. These are in good agreement with the more accurate Gibbs energy crossing point procedure used here. We note that an accurate CO adsorption energy is needed for accurate reversible potential prediction using either theory. The adsorption energy at the bridging site is closer to King's finding for the vacuum interface and if this represents the adsorption energy at the electrochemical interface, then, the predictions for the bridging site may be more accurate, respectively, \approx -0.9 V from the curve crossing method and \approx -0.7 V from applying LGER.

Previous calculations in this lab have predicted small activation barriers for oxidation reactions $\approx 0.1 - 0.2 \text{ eV}$,^{51,52} at the reversible potentials for several reactions involving O-H bonds. The potential dependencies of the activation energies are represented in Figure (5.4). Adsorbed formyl is oxidized to CO at a quite negative potential, $U_{\text{surf}}^{\text{rev}} = -0.7 \text{ V}$. In an alcohol fuel cell, $U^{\circ} \geq 0.0 \text{ V}$ and so if the reaction proceeds at this potential, the activation energy will, from Figure (5.4), be very small and not rate limiting.



Figure 5.4 Dependency of activation energy on electrode potential.

5.5 Conclusion

For formyl oxidation on Pt (111) electrode, the LGER theory and Gibbs energy curve crossing procedure, both give $U_{\text{surf}}^{\text{rev}}$ prediction within 0.1-0.2 V of one another. This is strong independent support for the very useful LGER theory. Since the potential is so negative, formyl oxidation will not contribute to the overpotential in alcohol fuel cell.

Appendix

Interface 1.0

Self-consistent two-dimensional functional band theory code, has been developed in Anderson's lab by Dr. R. Jinnouchi. It is capable of predicting accurate reversible potential at the liquid-solid interface. The code is for Prof. Anderson's lab and not available online. For more information about the interface 1.0, please contact Prof. Alfred B. Anderson:

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Gaussian 09

It is the latest version of Gaussian computational program series. The series is widely used in computational chemistry. They use quantum mechanics laws to model variety of systems and to predict electronic structures, energies, and vibrational frequencies in addition to many other features epically in the last version.⁴⁹

Helmholtz Double Layer (Parallel-Plate Condenser Model)

This model was the first and the simplest approximation for the double layer structure. The countercharges in this model form a layer at a fixed distance from the surface. However, experiments indicate a variable distribution of charges as a function of potential. This limitation of the model leads to the second model.¹⁹

Gouy and Chapman Model (Diffuse-Layer Model)

This model suggests that ions are highly mobile point charges and tend to diffuse far from the surface but as a result of the electrostatic attraction they stay close to the metal surface. Independently, Gouy and Chapman combined the Poisson equation of electrostatics with the Boltzmann statistics to describe the electrostatic potential and the charge distribution of ions as a function of the distance from the charged metal surface. Major deficiency of this model is that it predicts very high concentration of counter ions at the surface based on the assumption of point charges that neglects the finite size of ions.¹⁹

Stern Model (Compact Diffuse-Layer Model)

To model a more realistic double layer region, Stern, in 1924, combined the two previous models in one theory. He divided the double layer into two layers. One is called a Stern layer, a compact or a rigid layer where ions are close to the surface with a possibly for being adsorbed. In the second layer, ions tend to diffuse away from the surface. The two layers are separated by a distance equals the counterion radius.¹⁹

Explicit solvation models

All solvent molecules are represented in explicit details of each molecule. Although calculations using this model are generally accurate, they are time consuming and require a large scale sampling.⁹⁷

Implicit solvation models

Implicit solvations treats the solvent as a continuous medium described by the dielectric constant and the solute or the slab is surrounded by a cavity in the continuum. Unlike the explicit representation of the solvent, these models do not require a large scale sampling this makes them used widely in calculations. However, they are approximate because since they take into account a fewer degrees of freedom for solvent molecules and they do not include strong hydrogen bonding stabilizations. An essential difference between the models presently available is the way they mathematically describe the interaction between the solute and the dielectric continuum.^{97,98}

Hybrid solvation models (Super molecule)

In hybrid models, a solvation sphere of coordinated molecule is included, forming a "supermolecule" which is then embedded in a cavity in the continuum. ⁹⁷
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