INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI
University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700  800/521-0600
The electrochemistry of carbon monoxide

Lin, Shioujenq Andrew, Ph.D.

Case Western Reserve University, 1991
THE ELECTROCHEMISTRY OF CARBON MONOXIDE

BY

SHIOUJENQ ANDREW LIN

Submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

Thesis Advisor: Ernest B. Yeager

Department of Chemistry
CASE WESTERN RESERVE UNIVERSITY
August 1991
CASE WESTERN RESERVE UNIVERSITY

GRADUATE STUDIES

We hereby approve the thesis of

SHIOUJENQ ANDREW LIN

candidate for the Ph.D.

degree. *

Signed:  

(Chairman)

Date  

June 17, 1991

*We also certify that written approval has been obtained for any proprietary material contained therein.
I grant to Case Western Reserve University the right to use this work, irrespective of any copyright, for the University's own purposes without cost to the University or to its students, agents and employees. I further agree that the University may reproduce and provide single copies of the work, in any format other than in or from microforms, to the public for the cost of reproduction.

[Signature]
THE ELECTROCHEMISTRY OF CARBON MONOXIDE

Abstract
by
SHIOUJENQ ANDREW LIN

The electrochemical oxidation of CO and the reduction of the product (CO₂) have been studied using in situ FTIR spectroscopic techniques and electrochemical methods. A number of experimental conditions have been studied. These include the pretreatment of the electrode, the way in which CO is adsorbed, the solution composition, the CO adsorption potential, and various crystallographic orientations using single crystals.

There were significant differences observed in the CO oxidation peak structures for different CO adsorption conditions. It is likely that the CO adlayer structure has an influence on the CO oxidation mechanism. The surface CO layers formed in the hydrogen adsorption/desorption and double layer potential regions have been examined. The in situ FTIR-RAS technique was used to study the nature of bonding of the adsorbed CO to the surface and the orientation of the adsorbate on the electrode surface. Often the IR absorption band associated with the linearly bound CO was observed. The multiplicity of oxidation peaks in the cyclic voltammetry may not
be interpreted solely in terms of the bonding structure of the adsorbed CO. An alternative explanation for the multiple oxidation peak features is proposed.

The catalytic activity of the low index Pt surfaces for both CO oxidation and CO\textsubscript{2} reduction decreased in following order: (100) > (110) > (111). On Pt(110), the only detectable reduction product of CO\textsubscript{2} was adsorbed CO in linear form and simultaneously in linear and bridge bound forms on Pt(100). The oxidation of the reduction product (i.e. adsorbed CO) indicated similar oxidation peak features in the voltammetry curves to those of the oxidation of CO (from the electrolyte) on those single crystal surfaces. The presence of strongly adsorbed anions such as phosphate anion or chloride either give rise to the steric hindrance, impeding attack by oxygen donors or inhibit the formation of Pt surface hydroxide, resulting in the retardation of the CO oxidation peaks.

The nature of the very sharp CO oxidation peak was interpreted as being due to the coupling of two surface processes. Based on the number of the electrons transferred during the electrochemical process, the reaction mechanisms for oxidation of surface adsorbed CO and solution phase CO were proposed.
DEDICATION

To my parents and family

謹以此論文獻給在台灣的雙親及家人
ACKNOWLEDGEMENTS

I would like to thank my advisor Professor Ernest B. Yeager for his guidance, instruction, encouragement, and support throughout my graduate work.

Special thanks go to Dr. Donald Tryk for his suggestion in my thesis writing and helpful discussions. I would also like to thank Professor Boris Cahan for his advice and the use of his laboratory equipment. Thanks also to Dr. Radoslav Adzic for his expertise in single crystal studies during his visit in CCES.

I thank all my colleagues and personnel in Case Center for Electrochemical Sciences for their assistance and the special scientific environment which they create.

I thank my wife, Mindy for her helping at most of drawings in this thesis, and her support with love.

An acknowledgement should be made to my parents for their encouragement and endless love.

The financial support for this work by the Office of Naval Research is greatly acknowledged.
TABLE OF CONTENTS

ABSTRACT.................................................................ii
ACKNOWLEDGES............................................................v
TABLE OF CONTENTS.......................................................vi
LIST OF FIGURES...........................................................ix
LIST OF TABLES.............................................................XV

Chapter 1
Introduction

1.1 Objectives..............................................................1
1.2 Review of Prior Research on the Electrochemical Oxidation of CO on the Platinum Electrode..............2
  1.2.1 Electrochemical Oxidation of CO on Polycrystalline Pt Surface..............................................2
  1.2.2 Electrochemical Oxidation of CO on Pt Single Crystal Surfaces.............................................6
1.3 Review of CO Oxidation on Platinum Metal Surfaces in the Ultra-High Vacuum Environment..........11
1.4 Review of CO₂ Reduction as the Reverse Reaction of the CO Electrooxidation Reaction on Platinum Surfaces.................................................................16
1.5 Physical and Chemical Properties of CO and Statement of Problems...........................................18
  1.5.1 Physical and Chemical Properties of CO..................18
  1.5.2 Physical and Chemical Properties of Adsorbed CO on Single Crystal Pt Surfaces.........................19
1.5.3 Statement of Problem.................................20

Chapter 2
Experimental Methods
2.1 Single Crystal Surface Preparation.........................25
2.2 Ultrapure Water Preparation...............................31
2.3 Electrolyte Solution Preparations.........................32
2.3.1 Phosphoric Acid......................................32
2.3.2 Perchloric Acid.......................................34
2.3.3 Acetonitrile in dry box.................................34
2.4 Gas Handling..............................................35
2.4.1 Carbon monoxide safety monitor........................35
2.4.2 Gases................................................36
2.5 Carbon Monoxide Solubility in Electrolyte...............36
2.6 Linear Sweep Cyclic Voltammetry........................37
2.7 In Situ Fourier Transform Infrared Spectroscopy.......38
2.7.1 Cell Design..........................................40
2.7.2 Data Acquisition....................................44

Chapter 3
Results and Discussion
3.1 Carbon Monoxide Electrooxidation on Polycrystalline
   Platinum Surface in 0.1 M Perchloric Acid..............50
3.1.1 The Use of Hanging Meniscus Rotating Disk (HMRD)
   for the Oxidation of CO on Polycrystalline Pt........67
3.1.2 The Chloride Anion Effects............................82
3.1.3 Infrared Spectroscopic Studies of Carbon Monoxide Oxidation on the Polycrystalline Pt Surface......90

3.2 Carbon Monoxide Oxidation on the Three Low Index Pt(111), Pt(100) and Pt(110) Surfaces in 0.1 M Perchloric Acid.................................................98

3.2.1 Infrared Spectroscopy Studies of Carbon Monoxide Oxidation on the Single Crystal Pt Surfaces......109

3.3 Carbon Monoxide Oxidation on the Three Low Index Pt Surfaces (111), (100), and (110) in Phosphoric Acid Electrolyte.................................115

3.3.1 $^{13}$C NMR Measurement............................................116

3.3.2 Water Effect..........................................................119

3.3.3 Anions and Hydrogen co-adsorption Effect............123

3.3.4 Infrared Spectroscopy Studies of Carbon Monoxide Oxidation in Phosphoric Acid Electrolyte........132

3.4 Summary of Infrared Spectroscopy Studies..............143

3.4.1 Comparison in the Oxidation of Reduction Product of Carbon Dioxide and Carbon Monoxide Oxidation on Three Low Index Pt Surfaces......................150

3.5 Carbon Dioxide Reduction on the Three Low Index Pt(111), (100), and (110) Surfaces in 0.1 M Perchloric Acid........................................151

3.5.1 Infrared Spectroscopy Studies of Reduction of Carbon Dioxide on the Single Crystal Pt Surfaces.........................................................158

3.6 Carbon Monoxide Oxidation on the Three High Index
Pt surfaces(311), (332), and (755) in 0.1 M Perchloric Acid.................................163

3.7 Overall Discussion...........................169

Chapter 4
Summary and Conclusions
Electrolyte Effects..............................175
Surface Structure Sensitivity...................176
Islands Mechanism...............................177
Reactions Mechanism............................178

Reference........................................180
Chapter 1:

Fig. 1.1. CO bonding in 1-fold, 2-fold and 3-fold sites on the Pt(111) surface. [model used by A. B. Anderson and S.-F. Jen, J. Phys. Chem. 94, 1607 (1990)]

Fig. 1.2. CO bonding in 1-fold, 2-fold and 4-fold sites on the Pt(100) surface. [model used by A. B. Anderson and S.-F. Jen, J. Phys. Chem. 94, 1607 (1990)]

Fig. 1.3. 5σ donation and back-donation to π* for CO adsorbed to a surface metal atom. [from A. B. Anderson, in Chapter 10 of "Theoretical Aspects of Heterogeneous Catalysis" Ed. J. B. Moffatt (1989)]

Chapter 2:


Fig. 2.2 Schematic diagram of the ultra high vacuum system.

Fig. 2.3 Illustration of the electrochemical infrared cell used in the FTIR studies of adsorbates on single crystal Pt surfaces. (A) Tefzel electrode holder (B) Pt counter electrode lead wire (C) luggin Teflon capillary (D) CaF₂ optical windows (can be relaced by dove prism in Fig. 2.4) Tefzel cell body (F) N₂ gas inlet (G) N₂ gas outlet (H) Viton o-rings (I) Micrometer (J) Cell mount for fastening to optical table.

Fig. 2.4 Schematic diagram of the optical arrangement used in the FTIR studies. (with the CaF₂ 43 dove prism)

Fig. 2.5 Various potential program schemes for in situ FTIRRAS; E_s and E_r are the sample and the reference potentials respectively. The potential change is followed by a time delay of 1-5 sec to remove nonfaradaic components. a) Square wave train, one normalized spectrum at the end of the train. b) Single potential step. c) linear sweep at a very slow rate(1 mv/s), one spectrum over

x
Chapter 3:

Fig. 3.1 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with nitrogen [solid line] and saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s.

Fig. 3.2 Carbon monoxide coverage (estimated by the CO charge current and hydrogen adsorption/desorption charge area) vs. CO adsorption potentials.

Fig. 3.3 Carbon monoxide coverage (estimated by the CO charge current and hydrogen adsorption/desorption charge area) vs. holding time (CO adsorption time).

Fig. 3.4 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 150 mV. Holding time = 1, 3, 5, 10 min [solid line].

Fig. 3.5 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 450 mV. Holding time = 1, 3, 5, 10 min [solid line].

Fig. 3.6 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potentials = 200 mV. Negative [dash-point] and positive [solid] sweep.

Fig. 3.7 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 300 mV. Negative [dash-point] and positive [solid] sweep.

Fig. 3.8 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 450 mV. Negative [dash-point] and positive [solid] sweep.
Fig. 3.9 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with N₂ gas at 1 atm at rotating rate= 0 rpm [solid line], 3600rpm [dash line], 4900rpm [dash-point line]. Sweep rate = 50 mV/s.

Fig. 3.10 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm at rotating rate= 400 rpm [solid line], 900rpm [dash-point line], 1600 rpm [dash-double-point line], 2500rpm [dash line], 3600rpm [long-dash line]. Sweep rate = 50 mV/s.

Fig. 3.11 CO coverages vs. reciprocal root square of rotation speed. (Data points taken from Fig. 3.10.)

Fig. 3.12 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm. Rotating rate= 900 rpm [dashed line]. Sweep rate = 50 mV/s. Holding time= 30 sec. Holding potential= 200 mV [solid line].

Fig. 3.13 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm. Rotating rate= 900 rpm [dashed line]. Sweep rate = 50 mV/s. Holding time= 30 sec. Holding potential= 450 mV [solid line].

Fig. 3.14 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with 100% CO at 1 atm. Rotating rate= 400 rpm [solid line], 900rpm [dash-point line], 1600 rpm [dash-double-point line], 2500rpm [dash line], 3600rpm [long-dash line]. Sweep rate = 50 mV/s. Potential window opened to 1.4V.

Fig. 3.15 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with 100% CO at 1 atm. Rotating rate= 400 rpm [solid line], 900rpm [dash-point line], 1600 rpm [dash-double-point line], 2500rpm [dash line], 3600rpm [long-dash line]. Sweep rate = 50 mV/s. Potential window opened to 1.15V.

Fig. 3.16 Plot of 1/i vs. 1/vf for CO adsorbed on polycrystalline Pt surface in 0.1 M HClO₄. Data points taken at the potentials of 0.95, 1.0, 1.1, 1.2, 1.3 V (vs. RHE) from Fig. 3.11.
Fig. 3.17 Voltammetry curves of polycrystalline Pt electrode in (a) 0.1 M HClO₄ and (b) 0.1 M HClO₄ + 10⁻⁴ M Cl⁻ and (c) 0.1 M HClO₄ + 10⁻³ M Cl⁻ saturated with mixture of 1% CO in N₂ [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 3 min.

Fig. 3.18 Voltammetry curves of polycrystalline Pt electrode in (b) 0.1 M HClO₄ + 10⁻⁴ M Cl⁻ saturated with mixture of 1% CO in N₂ [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 3 min.

Fig. 3.19 Voltammetry curves of polycrystalline Pt electrode in (c) 0.1 M HClO₄ + 10⁻³ M Cl⁻ saturated with mixture of 1% CO in N₂ [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 3 min.

Fig. 3.20 Voltammetry curves of polycrystalline Pt electrode in (a) 0.1 M HClO₄ and (b) 0.1 M HClO₄ + 10⁻⁴ M Cl⁻ and (c) 0.1 M HClO₄ + 10⁻³ M Cl⁻ saturated with mixture of 1% CO in N₂ at rotation rate = 400 rpm [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 1 min.

Fig. 3.21 Voltammetry curves of polycrystalline Pt electrode in (b) 0.1 M HClO₄ + 10⁻⁴ M Cl⁻ saturated with mixture of 1% CO in N₂ at rotation rate = 400 rpm [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 1 min.

Fig. 3.22 Voltammetry curves of polycrystalline Pt electrode in (c) 0.1 M HClO₄ + 10⁻³ M Cl⁻ saturated with mixture of 1% CO in N₂ at rotation rate = 400 rpm [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 1 min.

Fig. 3.23 FTIR spectra of CO adsorption on polycrystalline Pt in different adsorption periods. 0.1 M HClO₄ + 10⁻³ M CO. Holding at 150 mV vs RHE for 1, 3, 5 min. Single step at reference 450 mV & sample 1000 mV. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.

Fig. 3.24 FTIR spectra of CO adsorption on poly-
crystalline Pt in different adsorption periods.
0.1 M HClO₄ + 10⁻⁵ M CO. Holding at 450 mV vs RHE for 1, 3, 5 min. Single step at reference 450 mV & sample 1000 mV. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.

Fig. 3.25 FTIR spectra of CO adsorption on polycrystalline Pt vs electrode potentials. 0.1 M HClO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101st scan of 200 scans) Holding at 150 mV vs RHE for 5 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.

Fig. 3.26 FTIR spectra of CO adsorption on polycrystalline Pt vs electrode potentials. 0.1 M HClO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101st scan of 200 scans) Holding at 450 mV vs RHE for 5 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.

Fig. 3.27 Voltammetry curves of Pt(111) and Pt(100) electrode in 0.1 M HClO₄ saturated with N₂ (full line). The dash line and dash-point line 100 show the negative sweep curves after 3 min holding time starting at holding potential 0.15 V and 0.45V.

Fig. 3.28 Voltammetry curves of Pt(111) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ (dashed line). Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 150, 450 mV. Negative sweep.

Fig. 3.29 Voltammetry curves of Pt(100) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ (dashed line). Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 150, 450 mV. Negative sweep.

Fig. 3.30 Voltammetry curves of Pt(110) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ (dashed line). Sweep rate = 50 mV/s. Holding time = 3, 5, 7, 10 min. Holding potential = 450 mV. Negative sweep.

Fig. 3.31 Voltammetry curves of Pt(110) electrode
in 0.1 M HClO$_4$ saturated with mixture of 1% CO in N$_2$ [dashed line]. Sweep rate = 50 mV/s. Holding time= 3, 5, 7, 10 min. Holding potential= 150 mV. Negative sweep.

Fig. 3.32 Voltammetry curves of Pt(110) electrode in 0.1 M HClO$_4$ saturated with mixture of 1% CO in N$_2$ [dashed line]. Sweep rate = 50 mV/s. Holding time= 3 min. Holding potential= 100 mV. Negative[dash-point line] and positive[solid line] sweep.

Fig. 3.33 Voltammetry curves of Pt(110) electrode in 0.1 M HClO$_4$ saturated with mixture of 1% CO in N$_2$ [dashed line]. Sweep rate = 50 mV/s. Holding time= 3 min. Holding potential= 200 mV. Negative [dash-point line] and positive [solid line] sweep.

Fig. 3.34 Voltammetry curves of Pt(110) electrode in 0.1 M HClO$_4$ saturated with mixture of 1% CO in N$_2$ [dashed line]. Sweep rate = 50 mV/s. Holding time= 3 min. Holding potential= 300 mV. Negative [dash-point line] and positive [solid line] sweep.

Fig. 3.35 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 0.1 M HClO$_4$ + 10$^{-5}$ M CO. Holding at 135, 408 mV vs RHE for 10 min. Single step at reference 450 mV & sample 1000 mV vs RHE. NSS= 400. RES= 8 cm$^{-1}$. SMF= 0. Incident angle(air/ CaF$_2$)= 50$^\circ$.

Fig. 3.36 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 0.1 M HClO$_4$ + 10$^{-5}$ M CO. Holding at 200, 400 mV vs RHE for 10 min. Single step at reference 450 mV & sample 1000 mV vs RHE. NSS= 400. RES= 8 cm$^{-1}$. SMF= 0. Incident angle(air/ CaF$_2$)= 50$^\circ$.

Fig. 3.37 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 0.1 M HClO$_4$ + 10$^{-5}$ M CO. Linear sweep cyclic voltammetry at sweep rate= 1 mV/sec. Potential recorded halfway through each spectral collection( at 101th scan of 200 scans) Holding at 400 mV vs RHE for 10 min. NSS= 200. RES= 8 cm$^{-1}$. SMF= 0. Incident angle (air/ CaF$_2$)= 50$^\circ$. First spectrum is the reduction of in situ generation CO$_2$ at 950 mV.

Fig. 3.38 FTIR spectra of CO adsorption on Pt(110) vs electrode potentials. 0.1 M HClO$_4$ + 10$^{-5}$ M CO. Holding at 150, 450 mV vs RHE for 10 min. Single step at reference 450 mV & sample 1000 mV vs RHE.
NSS = 400. RES = 8 cm\(^{-1}\). SMF = 0. Incident angle (air/ CaF\(_2\) ) = 50°.

Fig. 3.39 \(^{13}\)C NMR (400 MHz) chemical shift at 184.887 ppm show \(^{13}\)CO presence in D\(_2\)O.

Fig. 3.40 \(^{13}\)C NMR (400 MHz) chemical shift at 182.225 ppm (in 4, 8, 12, and 16 hrs accumulating periods) and 184.025 ppm show \(^{13}\)CO presence in 10 M D\(_3\)PO\(_4\) in D\(_2\)O.

Fig. 3.41 Voltammetry curves of (a) Pt(111) (b) Pt(100) and (c) Pt(110) electrode in 10 M H\(_3\)PO\(_4\) saturated with mixture of 1% CO in N\(_2\) [dashed line]. Sweep rate = 50 mV/s. Holding time = 6 min. Holding potential = 400 mV. Negative sweep [full line] following the holding.

Fig. 3.42 Voltammetry curves of polycrystalline Pt in Acetonitrile w/TEAP saturated with mixture of 1% CO in N\(_2\). Sweep rate = 50 mV/s. Holding potential = -1.0 V vs Ag/Ag\(^+\). Holding time = 15 min. In dry box (<1 ppm water) and in the air.

Fig. 3.43 Voltammetry curves of Pt(111) electrode in 5 M H\(_3\)PO\(_4\) saturated with mixture of 1% CO in N\(_2\) [dashed line]. Sweep rate = 50 mV/s. Holding time = 6 min. Holding potential = 300, 450 mV. Negative sweep [full line] following the holding.

Fig. 3.44 Voltammetry curves of Pt(100) electrode in 5 M H\(_3\)PO\(_4\) (a) nitrogen saturated [full line] and saturated with mixture of 1% CO in N\(_2\) [dashed line]. Sweep rate = 50 mV/s. (b) Holding time = 6 min. Holding potential = 150, 250, 350 mV. Positive sweep [full line] following the holding.

Fig. 3.45 Voltammetry curves of Pt(100) electrode (a) in 1 M H\(_3\)PO\(_4\) saturated with mixture of 1% CO in N\(_2\) [dashed line]. Sweep rate = 50 mV/s. Holding time = 6 min. Holding potential = 450, 500, 550 mV. Positive sweep [full line] following the holding. (b) in 0.01 M H\(_3\)PO\(_4\) saturated with mixture of 1% CO in N\(_2\) [full line]. Sweep rate = 50 mV/s. Holding time = 1 min. Holding potential = 150, 300, 350, 400, 450 mV. Positive sweep following the holding.

Fig. 3.46 Voltammetry curves of Pt(111) electrode in 1 M H\(_3\)PO\(_4\) (a) nitrogen saturation [full line] and saturated with mixture of 1% CO in N\(_2\) [dashed line]. Sweep rate = 50 mV/s. (b) Holding time = 6
min. Holding potential = 150, 450 mV. Positive sweep following the holding.

Fig. 3.47 Voltammetry curves of Pt(111) electrode in 0.01 M H₃PO₄ saturated with mixture of 1% CO in N₂ [full line]. Sweep rate = 50 mV/s. (a) Holding time = 1 min. Holding potential = 150, 200, 250, 300 mV. Positive sweep [full line] following the holding. (b) Holding time = 3 min. Holding potential = 150, 500 mV. Positive sweep [full line] following the holding.

Fig. 3.48 Voltammetry curves of Pt(110) electrode (a) in 1 M H₃PO₄ saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. Holding time = 1 min. Holding potential = 125, 250, 400 mV. Positive sweep [full line] following the holding. (b) in 0.01 M H₃PO₄ saturated with mixture of 1% CO in N₂ [full line]. Sweep rate = 50 mV/s. Holding time = 1 min. Holding potential = 125, 225, 400 mV. Positive sweep following the holding.

Fig. 3.49 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 1 M H₃PO₄ + 10⁻³ M CO. Holding at 146, 410 mV vs RHE for 15 min. Single step at reference 146 mV, 410 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm⁻¹. SMF = 0. Incident angle (air/ CaF₂) = 50°.

Fig. 3.50 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans) Holding at 146 mV vs RHE for 5 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.

Fig. 3.51 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans) Holding at 400 mV vs RHE for 5 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.

Fig. 3.52 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Holding at 146 mV vs RHE for 15 min and reduction of in situ generation CO₂ at 91 mV for 5 min.

xvii
Single step at reference 146 mV, 91 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm⁻¹. SMF = 0. Incident angle (air/ CaF₂) = 50°.

Fig. 3.53 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Holding at 270, 400 mV vs RHE for 10 min. Single step at reference 270 mV, 400 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm⁻¹. SMF = 0. Incident angle (air/ CaF₂) = 50°.

Fig. 3.54 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans) Holding at 132 mV vs RHE for 10 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.

Fig. 3.55 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans) Holding at 411 mV vs RHE for 10 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.

Fig. 3.56 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Holding at 270 mV vs RHE for 10 min and reduction of in situ generation CO₂ at 90 mV for 5 min. Single step at reference 270 mV, 90 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm⁻¹. SMF = 0. Incident angle (air/ CaF₂) = 50°.

Fig. 3.57 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Holding at 336 mV vs RHE for 10 min and reduction of in situ generation CO₂ at 86 mV for 5 min. Single step at reference 336 mV, 86 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm⁻¹. SMF = 0. Incident angle (air/ CaF₂) = 50°.

Fig. 3.58 FTIR spectra of CO adsorption on Pt(110) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Holding at 180, 289, 440 mV vs RHE for 15 min. Single step at reference 180 mV, 289, 441 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm⁻¹. SMF = 0. Incident angle (air/ CaF₂) = 50°.
Fig. 3.59 FTIR spectra of CO adsorption on Pt(110) vs electrode potentials. 1 M H$_3$PO$_4$ + 10$^{-5}$ M CO. Holding at 289 mV vs RHE for 10 min and reduction of in situ generation CO$_2$ at 90 mV for 5 min. Single step at reference 289 mV, 90 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm$^{-1}$. SMF = 0. Incident angle (air/ CaF$_2$) = 50°.

Fig. 3.60 Voltammetry curves for Pt(100) in a CO$_2$-saturated solution without [dash line] and with [full line] holding at 130 mV for 5 min. Sweep rate = 50 mV/s.

Fig. 3.61 Voltammetry curves for Pt(110) in a CO$_2$-saturated solution without [dash line] and with [full line] holding at 110 mV for 5 min. Sweep rate = 50 mV/s.

Fig. 3.62 Voltammetry curves for Pt(111) in the absence [dash line] and presence of CO$_2$-saturated solution without [dash point line] and with [full line] holding at 130 mV for 5 min. Sweep rate = 50 mV/s.

Fig. 3.63 Potential difference FTIRRAS spectra obtained in a CO$_2$-saturated 0.1 M HClO$_4$ solution with reference potential at 0.10 V and sample potentials at 0.60, 0.70, and 0.90 V for Pt(100), Pt(111), and Pt(110), respectively. The electrode was pushed close to the optical window at 0.10 V after holding this value for 2 to 10 min.

Fig. 3.64 Potential difference FTIRRAS spectra obtained in a CO$_2$-saturated 0.1 M HClO$_4$ solution with reference potential at 0.50 V and sample potential at 0.10 V. The electrode was pushed close to the optical window at 0.50 V and a reference spectrum collected; the potential was then shifted to 0.10 V without moving the electrode.

Fig. 3.65 Voltammetry curves of Pt(311), (322), (755) electrode in 0.1 M HClO$_4$ saturated with nitrogen. Sweep rate = 50 mV/s.

Fig. 3.66 Voltammetry curves of Pt(311) electrode in 0.1 M HClO$_4$ saturated with mixture of 1% CO in N$_2$ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 200, 300, 400 mV. Holding time = 3 min.

Fig. 3.67 Voltammetry curves of Pt(755) electrode in 0.1 M HClO$_4$ saturated with mixture of 1% CO in
\[ \text{N}_2 \text{ gas at 1 atm [dash line]. Sweep rate} = 50 \text{ mV/s. Holding potential} = 100, 400 \text{ mV. Holding time} = 6 \text{ min.} \]

Fig. 3.68 Voltammetry curves of Pt(755) electrode in 0.1 M HClO\(_4\) saturated with mixture of 1% CO in \(\text{N}_2\) gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 100 or 400 mV. Holding time = 3[dash-point], 9[solid line] min.

Fig. 3.69 Voltammetry curves of Pt(322) electrode in 0.1 M HClO\(_4\) saturated with mixture of 1% CO in \(\text{N}_2\) gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 100, 400 mV. Holding time = 9 min.

Fig. 3.70 Voltammetry curves of Pt(322) electrode in 0.1 M HClO\(_4\) saturated with mixture of 1% CO in \(\text{N}_2\) gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 400 mV. Holding time = 3, 6, 9 min.

Fig. 3.71 Voltammetry curves of Pt(322) electrode in 0.1 M HClO\(_4\) saturated with mixture of 1% CO in \(\text{N}_2\) gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 100 mV. Holding time = 3, 6, 9 min.
CHAPTER 1
INTRODUCTION

1.1 Objectives

The adsorption and electrochemical oxidation of carbon monoxide on platinum electrodes in acid solutions has been investigated for several decades and reported in more than 100 papers [1]. The electrochemical oxidation of carbon monoxide is important for energy conversion using C₁ fuels in fuel cells [2-3]. Not only can CO itself be a fuel but it may also be a by-product of other hydrocarbon fuels, such as CH₄, and CH₃OH [3-8]. Carbon monoxide is strongly adsorbed on platinum surfaces both from the gas phase and electrochemical environments. The adsorption of CO is sufficiently strong that further reactions are inhibited.

The objective of the thesis work has been to characterize and understand the factors controlling the adsorption of CO and its oxidation to CO₂ in electrochemical systems. The dependence of the electrochemical behavior of CO on surface morphology and on the nature of the adsorbed species have been studied in this thesis research. The present work has been motivated by recent developments coupling in situ FT-IR spectroscopic measurements with simultaneous electrochemical measurements.
[9,10], and by the rapid process in the understanding of electrochemistry on single crystal electrode surfaces [11].

1.2 Review of Prior Research on the Electrochemical Oxidation of CO on the Platinum Electrode

1.2.1 Electrochemical Oxidation of CO on Polycrystalline Pt Surface

An earlier mechanism for CO oxidation, proposed by Gilman [12] and still referred to, involves the reaction of linearly adsorbed CO with an adjacent water molecule as the oxygen donor. He believed that the oxidation of CO(ads) must be completed before the oxidation of the Pt surface can take place. McCallum et al. [13] studied the oxidation of CO by stepping the potential into the region where oxidation of the Pt surface takes place simultaneously with CO(ads) oxidation. They concluded that the oxidation of CO(ads) occurs at the perimeter of the growing islands of platinum oxide, which acts as the oxygen donor.

The electrooxidation of carbon monoxide adsorbed on polycrystalline platinum is known to be a complex process, the mechanism of which depends on various experimen-
tal conditions. The experimental parameters that have been examined include the pre-treatments of the electrode, the composition of the electrolyte, the adsorption potentials and the coverage. Experiments have been done over a broad range of roughness factors, ranging from about 1 for smooth platinum electrodes [14,15] to large values for platinized Pt electrodes [16,102]. Studies of carbon monoxide adsorption on Pt electrodes have used CO saturated electrolyte either with open circuit or controlled potential and a range of adsorption times (e.g. 2 min to 1 h) [17]. Many of these studies have concluded that the final product of CO(ads) electrooxidation is carbon dioxide.

Even though extensive work has been carried out, the structure of adsorbed CO on the Pt surface is still not completely understood [18,19]. After Gilman [12] introduced the concept of the linearly bonded and bridged-bonded forms of adsorbed CO, these bonding structures of the CO were used to interpret the electrochemical data. Several infrared studies [15,19,31-33,36] indicated that the IR bands associated with these two different species occur at different frequencies. It is generally accepted that the predominant adsorbed species at potentials in the double layer region on Pt is linearly bonded CO, with relatively small amounts of bridge-bonded adsorbed CO. Czerwinski and Sobkowski [20] pro-
posed that CO adsorption on platinized Pt in acid solution leads to at least three different species: CO bonded to Pt in the bridged form, the linear form, and adsorbed COOH radicals arising from the interaction of adsorbed CO with co-adsorbed hydrogen. In addition to the linearly bonded and bridge-bonded adsorbed CO, other species such as CO monohydrate [23] and HCO [24], have been proposed for adsorbed CO at potentials in the hydrogen adsorption/desorption region [21-24].

The profile of the CO oxidation region in the electrochemical current-potential curves, which can include at least two distinct peaks, has been interpreted as being due to the oxidation of linearly and bridge-bonded CO on the Pt surface [25-27]. On the other hand, the multiplicity of oxidation peaks may not necessarily be interpreted only in terms of the simultaneous presence of linearly and bridge-bonded CO[28-30].

Leiva et al. [37] have described CO adsorption on electrochemically faceted Pt surfaces in acid solution. For CO adsorbed at potentials in the hydrogen region, two types of adsorbed CO were observed, a more weakly bound species and a more strongly bound species, which were oxidized at 0.4 V (vs NHE) and 0.6 V respectively. A CO adsorption potential in the double-layer region led to
only strongly bound CO, which required an even higher oxidation potential. Kunimatsu et al. [38,39] have also examined the CO electrooxidation on a smooth polycrystalline platinum surface in acid solution. The CO adsorption potentials used were in the double layer region (0.4 V vs NHE) and in the hydrogen adsorption/desorption region (0.05 V vs. NHE). They hypothesized that a structural change in the Pt surface occurs in the hydrogen adsorption/desorption potential region, which favors the formation of bridged CO(ads). They also showed that the co-adsorption of deuterium (electrosorbed in D₂O solution) and CO(ads) led to a shift in the oxidation potential compared to that in non-deuterated acid. They proposed that this was due to the involvement of adsorbed hydrogen in the oxidation process.

From the potential dependence of the infrared spectra for CO adsorbed on Pt, Kunimutsu et al. [43] reported that there were two types of CO adlayers. One was produced in the double layer region (0.4V vs. NHE) and the other was produced in the hydrogen adsorption region (0.05V vs. NHE). For the layer formed at 0.4V, they concluded that the reaction proceeds at the edge of CO islands. For the layer produced at 0.05V, the oxidation proceeds randomly in the adsorbed CO adlayer.

In a more detailed study, Kunimatsu et al. [8,45]
proposed that there are two types of adsorbed CO surface layers present at 0.05V, which are responsible for the oxidation behavior of CO adsorbed at this potential. The CO which is adsorbed in the hydrogen region produces a higher surface concentration of bridged CO(ads), which occupies more Pt sites. The oxidation of CO is thought to proceed randomly within the adsorbed CO layer domain. For the layer produced at 0.4V, in which the linear form predominates, the oxidation of CO is thought to proceed at the boundary of the adsorbed CO islands. They also proposed that the potentials of the current peaks in the voltammograms are not affected by potential cycling into the oxide regions which produces surface roughness. The electrooxidation of CO is not a structure-sensitive reaction [Table 1] according to Kunimutsu et al. even though CO is strongly adsorbed [48-54].

1.2.2 Electrochemical Oxidation of CO on Pt Single Crystals Surfaces

Great progress has been made in the last several years in the preparation of clean, well-defined Pt single crystal surfaces and using electrochemical methods with various ex situ surface physical techniques such as LEED and AES in ultrahigh vacuum. Small organic molecules adsorbed on Pt single crystals have been studied intensively. The quality of the single crystal Pt surface can
Table 1. Potentials for CO Oxidation on Pt Surfaces from Voltammetry and IR Spectral Studies.

<table>
<thead>
<tr>
<th>CONDITIONS</th>
<th>$E_{\text{peak}}$ (V vs. RHE)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Poly. Pt</td>
<td>Pt(111)</td>
</tr>
<tr>
<td>50 mV/s</td>
<td>0.69</td>
<td>0.68</td>
</tr>
<tr>
<td>5V/s</td>
<td>0.97</td>
<td>1.002</td>
</tr>
<tr>
<td>10V/s</td>
<td>1.00</td>
<td>1.06</td>
</tr>
<tr>
<td>Steady State</td>
<td>0.65</td>
<td>0.57</td>
</tr>
<tr>
<td>Steady State</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Steady State</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>Steady State</td>
<td>0.60</td>
<td></td>
</tr>
</tbody>
</table>

Note: The potentials are referred to RHE. The potentials at which the CO was adsorbed were in the double layer region (ca. 0.4V vs. RHE) unless stated otherwise. The CO peak potentials obtained from the IR measurements (at steady state current for the recorded spectra) are those at which the IR signal decreased most rapidly.

References (and electrolyte used) for Table 1:
48(in 0.1M HClO₄); 49(in H₂SO₄; E(ads)=0.05V); 50(in 0.5M HClO₄); 51(in 0.5M H₂SO₄); 52(in 0.5M H₂SO₄); 53(in 1M HClO₄); 54(in 0.1M HClO₄).
be verified using LEED and linear sweep voltammetry. The latter yields highly reproducible characteristic hydrogen adsorption/desorption features in sulfuric and perchloric acid solutions. Due to the ability to prepare the crystals with the relatively simple flame annealing techniques and to check their quality using voltammetry, in situ infrared spectroscopy on such crystals has become more practical [10]. After Lamy and Clavilier et al. [46] reported the oxidation of CO, HCOOH and CH₃OH on single crystal Pt electrodes, studies of surface crystallographic effects on the reactions of small organic molecules became an active area.

The vibrational frequency for adsorbed CO depends on the CO coverage, binding structure of CO to Pt and surface electric field [31-32,36,40-42]. For example, the types of adsorbed CO include linearly and bridge-bound CO, which are observed in infrared spectra at 2100-2000 cm⁻¹ and 1860-1850 cm⁻¹ respectively. Ito et al. pointed out that the interconversion of linearly and bridged-bound CO(ads) on Pt(100) could be induced by changes in the electrode potential. Weaver et al. [55] observed that adsorbed CO on Pt(111) crystal was a function of CO coverage and electrode potential: the CO band frequency increased approximately linearly with both increasing coverage and potential. They concluded that
the vibrational characteristics of the surface adsorbate yielded insights into the chemical reactivity as well as correlations between the electrochemical interface and the corresponding UHV surface. The electrochemically measured CO coverages at saturation were the same within \( \approx 10\% \) as those obtained in UHV for all three faces. The linear C-O stretching frequency and band intensity are dependent on the crystallographic orientation at a given electrode potential[55-64] [Table 2].

The results of CO experiments obtained under electrochemical conditions cannot be compared directly with the data obtained in the UHV environment because of the CO pressure difference, the presence of the solution and the applied potential. Clavilier et al. [103] argued that the electrochemical approach (e.g. number of electrons per hydrogen atom on Pt) provides the necessary information for the interpretation of the in situ spectroscopic results in terms of CO bonding mode. From the charge consumed in CO oxidation charge obtained by integrating the area under the voltammetry peak vs. the charge consumed in hydrogen adsorption, the number of adsorbed CO molecules can be compared directly to the number of Pt sites occupied by hydrogen, so that the proportion of linear vs. bridge-bound CO can be estimated. They proposed that two types of distributions of CO
Table 2. Infrared Stretching Frequencies for Adsorbed CO on Single Crystal Pt Surfaces at Selected Coverage in Electrochemical and UHV Environments at 300 K.

### UHV environment

<table>
<thead>
<tr>
<th>Coverage</th>
<th>IR</th>
<th>Coverage</th>
<th>IR</th>
<th>Coverage</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2095</td>
<td>0.8</td>
<td>2097</td>
<td>0.9</td>
<td>2117</td>
</tr>
<tr>
<td>0.3</td>
<td>2091</td>
<td>0.5</td>
<td>2091</td>
<td>0.6</td>
<td>2104</td>
</tr>
<tr>
<td>0.1</td>
<td>2085</td>
<td>0.2</td>
<td>2087</td>
<td>0.3</td>
<td>2094</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>2080</td>
</tr>
</tbody>
</table>

### Electrochemical environment; E(ads)= 0.0V vs. SCE

<table>
<thead>
<tr>
<th>Coverage</th>
<th>IR</th>
<th>Coverage</th>
<th>IR</th>
<th>Coverage</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>2066</td>
<td>0.85</td>
<td>2055</td>
<td>1.0</td>
<td>2074</td>
</tr>
<tr>
<td>0.4</td>
<td>2063</td>
<td>0.7</td>
<td>2046</td>
<td>0.6</td>
<td>2071</td>
</tr>
<tr>
<td>0.3</td>
<td>2058</td>
<td>0.5</td>
<td>2041</td>
<td>0.3</td>
<td>2063</td>
</tr>
<tr>
<td>0.2</td>
<td>2056</td>
<td>0.3</td>
<td>2042</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References: 55-60; 61-64 (coverages were estimated using the CO oxidation charge current with some assumptions).
* Frequency of infrared band in cm$^{-1}$. 
molecules exist on the Pt(111) surface. One type of adsorbed CO adlayer domain has many CO free-sites available for oxygen donors, but another type of CO adlayer structure has no CO free sites. The sizes of adsorbed CO islands and the compactness of these islands affect the steric hindrance of the reaction of oxygen donors at the Pt surface. The possibility of various degrees of steric hindrance on given surfaces leads to the multiplicity of CO oxidation peaks.

This interpretation is consistent with the island mechanism proposed by Kunimatsu et al. [45] on polycrystalline Pt surfaces which involve the coexistence of two different kinds of CO domains. Santos et al. [104] used the potential step method to characterize the kinetic behavior of CO on Pt(111) surface. They found that two different oxidation processes could be distinguished on the basis of the current-time transients even when only a single peak feature was evident in the CO oxidation peak structure. Although significant progress has been made, the nature of the adsorbed CO on different types of surface sites is still not completely clear.

1.3 Review of CO Oxidation on Platinum Metal Surfaces in the Ultrahigh Vacuum Environment

Even though there are fundamental differences
between the electrochemical and the ultrahigh vacuum (UHV) environments, such as the difference in the potential distribution across the interface and the coexistence of liquid and gas on the solid surface, it is still interesting to examine the surface oxidation reaction of CO in UHV environment in order to draw comparisons with the corresponding electrochemical reaction. Some ex situ studies were carried out to investigate such differences. Ex situ LEED and voltammetric studies of CO on Pt(111) were reported by Wieckowski et al [82]. They postulated that close-packed adlayer structures vs. various types of packing at partial coverage of CO could be responsible for the multiplicity of CO electrooxidation peaks in voltammetry. Wieckowski et al. also showed that the structure of CO adlayers on Pt(111) obtained by dosing from aqueous solutions was similar to those obtained with gas phase dosing. They also found that UHV exposure of CO adlayers obtained with solution phase dosing did not alter the electrooxidation behavior [84].

A review of UHV results will be presented and discussed in this section. The surface oxidation of CO in UHV has been investigated on metal single crystal surfaces as a model catalytic system[5]. Carbon monoxide has been used as an adsorbate for developing an understanding of adsorbate-substrate interactions and chemical
transformations that take place at the surface of a catalyst (substrate) in heterogeneous catalysis [6,7].

Following the initial work by Langmuir [65], the catalytic gas-phase oxidation of carbon monoxide on platinum was investigated extensively on polycrystalline Pt [66-70] and single crystal surfaces [71-77].

With the advent of the various surface physics techniques during the last two decades, the surface bonding mode of the adsorbate and the adlayer structure have been able to be studied as a basis for the understanding of catalytic oxidation of carbon monoxide [78]. The individual steps that are probably involved in the reaction may be formulated as follows:

1) $\text{CO} \leftrightarrow \text{CO(ads)}$

2) $\text{O}_2 \leftrightarrow 2 \text{O(ads)}$

3) $\text{O(ads)} + \text{CO(ads)} \leftrightarrow \text{CO}_2$

   (Langmuir-Hinshelwood mechanism)

4) $\text{O(ads)} + \text{CO} \leftrightarrow \text{CO}_2$

   (Eley-Rideal mechanism)

5) $\text{O}_2 + 2 \text{CO(ads)} \leftrightarrow 2 \text{CO}_2$

The question of whether the reaction takes place between two adsorbed species, CO(ads) and O(ads) (Langmuir-Hinshelwood mechanism) or between a gas phase CO molecule
and an oxygen adatom (Eley-Rideal mechanism) is still not completely resolved.

The chemisorption of carbon monoxide on the transition metal surface is generally accepted to occur via the coupling of the 2 $\pi^*$ and 5 $\sigma$ orbitals of CO to the metallic d-states. The bonding occurs through a concerted electron transfer from the highest filled molecular orbital (5$\sigma$) of CO to the metal and back-donation of metal electrons to the lowest unfilled orbital of CO(2$\pi^*$), as shown in Fig. 1.3 (Section 1.5.2). The adsorption energy depends on the geometric location and orientation of the adsorbed molecule on the surface, the crystallographic orientation of the surface, and the nature of the substrate metal [79].

Somorjai et al. [80] investigated CO adsorbed on Pt(111) in UHV using low energy electron diffraction (LEED). The CO molecules exhibited a metal-carbon bond length of $\approx 1.85$ Å and $\approx 2.08$ Å for atop and bridged sites respectively. Both modes exhibited a carbon-oxygen bond length of $\approx 1.15$ Å. Olsen and Masel [81] reported that both the linear and bridged modes were observed with infrared spectroscopy for CO on Pt(111) in the UHV environment.
Various studies have examined the effects of co-adsorption of other species on the adsorption of CO. Ehlers et al. [82] reported that adsorbed CO remained on Pt(111) and was not removed by coadsorbed species such as methanol, water, and xenon. Schmieg et al. [86] showed that CO adsorbed on Pt(111) decreased the desorption temperature of water, indicating a lower adsorption energy of the water due to a hydrophobic interaction of the CO and water. They suggested that the co-adsorbates on Pt(111) separate into islands containing only water and islands containing only CO. Bradshaw et al. [87] studied the coadsorption of CO and hydrogen on the Pt(111) surface. They found island formation of lower CO coverage (θ<0.25) with the absence of bridge-bonded CO.

Behm et al. [88] studied the oxidation of CO on Pt(100). They found that CO oxidation was much more rapid when the surface was first exposed to O₂ to form O(ads) and then to CO to form CO(ads) rather than vice versa. The boundary region between O(ads) and CO(ads) islands was the area permitting the reaction. They concluded that the reaction rate for CO oxidation depends on the rate of CO adsorption. Ku and Bonzel [89] examined CO oxidation on Pt(110). They showed that two different mechanisms were involved depending on the experimental conditions. The reaction exhibited the Langmuir-Hinshelwood mechanism at 100K<T<200K when CO
was pre-adsorbed on the Pt surface, and the subsequent adsorption of oxygen was competitive. When oxygen was preadsorbed on the Pt surface, the subsequent reaction exhibited an Eley-Rideal mechanism on the basis of the dependence on the gas CO dosage. Campbell et al.[90] used a molecular beam - surface scattering experiment to study CO catalytic oxidation on Pt(111). They showed that an adsorbed CO molecule combines with an adsorbed oxygen via a Langmuir-Hinshelwood mechanism.

1.4 Review of CO₂ Reduction as the Reverse Reaction of the CO Electrooxidation Reaction on Platinum Surfaces

The initial investigations of the feasibility of electrochemical reduction of CO₂ were carried out as early as the late nineteenth century[91]. In recent years, interest in the electroreduction of carbon dioxide has attracted much attention in connection with some practical problems, particularly in liquid fuel energy cycles that would make use of CO electrooxidation in fuel cells. [92-93]. Since the first report by Giner [94], the nature of the reduced species formed during CO₂ reduction taking place in the hydrogen adsorption potential region on the Pt surface has been investigated by several authors [95-101].
Sobkoski et al. [95] have reported that the adsorbed reduction product of CO$_2$ on a Pt electrode is not desorbed into solution. Electrochemically modulated infrared spectroscopy (EMIRS) data obtained by Beden et al. [15] and electrochemical data obtained by Giner [94] provided evidence that the product is carbon monoxide. Baruzzi et al. [96] and Marco et al. [97] studied the electrooxidation of reduced CO$_2$ on a platinum electrode and showed that two distinguishable reduced forms of CO$_2$ react with the surface oxide (PtOH). Shlepakov et al. [98] have proposed that there is only a single species adsorbed in two different adsorbate geometries. Kazarinov et al. [99] suggested that the adsorbed species is COH in two different forms on the surface. Bockris et al. [100] showed that the electroreduction of carbon dioxide in acetonitrile involved the CO$_2^-$ (ads) radical anion. Arvia et al. [101] studied the electroreduction of CO$_2$ on Pt in acid solution. Since the reduction of CO$_2$ involves an interaction with adsorbed hydrogen, the nature of the adsorbed product is thought to depend on the nature of the adsorbed hydrogen. They proposed that the electrosorption of strongly bound H adatoms resulted in the formation of a strongly bound reduced CO$_2$ species. A weakly bound H adatom leads to the formation of weakly bound reduced CO$_2$.

An understanding of the products of CO$_2$ electrore-
duction will lead to further insight into the CO/CO$_2$
 electrochemical system on Pt surfaces. Due to the de-
pendence of this reaction on the nature of coadsorbed
hydrogen, it should be particular interesting to examine
the effects of different Pt single crystal surfaces
because of their individual unique hydrogen adsorption
behavior. Detailed studies along these lines have al-
ready been carried out [103-104] and are discussed in
Chapter 3.

1.5 Physical and Chemical Properties of CO and A State-
ment of the Problems

1.5.1 Physical and Chemical Properties of CO

Carbon monoxide has a low electric dipole moment
(0.10 Debye) and a short interatomic distance(1.13 Å)
with a relatively high bond strength(1,072 kJ/mol).
Although in principle it is an anhydride form of formic
acid (HCOOH), it is unreactive with water and is only
slightly soluble (0.96 X 10$^{-3}$ M, at 25°C) [115]. It
absorbs radiation in the infrared region corresponding to
the vibrational excitation of the electronic ground state
of the molecule. For instance, 2143.3 cm$^{-1}$ is the funda-
mental vibration transition for gas phase CO ( $X^1\Sigma_g^+$,
v' = 1 -> v" = 0), and 2133 cm$^{-1}$ is the IR band position for
carbon monoxide in solution. The frequency of 2143 cm\(^{-1}\) for free CO is shifted to lower frequencies for the most of the metal carbonyl complexes (ca. 2100-1800 cm\(^{-1}\)). The frequency range of 1860-1700 cm\(^{-1}\) for bridge-bonding of CO to two metals is lower than that of 2125-1850 cm\(^{-1}\) for terminal CO [12-15]. The standard reversible potential for the reaction CO(g) + H\(_2\)O(1) \(\leftrightarrow\) CO\(_2\)(g) + 2 H\(^+\) + 2e\(^-\) is \(-0.106\) V (vs. SHE). CO is not oxidized on Pt at an appreciable rate until around +0.8V vs RHE in acid solution, however.

1.5.2 Physical and Chemical Properties of Adsorbed CO on single crystal Pt surfaces

The bonding energy of CO to Pt(111) at the solid-gas interface is estimated experimentally to be about 33 kcal/mol (138 kJ/mol). Energies of CO adsorption measured for the Pt single crystal are 138, 134, and 108 kJ/mol for the (111), (100), and (110) planes, respectively [142]. Carbon monoxide can bond to 1-, 2-, or possibly 3-fold sites on Pt(111), standing vertically with the carbon end down (Fig. 1.1). For 1-fold linear bonding of CO on Pt(111), the C-O bond length is 1.15Å and the C-Pt bond length is 1.85Å. For 2-fold bridge-bonding of CO on Pt(111), the C-O bond length is the same, but the C-Pt bond length is 2.05Å, with a vertical distance of 1.55Å from carbon atom to the plane of the
centers of the Pt atom in the surface layer [80]. Thus the bridge bound CO lies closer to the surface than does linear bound CO. The distance between the nearest-neighbor CO molecules on the Pt(111) surface at a 1-fold site and a 2-fold site is 3.66Å and that between a 1-fold site and a 3-fold site is 3.20Å (Fig. 1.1). For the Pt(100) surface, carbon monoxide binding sites can be 1-fold, 2-fold or 4-fold (Fig. 1.2). The bonding description of carbon monoxide bonded vertically on the Pt surface involves two interactions, CO 5σ donation to Pt surface band orbitals and back-donation from these orbitals to the CO π* orbital (Fig. 1.3).

1.5.3. Statement of the Problem

An understanding of possible multiple steps and pathways of the oxidation of CO to CO₂ on electrode surfaces as well as possible intermediates or strongly adsorbed species is the central focus of the present research. Although CO oxidation occurs at potentials where the formation of platinum oxides occurs, the involvement of surface oxide acting as a source of oxygen is still debatable. There is the possibility that the oxides have their own catalytic properties. Also, the inertness of stabler Pt oxides can lead to a lower electrocatalytic activity.
Fig. 1.1. CO bonding in 1-fold, 2-fold and 3-fold sites on the Pt(111) surface. [model used by A. B. Anderson and S.-F. Jen, J. Phys. Chem. 94, 1607 (1990)]
Fig. 1.2. CO bonding in 1-fold, 2-fold and 4-fold sites on the Pt(100) surface. [model used by A. B. Anderson and S.-F. Jen, J. Phys. Chem. 94, 1607 (1990)]
Fig. 1.3. 5σ donation and back-donation to π* for CO adsorbed to a surface metal atom. [from A. B. Anderson, in Chapter 10 of "Theoretical Aspects of Heterogeneous Catalysis" Ed. J. B. Moffatt (1989)]
Some experimental evidence for adsorbed hydrogen playing a role in CO oxidation is based on the holding potential effects in the voltammetry (i.e. dependence of CO oxidative desorption peak features on the CO adsorption potential). It is possible that hydrogen adsorption is coincidental, and the influence of potential results from the structure of the double layer or the orientation of CO and H$_2$O molecules. The difference between hydrogen adsorption on a surface preadsorbed with CO and CO adsorption on a surface preadsorbed with hydrogen should be distinguished.

A number of experimental conditions have been studied. These include the pretreatment of the electrode, the way in which CO is adsorbed, the solution composition and the CO adsorption potential. This thesis will cover these variables for the studies of CO electrochemical oxidation.
2.1 Single Crystal Surface Preparation

The electrochemical oxidation of carbon monoxide in aqueous media is sensitive to structural properties of the electrode surface such as surface morphology (e.g. single crystal character), and therefore the surface characterization is important for the understanding of what is occurring at the atomic level during CO electrooxidation. Single crystal platinum surfaces with low Miller indices, namely Pt(100), (111), (110), have been used in these studies.

The quality of the results obtained from electrochemical studies of a single crystal electrode is strongly depend upon the cleanliness and the state of the crystal surfaces. Therefore, the preparation of the electrode surface is a crucial part of single crystal studies.

The pre-grown platinum single crystals were purchased from Metal Crystal and Oxide Ltd. All of the crystals were cylindrically-shaped (approximately 6.35 mm in diameter x 6.35 mm in length and 10.00 mm in diameter x 3.00 mm in length) and guaranteed 99.999% pure.
Large crystals have been used in this work in order to provide a larger working area to facilitate infrared studies. There are three steps in the surface preparation process: orientation, polishing and annealing. Each crystal was glued to an aluminum disk with a fast-setting epoxy cement and the disk was screwed onto a polishing jig. Next the jig was placed on a V-block and fastened to the X-ray track of a Laue backscattering apparatus (General Electric XRD-5). The crystals were oriented to within 0.5°. The method by which the crystal were mounted for polishing and orienting were developed by Professor B. D. Cahan, modifying the techniques originally developed by D. M. Zehner of the Oak Ridge National Laboratory [106].

The surface crystallographic orientation was maintained throughout the mechanical polishing process. All of the polishing materials were purchased from Buehler. Each crystal was polished sequentially with increasingly finer grades of Emery paper (0, 00, 000, 0000), then 1200 grit Si-C paper, diamond paste (6, 3, 1μm) and finally alumina powder (0.3 and 0.05 μm) to obtain a mirror finish. An optical metallograph was used to verify that each polished surface was free of scratches and pits.

A Buehler Whirlimet Automatic Polishing Device was
used to polish the crystals. After polishing, the crystals were cleaned in a hot solution of one part concentrated nitric acid to one part concentrated sulfuric acid, followed by thorough rinsing with distilled-reverse osmosis water.

A modified flame-annealing method [107] was used to anneal the crystal in order to avoid thermal stressing of the large Pt crystal. A slow cooling in a hydrogen stream down to the room temperature is required. Each crystal was annealed for 10 min (20 min may be desired for larger crystals) in a hydrogen-oxygen flame to reach a temperature of 950-1050 °C, which was measured with a chromel-alumel thermocouple in contact with the back of the Inconel 600 crystal holder.

After removal from the flame, the crystal was rapidly transferred into a closed Pyrex tube purged with flowing hydrogen (Matheson ultrapure grade 99.999%) where it remained for 2 min to cool. The crystal was removed with the surface protected by a drop of ultrapure water in order to prevent any impurities from the air and from the surface of the solution from contaminating the single crystal surface during the transfer process.

The crystal surface was characterized using voltammetry in the hydrogen electroadsorption/electroodesorption region in 0.1M HClO₄, and following ex-vacuo transfer
(see below) to the ultrahigh vacuum chamber, using low energy electron diffraction in order to ascertain the quality of the well-ordered surfaces.

The flame-annealed electrode was quickly fitted into a special rotating disk electrode holder (Fig. 2.1), and then brought into contact with the electrolyte in the electrochemical cell. The assembled rotating disk electrode was attached to a Pine ASR-2 rotator. The electrode was lowered into the cell until contact was made with the electrolyte and then raised slightly so that a meniscus formed between the electrode face and the electrolyte. Care was taken not to wet the sides of the crystal. A particular reproducible shape of the steady state cyclic voltammetry can be obtained for each of the low index and stepped Pt single crystal surfaces, and there are indicative of the quality and cleanliness of the crystal surface.

The flame-annealed crystal was also transferred into a closed Pyrex transfer vessel purged with flowing hydrogen (Matheson, ultrapure grade 99.999%) before it was ex vacuo transferred into the three-chamber ultrahigh vacuum system (Fig. 2.2) for LEED analysis. The pressure in the surface physics chamber was less than 2 x 10^{-9} Torr. The crystal was radiatively heated to 400 °C.
Fig. 2.2 Schematic diagram of the ultra high vacuum system.
to desorb impurities and then reexamined with LEED.

The LEED apparatus used in the surface physics chamber was comprised of a Varian electron gun and four-grid optics system. The electrode gun was operated in a constant filament voltage mode with an emission current of generally a few tenths of a μA (e.g., 0.3 μA at a beam energy of 53 eV).

The diffraction patterns were imaged on a fluorescent screen. This image was photographed with a 35 mm camera and all photographs were taken with an f-stop of 3.5 with Kodak Panatomic-X or Kodak T-Max 400 film for times periods of 600-800 s or 30-120 s, respectively.

2.2 Ultrapure Water Preparation

The problem of removal of impurities from water used for single crystal electrochemical studies is an important issue [108]. A relatively inexpensive continuous duty water purification system has been used and tested in our laboratory. This system produces 15-20 liters per day of high purity water directly from the city water supply. The design of the this system is based on an efficient design which is commercially available [109]. The original design was modified for us by Gilmont Instruments Inc. to our specifications to allow
for operation under a nitrogen atmosphere.

The feed should have a sufficiently low concentration of Ca$^{2+}$ and Mg$^{2+}$ ions to prevent scale formation even after concentration by the distillation process. The condensed vapor should be collected at the boiling point and the condensate is collected in the alembic in order to prevent a loss of the product by refluxing back to the separator. The quality of the water is monitored at various stages in the process using three conductivity meters: one after the tap water filtration, one after the reverse osmosis membrane filtration and one after the final distillation. The final resistance is no lower than 18MΩ. The water quality criteria are more stringent than the American Society of Testing and Materials (ASTM) electronic-grade standard [110-111].

2.3 Electrolyte Solution Preparations

2.3.1 Phosphoric Acid

In order to remove oxidizable organics and lower oxyacids of phosphorus, analytical reagent grade phosphoric acid (84.7% from Mallinckrodt) was added to 50% hydrogen peroxide (Hach) and heated up to 50°C until vigorous gas evolution ceased. The solution was heated to 160°C to remove any unreacted hydrogen peroxide and to
evaporate the excess water. After cooling, the solution was placed in a round bottom flask equipped with a sintered glass bubbler.

The solution was deoxygenated by rapidly bubbling nitrogen for 15 minutes. Platinum black (Engelhard fuel cell grade, with an area of \( \sim 35 \text{ m}^2/\text{g} \) ) was added (1 g per 500 mL of solution), and hydrogen was bubbled through the solution for more than 48 h. The acid was filtered through a 0.2 \( \mu \text{m} \) pore size membrane and the bubbling of hydrogen was continued during the filtration process. The resulting concentration of phosphoric acid can be determined by titration to a phenolphthalein endpoint. The single crystal experiments were carried out in various concentrations from 85\%(\sim 15\text{M}), 10\text{M}, 5\text{M}, 1\text{M} \) through 0.01\text{M} by diluting with ultrapure water.

The purity of the 85\% phosphoric acid can be tested with cyclic voltammetry. After voltammetric cycling of the electrode in the acid at 150 \( \text{C} \), a small peak was observed in the double layer region but at room temperature the peak became negligible. A likely explanation for this behavior is that 85\% phosphoric acid is relatively viscous at 25 \( \text{C} \) and the diffusion rate of impurities to the electrode is slow enough that the peak is not observed. The species could not be eliminated by further
purification and was judged to be intrinsic to phosphoric acid [112-113]. The cyclic voltammetry for the Pt single crystals was indicative of acceptable purity for the purified acid in various concentrations at room temperature.

A pre-electrolysis procedure had been used to purify the phosphoric acid after the hydrogen peroxide treatment instead of the platinum black method. A potential in the hydrogen generation range was applied to a platinum gauze electrode and purified nitrogen was used to force solution through the Pt gauze at a stable flow rate for 72 hours. The purity was shown to be similar to that obtained using the Pt black method.

2.3.2 Perchloric Acid

Ultrapure (Ultrex grade) perchloric acid (J. T. Baker Chemical Co.) was used in this work and no further purification was applied. A pre-electrolysis procedure with a continuous flow system had been used to check the purity level. Cyclic voltammetry showed no difference before and after the pre-electrolysis process. The purity of the perchloric acid was thus judged to be suitable for this single crystal work.

2.3.3 Acetonitrile in Dry Box
Aldrich chemical company Gold Label anhydrous 99.9+% (with less than 0.00005% water) acetonitrile was used inside of a Vacuum Atmospheres HE-43 series "Dri-Lab" dry box. The dry box was used in order to provide a working area with an inert atmosphere free of moisture and oxygen. Before operation, the catalyst was activated by heating with a 1% ultrapure hydrogen [balanced with ultrapure argon (Matheson 99.999%)] gas mixture. During the sample transfer operation, care was taken to evacuate the antechamber. The water sensor inside the dry box showed less than 1 ppm water present. Tetrabutylammonium perchlorate (Electrometric grade from Southwestern Analytical Chemicals Inc.) was used as the supporting electrolyte. It was dried under vacuum at ≈80°C for 12 h and stored in a desiccator or in the dry box.

2.4 Gas Handling

2.4.1 Carbon Monoxide Safety Monitor

A Model 2006 carbon monoxide monitor (Sierra Monitor Corporation) was used to monitor CO in the laboratory air for safety purposes. The sensor is a sintered n-type metal-oxide semiconductor, the conductivity of which increases in the presence of carbon monoxide. The Model
2006 is factory-calibrated so that the alarm sounds at 100 ppm CO. Standard laboratory procedure required that the monitor be activated during CO gas operation, particularly in the FTIR laboratory, in which there was in a closed air circulation loop.

2.4.2 Gases

Ultrahigh purity grade (UHP) nitrogen (Matheson 99.999%) was used in all deoxygenation procedures in this work. Carbon monoxide (Matheson purity grade, 99.99%) was used in all of the high concentration CO experiments. The gas mixture (Certified Standard grade, with 10% component preparation tolerance) of 1.04% (±0.02%) carbon monoxide (Matheson purity, 99.99%) with 99% nitrogen (UHP grade) was used in low concentration CO experiments. Due to the similar densities of carbon monoxide and nitrogen, the latter is a good candidate for maintaining the proper gas mixture ratio while the gas is withdrawn from the cylinder. In the solubility test, 99.3 atom % $^{13}$C-labeled (with 8.0 atom % $^{18}$O) carbon monoxide (from Isotec Inc.) was used in the 400 MHz $^{13}$C NMR measurements [114].

2.5 Carbon Monoxide Solubility in Electrolyte

In the electrochemical cell, gas (either pure N$_2$ or CO-N$_2$ mixture) was bubbled directly through the electro-
lyte using a glass grit gas dispersion tube. During the experimental measurements, the gas was passed above the electrolyte to maintain gas saturation in the solution. The carbon monoxide solubility in water is dependent on the temperature. At 0°C it is 3.54 mL/100 mL (1.7 x 10^{-3} M), at 20°C 2.32 mL/100 mL (1.05 x 10^{-3} M), and at 25°C 2.14 mL/100 mL (0.96 x 10^{-3} M) [115].

The presence of CO in phosphoric acid has been checked using 400 MHz $^{13}$C NMR. $^{13}$C-labeled carbon monoxide was used to saturate the deuterated phosphoric acid, 85% D$_3$PO$_4$ in D$_2$O (99 + atom% from Aldrich) which was diluted by deuterium oxide (D$_2$O with 99.8% D from Norell Inc.) to prepare 10 M, 5M, 1M solutions for $^{13}$C NMR measurements. The solubility measurements will be discussed in more detail in Chapter 3.

2.6 Linear Sweep Cyclic Voltammetry

After the flame-annealed crystal was fitted into the special Kel-F holder and mounted in a Pine ASR-2 rotating disk electrode rotator, a meniscus was formed, with the disk surface protected with an ultrapure water droplet, on the crystal face about 3 mm above the electrolyte level under potential control at +0.04V vs. RHE. Experiments were performed in nitrogen-saturated electro-
lyte with $N_2$ flowing above the electrolyte. A cyclic voltammogram was taken to check the quality of the single crystal surface. Introduction of CO(1%) was carried out by flowing the gas above the electrolyte for 30–60 min. Cyclic voltammetry was used to continuously monitor the saturation level. The potential was held at a fixed potential in the Pt double layer region (typically at +0.4 V), for a given time period (e.g. 1 min) and then the positive sweep was recorded. After the CO oxidation peak current reached a limiting value, the solution was considered to be saturated. A steady-state continuous-sweep voltammogram was recorded as a background curve (see Fig. 1 of Chapter 3). Various holding potentials and times were then used to control the coverage of CO on the surface.

The electrochemical measurements were carried out in a conventional three-compartment Pyrex cell. A platinum gauze electrode served as the counter electrode and was separated from the main cell body by a porous frit. The reference electrode was a reversible hydrogen electrode (RHE) in the same medium, which was brought in contact with the main working electrode compartment via a Luggin capillary. Cyclic voltammograms were recorded at a sweep rate of 50 mV/s.

2.7 In Situ Fourier Transform Infrared Spectroscopy
A great variety of heterogeneous processes has been investigated and elucidated by both surface chemists and electrochemists. Electron spectroscopic techniques have enabled one to obtain information on surface processes at gas-solid interfaces. Due to the very small mean free path of electrons in liquid electrolytes, liquid-solid interfacial electrochemical studies cannot make direct use of electron spectroscopic techniques. Infrared reflectance techniques have thus been considered and widely implemented for the study of the structure and dynamics of solid metal/liquid electrolyte interfaces. Because of strong infrared absorption of aqueous solutions used in electrochemistry, in situ external reflection methods using a very thin layer of electrolyte were developed [116-117].

In order to gain molecular specificity for electrochemically adsorbed/desorbed species on electrode surfaces, infrared spectroscopic techniques were applied in addition to traditional current-potential measurements. The information obtained on vibrational properties of adsorbates can be interpreted in terms of adsorbate structure and bonding so that, using the surface selection rules, IR spectra can determine the molecular identity and binding orientation of adsorbed species on electrode surfaces at the given applied potentials [118].
The primary goal of in situ methods in studying electrode-solution interfaces is to characterize the adsorbed species in the electrical double layer and species in the reaction-diffusion layer near the electrode surface. Spectrometers capable of measuring absorbances on the order of $10^{-2}$ to $10^{-6}$ are required for the detection of these species. Because of the large absorption of IR radiation by the bulk solvent (i.e. water) and less than monolayer surface concentration of adsorbed species ($<2 \times 10^{-9}$ mol/cm$^2$), the sensitivity of the measurement must be improved by cell design, data acquisition and experimental methods [119–121].

2.7.1 Cell Design

To minimize the IR absorption of the solvent, a cell was used which is capable of forming a very thin layer of electrolyte in contact with an infrared-transparent CaF$_2$ flat window, which is mounted at one end of the cell (Fig. 2.3). A CaF$_2$ dove prism can replace the flat window in order to improve the sensitivity. This is because the IR absorption coefficient for metal surfaces is a strong function of the angle of incidence for paral
(G) Nitrogen gas outlet  
(B) Pt counter electrode wire  
(E) Tefzel cell body  
(I) Micrometer  
(D) Ca F₂ window  
(A) Tafzel electrode holder  
(H) Viton O-ring  
(C) Luggin teflon capillary  
(F) Nitrogen gas inlet  
(J) Cell mount for fastening to Optical table

Fig. 2.3 Illustration of the electrochemical infrared cell used in the FTIR studies of adsorbates on single crystal Pt surfaces. (A) Tefzel electrode holder (B) Pt counter electrode lead wire (C) luggin Teflon capillary (D) CaF₂ optical windows (can be replaced by dove prizm in Fig. 2.4) Tefzel cell body (F) N₂ gas inlet (G) N₂ gas outlet (H) Viton o-rings (I) Micrometer (J) Cell mount for fastening to optical table.
polarized radiation (p-polarized). The dove prism allows one to conveniently use a relatively large angle of incidence (e.g. 60° to surface normal), while a flat window decreases the incident angle at the metal surface due to refraction. The reflected light combines with the incident light to produce a standing wave electric field at the metal surface, into which the thin absorbing layer is introduced. The cell design and optical path provide an optimum value of the angle of incidence and the state of polarization of the incident light to maximize the absorption in the reflected beam, in order to gain the most sensitivity to the adsorbed species on the reflecting metal surface.

The infrared radiation was p-polarized using a KRS-5 wire grid polarizer and was incident on the CaF$_2$ window of the electrochemical cell at an angle of 60° to the surface normal. The Tefzel (Du Pont) fluoropolymer cell was mounted on an adjustable reflection attachment optical table which was placed in the sample compartment of the FTIR instrument. The optical path of the infrared beam is schematically shown in Fig. 2.4.

The instrument used in this work is an IBM IR/98 FTIR spectrometer equipped with a Globar light source and a liquid nitrogen-cooled solid state mercury-cadmium-tellurium detector. KBr windows mount on either side of
Calcium Fluoride Dove Prism

1. Angle between the base plane(abhg) and the side plane(aceh and bdgf) is 60 degree.

2. Optical planes: base plane(abhg) and two side planes(aceh and bdgf). Two side planes(aceh and bdgf) are at 60 degree.

Fig. 2.4 Schematic diagram of the optical arrangement used in the FTIR studies. (with the CaF$_2$ dove prism)
the sample compartment with O-ring compression seals so that vacuum can be maintained in the source and detector compartments. The sample compartment was continuously purged with nitrogen during the measurements in order to decrease IR absorption from CO₂ and H₂O in air.

2.7.2 Data Acquisition

Signal-to-noise enhancement is accomplished through signal averaging techniques. A number of interferograms are obtained typically at one potential and then at a second potential, and this process is repeated until the desired signal-to-noise ratio is obtained. The two single beam spectra, recorded with p-polarized light with the same specified number of interferometric scans at each potential, are subtracted from each other and ratioed to the intensity at one potential to obtain the final normalized spectrum as in the following expression:

\[ \frac{dR(v)}{R} = \frac{R_2(v) - R_1(v)}{R_1(v)} \]

\( v \): frequency, \( R \): reflectance

This is so-called subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS). Three types of electrochemical measurements were used in
the acquisition of SNIFTIRS spectra: single potential step, multiple potential step and slow linear sweep cyclic voltammetry.

The procedure employed was as follows: A reference potential $E_r$ was set at which CO adsorbed on the surface. Then the electrode was pushed against the CaF$_2$ window, forming a thin layer cell, and the spectroscopic measurements were taken synchronously with changes in the electrochemical potential. For the potential step technique, the experiment was continued as follows. After twenty interferometer scans were completed, the counter/triggering device sent a trigger pulse to the potentiostat, resulting in an electrode potential change to the sample potential ($E_s$) at which complete oxidation of CO occurs. A two second time delay was observed prior to triggering the interferometer. After collecting twenty spectral scans at $E_s$, the electrode potential was changed back to $E_r$, and the process was repeated. A total of 400 to 1000 scans was obtained (depending on the coverage of CO) at $E_r$ and $E_s$ by alternately collecting 20 scans at each potential. These two sets of data were subtracted and ratioed to give a SNIFTIRS spectrum. The coupling of the spectral acquisition with the electrochemical potential step technique is shown schematically in Fig. 2.5a for the multiple step method.
Fig. 2.5 Various potential program schemes for in situ FTIRRAS; $E_\text{s}$ and $E_\text{r}$ are the sample and the reference potentials respectively. The potential change is followed by a time delay of 1–5 sec to remove nonfaradaic components. a) Square wave train, one normalized spectrum at the end of the train. b) Single potential step. c) linear sweep at a very slow rate (1 mV/s), one spectrum over $\approx$100 mV potential span.
In the single step method (Fig. 2.5b), the sample potential spectrum and the reference potential spectrum were taken in sequence without alternately shifting the potentials during the spectral scans. This can lead to artifactual CO$_2$ and/or H$_2$O peaks if these species change their concentrations in the gas phase (principally N$_2$) in the spectrometer sample chamber. The multiple step technique reduces the magnitude of such artifacts, as well as other factors such as thermal drift, to a greater degree than dose the single step method. Thus the single step FTIR technique requires that the system is stable without significant changes in water vapor, CO$_2$ concentration or instrumental drifts.

The coupling of slow sweep cyclic voltammetry (Fig.2.5c) with FTIR spectroscopy allows one to obtain spectral information corresponding to voltammetric current-potential features in greater detail. A reference spectrum was taken at a reference potential $E_r$ at which CO adsorbs on the surface using the same number of scans (i.e. 200 scans), which was to be taken during the slow linear potential sweep over specified potential range (e.g. 100 mV). The potential was swept positively at a rate of 1 mV/s and a series of sample spectra was collected synchronously with the potential sweep in each 200 interferogram scans. The electrode potential values displayed with each spectrum were the midpoint potential
(i.e. at 101th interferogram scans) through the acquisition of 200 scans. The linear sweep CV method allow for a detailed matching of cyclic voltammetric features with the spectral information.

After being protected by a drop of purified water on the polished face, the flame-annealed Pt electrodes (including both polycrystalline and single crystal Pt) were inserted into a Tefzel electrode and held by a viton O-ring. Using a micrometer, the Tefzel holder with crystal was advanced to a point close to the CaF₂ window, forming a thin layer electrochemical cell for the spectral measurement. The position and orientation of the crystal face and light path had been carefully adjusted for optimum IR energy detection before introducing electrolyte into the cell.

The electrolyte was deaerated with nitrogen prior each experiment. A reversible hydrogen electrode was used as the reference electrode. The working electrode (crystal) was spot-welded on the rear side to a Pt lead wire. The potential was controlled by a PAR 175 programmer with a PAR 173 potentiostat. A stable voltammogram was obtained before collecting spectra. Nitrogen with 1% CO was introduced into the cell directly for more than 30 minutes while the electrode was pulled back from the
window. A linear potentials sweep was applied during the CO introduction process until a stable voltammogram was obtained. The potential was held for various time periods to control the CO coverage and then the electrode was pushed toward the window, forming a thin layer cell for spectral acquisition.
CHAPTER 3
RESULTS AND DISCUSSION

3.1 Carbon Monoxide Electro-oxidation on Polycrystalline
Platinum Surface in 0.1 M Perchloric Acid.

The preparation of experimental materials has been
described in Chapter 2, "Experiment and Methods" in this
thesis. The working electrode was a polycrystalline
platinum disk of the same size (0.34 cm² surface area) as
the single crystal electrode and annealed with the same
procedure. In order to reduce the anion coadsorption
effect, 0.1 M HClO₄ was used as the supporting electro-
lyte. This was prepared from Baker Ultrex grade per-
chloric acid with distilled reverse osmosis water. The
annealed polycrystalline Pt disk was mounted in a spe-
cially adapted rotating disk electrode (RDE) assembly as
described in Chapter 2 for single crystal electrodes.
The RDE was attached to a Pine ASR-2 rotator and lowered
into the electrochemical cell. The electrode surface had
been protected with a drop of pure water and then the
electrode was lowered until the water drop just made
contact with the surface of the electrolyte solution.
Care was taken not to wet the cylindrical side of the
electrode. The electrode was raised slightly to form a

50
hanging meniscus between the electrode face and the electrolyte. Before measurements were started, the electrode was cycled several times between 0.05 V and 1.50 V (vs RHE) at 50 mV/s to obtain voltammetry curves which were typical of a clean polycrystalline Pt electrode surface [122-124]. After several cycles the curves retraced themselves within the thickness of the pen tip (solid line in Fig.3.1).

Controlled experiments were carried out to check for any impurities in the electrolyte that would adsorb on the electrode surface under the conditions used for CO adsorption. First, the electrode was cycled in nitrogen-saturated electrolyte until the characteristic voltammetry of polycrystalline Pt was obtained. The potential was held for periods up to 10 min either in the hydrogen adsorption/desorption region (0.150 V vs RHE) or in the double layer region (0.450 V). When the potential sweep was resumed in the negative direction, the characteristic voltammetry of polycrystalline Pt was obtained immediately upon reversing the sweep direction at 0.050 V. This indicates the absence of significant amounts of adsorbed impurities.

The CO was introduced into the electrochemical cell in the following way. While continuously cycling the potential from the hydrogen adsorption/desorption region
(0.05 V) to the oxide region (1.50 V) at 50 mV/s, 1% CO (balance ultrapure nitrogen) was flowed above the electrolyte in the gas phase without perturbing the meniscus for 60 to 120 min. Saturation was achieved within 60 min. The anodic limit was more positive than needed to oxidize the CO which was adsorbed on the electrode surface from the electrolyte during the negative sweep period. Reproducible cyclic voltammograms were obtained with 10⁻⁵ M CO (ref. Section 2.5) present in the electrolyte (resulting from the equilibrium of the 1% CO in N₂ with the electrolyte). The voltammetry curves for polycrystalline Pt in 0.1 M HClO₄ without and with CO are shown in Fig.3.1.

After a stable background voltammogram was obtained in 1% CO saturated solution, various potential holding times were used to control the CO coverage on the Pt surface. These times varied from 1 to 10 min. After the potential holding time, the voltammograms were recorded as the potential was swept from the holding potential either in the positive or negative directions. Prior to reaching the potential range in which CO is oxidized, the negative sweep to 0.05 V(vs RHE) can show the decrease in the charge for the hydrogen adsorption and desorption due to blocking of the Pt surface by the co-adsorption of CO.
Fig. 3.1 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with nitrogen [solid line] and saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s.
The CO coverage is a function both of the holding potential and the time held at that potential (Fig. 3.2). The hydrogen adsorption/desorption charge (after subtraction of the estimated double layer charge) without CO present was taken. The decrease in the charge, when CO was adsorbed, was assumed to be due to one CO molecule blocking each H adsorption site on the Pt surface. The holding potentials used were 0.450 V and 0.150 V (vs RHE) and the holding times were 1, 3, 5, 7 min. At the ending of the holding time, the potential was swept first negatively and then positively, as described earlier. In the positive potential sweep after adsorption in the double layer region, multiple oxidation peaks were observed especially for the lower coverages (lower holding time). For the highest coverage (10 min holding time or longer), the potential sweep showed two main peaks, with a slight shoulder remaining in the lower potential (Fig. 3.5). At a holding potential in the hydrogen adsorption/desorption region, there were only two oxidation peaks at low CO coverages. At the highest coverage, a major peak was observed with a slight shoulder on the lower potential side (Fig. 3.4). For the same holding times for the two different holding potentials, the coverages of CO were estimated to be approximately the same. Thus at the same coverages, there are differences in the voltammetry due to the CO adsorption.
CO coverage vs. $E(\text{ads})$

Time(ads) = 3 min

Fig. 3.2 Carbon monoxide coverage (estimated by the CO charge current and hydrogen adsorption/desorption charge area) vs. CO adsorption potentials.
Fig. 3.3 Carbon monoxide coverage (estimated by the CO charge current and hydrogen adsorption/desorption charge area) vs. holding time (CO adsorption time).
Fig. 3.4 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential= 150 mV. Holding time= 1, 3, 5, 10 min[solid line].
Fig. 3.5 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 450 mV. Holding time = 1, 3, 5, 10 min [solid line].
In order to obtain further information concerning the relationship of the holding potential and subsequent potential sweep to oxidation peak structure, more detailed studies were carried out. Various holding potentials were used for 3 min periods to compare the shifts of the peak positions. There were found to be three different regions of holding potentials showing the dependence of the oxidation desorption peak positions upon CO adsorption potential: under 0.25 V; 0.25 to 0.40 V; and 0.45 V to 0.65 V. For the holding potentials less than 0.25 V, no difference was found in the oxidation desorption peak position when the sweep following the holding potential was either cathodic or anodic. After 3 min holding at 0.20 V, the positive sweep starting at the holding potential showed an oxidation peak feature centered at 0.70 V to 0.80 V. The negative sweep starting at the same holding potential after 3 min holding time showed an oxidation peak feature occurring over the same potential range with the same peak current (Fig. 3.6). The potential of the oxidation peak was found to remain the same for CO adsorption potentials less than 0.25 V.

For holding potentials more positive than 0.250 V, a sweep direction dependence was observed in the voltammetry. This potential is the beginning of the double layer region. After a 3 min holding period at 0.300 V, the positive sweep also showed the oxidation peak feature
Fig. 3.6 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 200 mV. Negative [dash-point] and positive [solid] sweep.
centered at 0.70 to 0.80 V. For the negative sweep, however, the oxidation peak was divided into two multiple peak regions, one centered at 0.70-0.75 V and the other at 0.80-0.85 V with approximately the same coverages (Fig. 3.7). This type of behavior was maintained for holding potentials from 0.25 V to 0.40 V. For adsorbed potentials ranging from 0.40 V to 0.65 V, positive sweep showed the two multiple peak features located at 0.70-0.75 V and 0.80-0.85 V. These two peaks were shifted about 30 mV negatively (for the lower potential peak) and 30 mV positively (for the higher potential peak) while sweeping the potential negatively to the hydrogen adsorption/desorption region. These was no significant change in the coverage (Fig. 3.8).

During the negative potential sweep after the holding period, CO continues to adsorb on the electrode surface. In the positive sweep experiment, the time available for the adsorption of CO is less. In order to obtain the same coverage for both negative and positive sweep experiments, the holding period was either increased for positive sweep experiment to match the longer time spent in the negative sweep experiment before returning to the holding potential, or decreased for negative sweep experiment to match the positive experiment. This assumes that the rates of adsorption and the structure of the adsorbed CO are not dependent on the poten-
Fig. 3.7 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 300 mV. Negative [dash-point] and positive [solid] sweep.
Fig. 3.8 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO$_4$ saturated with mixture of 1% CO in N$_2$ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 450 mV. Negative [dash-point] and positive [solid] sweep.
tial over the sweep range in these experiments. The behavior of the CO oxidation after this type of compensation was made is qualitatively the same as described earlier. A slight increase or decrease in the peak current was observed for the compensation experiment without any significant change in the voltammetry peak structure.

In order to examine the influence of the holding potential without perturbing the sweep process, at the end of holding period, the potential was either immediately stepped to 0.6V, a value just before the onset of CO oxidation and then scanned sweep or stepped first to a potential within the hydrogen adsorption/desorption region before stepping to 0.6V and then scanned continuously. There were slight decreases in the peak currents due to lower coverages as compared with the ordinary sweep experiments. In this potential step-sweep experiment, the behavior in the voltammetry peak structure of the CO oxidation was qualitatively the same as the earlier voltammetry curve.

Thus there were significant differences observed in the CO oxidation peak structures for the those different CO adsorption conditions: 1) CO adsorbed by holding the potential in the double layer region, 2) CO adsorbed by holding the potential in the hydrogen adsorption region
and 3) CO adsorbed by holding the potential in the double layer region but subsequently experiencing potentials in the hydrogen adsorption region. There are several possible explanations for these differences, including: 1) surface structural changes in the Pt surface due to H adsorption, 2) reaction of adsorbed H and adsorbed CO, 3) changes in the CO-Pt bonding structure, 4) changes in the CO adlayer structure. The first three possible explanations will be discussed in the following paragraph.

Regarding explanation 1, the in situ X-ray diffraction work of Fleischman and Mao [127] indicated that the changes in the structure of Pt surface layers are possible for "weakly" adsorbed hydrogen (discussed later in the Section of single crystal studies). The structure of Pt surface layer may also been changed for the adsorbed CO on Pt surface. Whether the adsorbed CO or the "weakly" adsorbed hydrogen cause the change in the surface nature of Pt is not sufficiently clear to use for interpreting the CO oxidation peak structures on polycrystalline surface. The sensitivity of CO oxidation to the surface geometrical structure have been studied further and will be discussed in the single crystal Section (3.2). Regarding explanation 2, no reduction or adsorption peak was observed in the region where could be attributed to CO(ads). Therefore, the chemical interaction between adsorbed CO and adsorbed hydrogen is weak. [reviews of
fuel cell studies in ref.125). Explanation 3 is unlikely because only one form of adsorbed CO(linear) was observed by the _in-situ_ FTIR studies of CO oxidation on polycrystalline Pt presented in Section 3.1.2. This result indicates that changes in the binding structure of CO caused by co-adsorbed hydrogen are relatively small.

It is likely that the CO adlayer structure has a major influence on the CO oxidation mechanism (explanation 4). Kunimatsu et al. [128] proposed that the surface CO layers formed in the hydrogen potential region undergo CO oxidation randomly within the adsorbed CO layer. For the CO adsorbed layer formed in the double layer potential region, however, the oxidation of CO is proposed to proceed at the purlieus of adsorbed CO islands [129]. As an extension of this type model, it is possible that the co-adsorption of hydrogen modifies the CO adlayer structure so that a greater number of small islands are formed, in which CO oxidation proceeds randomly within the island domains. The species at the purlieus of the islands may be more easily oxidizable resulting in a more negative peak (see Fig.3.4). The species at the central regions of the islands may be less easily oxidizable resulting in a peak with a more positive oxidation potential (see Fig.3.5). The CO adsorbed in the double layer region may form larger domains re-
sponsible for more positive oxidation potentials. When surface CO adsorbed in the double layer region experiences the potentials in the hydrogen adsorption/desorption region, such larger adlayer domains may redistribute into somewhat smaller island-type adlayer structures without a change in the coverage. The potential required to oxidize adsorbed CO with large islands is likely to be more positive than that for the smaller island ensemble. It is proposed that the differences in the CO oxidation energy requirements referred to above are due to differences in the interactions between adsorbed CO and adsorbed oxygen donors (adsorbed H$_2$O, OH and O).

3.1.1 The Use of Hanging Meniscus Rotating Disk (HMRD) for the Oxidation of CO on Polycrystalline Pt.

The hanging meniscus rotating electrode (HMRD) was used to obtain kinetic information [143-144]. Before the electrolyte was saturated with CO, the HMRD was rotated in a N$_2$ saturated electrolyte with a rotation rate up to 4900 rpm in order to check any impurity effect. The Fig. 3.9 shows voltammetry curves of rotation and non-rotation for polycrystalline Pt. The retardation of surface oxide formation at rotation rates of 3600 and 4900 rpm was caused by a small amount Cl$^-$ anion adsorption on the Pt. It was also evidenced by a small decrease of reduction peak at 0.75 V and a small change in the hydrogen adsorp-
Fig. 3.9 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with N₂ gas at 1 atm at rotating rate = 0 rpm [solid line], 3600 rpm [dash line], 4900 rpm [dash-point line]. Sweep rate = 50 mV/s.
The HMRD was used to study the electro-oxidation of CO with rotation rates up to 3600 rpm in a electrolyte of $10^{-5}$ M CO. Figure 3.10 shows results for five rotation rates. The oxidation peaks occurred at 725, 775, 800, 825, 850mV respectively for 400, 900, 1600, 2500, 3600 rpm. The rotation-induced increases in the peak current are consistent with an apparent increase of CO coverage on the surface which was evidenced by the decrease of hydrogen adsorption/desorption charge as seen in the figure. The adsorption of CO on the Pt surface is under diffusion control and the rate of CO adsorption increases with rotation rate (Fig.3.11). The positive shifts of the oxidation peaks with higher rotation rates are interpreted as being due to an increase of the CO coverage to form larger CO adlayer islands, which required higher oxidation potentials. At a rotation rate of 3600 rpm, the CO coverage reached a maximum (although less than full coverage), so that even higher rotation rates (4900 rpm) did not increase the peak current as compared with the peak current at 3600 rpm. The peak potential (850 mV) was also unchanged.

An alternative explanation for this result is also based on the increase of CO adsorption rate with rotation rate. At low rotation rates (e.g. 400 rpm), the adsorp-
Fig. 3.10 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm at rotating rate = 400 rpm [solid line], 900 rpm [dash-point line], 1600 rpm [dash-double-point line], 2500 rpm [dash line], 3600 rpm [long-dash line]. Sweep rate = 50 mV/s.
Fig. 3.11 CO coverages vs. reciprocal root square of rotation speed. (Data points taken from Fig. 3.10.)
tion of CO occurs both during the sweep in the range of double layer potentials and is co-adsorbed in the hydrogen adsorption region. Because the CO adsorbed in the hydrogen adsorption potential region uses different surface sites for the adsorption of CO, a less positive potential for the CO oxidation peak and the greater width of the oxidation peak can be expected. At a rotation rate of 3600 rpm, most of the CO adsorption occurs at potentials in the double layer. Thus the CO oxidation peak occurs at a more positive potential. The range of potential peak shifts from 725 mV to 850 mV and coincides with the multiple peak range appearing in the non-rotating potential-hold experiments (Fig. 3.4). This may mean that this particular potential range covers the potentials corresponding to different types of adsorbed CO [7]. The rotation rate dependence of the peak width may indicate a more uniform distribution of energetic states of adsorbed CO within the adlayer for higher coverages. This type of effect was also observed in the coverage dependent behavior of CO in potential hold experiments (Figs. 3.4 & 3.5).

The potential hold experiments involved a rotation rate of 400 rpm at 0.20 and 0.45 V each for 30 s. The background curve was a continuous sweep voltammogram recorded at a rotation rate of 400 rpm in 10^{-5} M CO, and showed a current peak at 0.725 V for the oxidation of ad-
sorbed CO. For the holding potential of 0.20 V showed a single spike was observed at 0.75 V (Fig. 3.12). The adsorbed CO oxidation peak shift to 0.80 V for the holding potential of 0.45 V (Fig. 3.13). Except for the single spike feature in the oxidation peak structure, the oxidation peak potentials for holding potential in the double layer region and the hydrogen region are similar to the non-rotating potential holding experiments.

The nature of the sharp peak is interpreted as being due to the coupling of two surface processes as follow.

\[ \text{Pt-CO} + \text{H}_2\text{O} \rightarrow \text{Pt} + \text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- \quad (3.1) \]

\[ \text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt-OH} + \text{H}^+ + \text{e}^- \quad (3.2) \]

Those surface processes can be expressed as follows:

\[ E = E^0_o - \frac{RT}{nF} \ln \left( \frac{\theta_{\text{Pt-CO}} \text{CO}_2(\alpha_{\text{H}^+})^2}{\theta_{\text{Pt-CO}}(\alpha_{\text{H}_2\text{O}})} \right) \]

\[ -2RT \left( \Sigma_{\text{Pt-CO}} \theta_{\text{Pt-CO}^+} \Sigma_{\text{Pt-OH}} \theta_{\text{Pt-CO}^+} (\Sigma_{\text{Pt-CO}} \theta_{\text{Pt-CO}})^2 \right) \]

\[ + (\Sigma_{\text{Pt-CO}, \text{Pt-OH}} \theta_{\text{Pt-CO}} \theta_{\text{Pt-OH}} + (\Sigma_{\text{Pt-OH}} \theta_{\text{Pt-OH}})^2) \]

Where \( \Sigma \) = Frumkin term; \( \theta \) = coverage;

\( \tau \) = electrosorption valence.
Fig. 3.12 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm. Rotating rate = 900 rpm [dashed line]. Sweep rate = 50 mV/s. Holding time = 30 sec. Holding potential = 200 mV [solid line].
Fig. 3.13 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm. Rotating rate = 900 rpm [dashed line]. Sweep rate = 50 mV/s. Holding time = 30 sec. Holding potential = 450 mV [solid line].
The interactions between adsorbed CO and surface oxide makes the energy of adsorption a function of surface coverage. According to the Frumkin isotherm [130], the cross terms of the coverage of adsorbed CO and surface oxide coverage are related to the adsorption energy. This coupling of surface adsorbed species is analogous to the phenomenon of chloride anion adsorption with the co-adsorption of hydrogen. The sharp peak observed in such cases is due to the favorable interaction of the two adsorption/desorption process. When $f \rightarrow 4.5$, the voltammetry peak becomes very sharp.

The rotation rate dependence experiment was carried out for higher CO concentrations ($10^{-3}$M) in 0.1 M HClO$_4$ with rotation rates of 400 to 3600 rpm. Only a single oxidation spike was observed at 950 mV regardless of the rotation rate (Fig.3.14) Almost no hydrogen adsorption features were found. The latter indicates full CO coverage. The oxidation of this layer occurred at higher oxidation potentials (0.95 V), compared to 0.85 V for the $10^{-5}$M CO concentration, indicating a higher energy requirement for the densely packed CO adlayer. The very narrow CO oxidation peak is interpreted in terms of the interactions between adsorbed CO and the surface hydroxide as described earlier. Right after the potential of the oxidation spike was reached, the surface adsorbed CO
Fig. 3.14 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with 100% CO at 1 atm. Rotating rate = 400 rpm [solid line], 900 rpm [dash-point line], 1600 rpm [dash-double-point line], 2500 rpm [dash line], 3600 rpm [long-dash line]. Sweep rate = 50 mV/s. Potential window opened to 1.4V.
was consumed completely and the oxidation of solution CO became evident, as seen by the rotation rate dependence of the current at potentials anodic to the sharp peak. The currents at potential anodic to the sharp peak began to decrease indicating a non-steady state transit of the production of OH(ads) and the consumption of CO(sol'n). With the increase of $\theta_{\text{Pt-OH}}$, the surface oxide film became a substrate for the oxidation of solution phase CO. The reverse cathodic sweep showed nearly potential-independent current plateaus. This indicates that these rotation rate dependent currents are caused by the oxidation of solution CO on the Pt(OH) substrate.

The cathodic sweep currents are related to the rotation rate $f$ by the expression [131-132]

$$\frac{1}{i} = \left(\frac{1}{i_k}\right) + \frac{1}{(B/\sqrt{f})} \quad (3.5)$$

where $B/\sqrt{f}$ is the diffusion limiting current, $B$ is the Levich coefficient (defined below), $f$ is the revolutions per min (rpm), and $i_k$ is the kinetic limiting current.

$$B = 0.20 \left(\frac{D_{CO}}{nFAC_{CO}}\right)^{2/3} \nu^{-1/6} nFAC_{CO} \quad (3.6)$$

where $D$ and $C$ are the diffusion coefficient and solubility of CO, $\nu$ is the kinematic viscosity, $A$ is the electrode area in cm$^2$, $F$ is the Faraday, and $n$ is the number of electrons transferred per molecule of CO diffusing through the Nernst boundary layer. The $i^{-1}$ vs. $w^{-1/2}$
Fig. 3.15 Voltammetry curves of polycrystalline Pt electrode in 0.1 M HClO₄ saturated with 100% CO at 1 atm. Rotating rate = 400 rpm [solid line], 900 rpm [dash-point line], 1600 rpm [dash-double-point line], 2500 rpm [dash line], 3600 rpm [long-dash line]. Sweep rate = 50 mV/s. Potential window opened to 1.15V.
plots should be linear for first-order kinetics [133]. Figure 3.16 shows such plots for the data from fig. 3.14 at 0.925, 1.0, 1.1, 1.2, 1.3V. The linearity of these plots is consistent with first-order kinetics with respect CO (sol’n). There was almost no potential dependence of the intercepts, which could indicate a chemical step as rate determining. The reciprocal of the slopes of these lines yield an average B value equal to 1.25 x $10^{-2}$ mA(rpm)$^{-1/2}$. To use this B value, the experimental diffusion coefficient of CO can be deduced by the equation 3.6. The kinematic viscosity was calculated from the viscosity of 1.002 x $10^{-2}$ g/s·cm (value for pure water at 20° C, ref.11) divided by the density of 1.005 g/cm$^3$ to be 9.97 x $10^{-3}$ cm$^2$/s. Based on these values and the present experimental data, a value for the diffusion coefficient of CO was calculated to be 8.89 x $10^{-6}$ cm$^2$/s, under assuming an n value of 2 and a CO concentration of 1.05 x $10^{-3}$M (see Chapter 2). If the number of electron transfer (n value) equals to 1, then the diffusion coefficient of CO was calculated to be 2.515 x $10^{-5}$ cm$^2$/s which is closer to the $D_{CO}$ value (2.03 x $10^{-5}$ cm$^2$/s at 25°C) from CRC Handbook [115].

Based on the above results, a possible mechanism for the oxidation of solution phase CO is as follows:

CO(sol’n) → CO(OHP) :outer Helmholtz plane
Fig. 3.16 Plot of $1/i$ vs. $1/\sqrt{f}$ for CO adsorbed on polycrystalline Pt surface in 0.1 M HClO$_4$. Data points taken at the potentials of 0.95, 1.0, 1.1, 1.2, 1.3 V (vs. RHE) from Fig. 3.14.
CO(OHP) + OH(ads) → CO₂ + H⁺ + e⁻

or

CO(OHP) + PtOₓHᵧ → PtOₓ₋₁Hᵧ + CO₂

In the cathodic sweep, the currents decreased following the plateau because the reduction of surface oxide and a recovery of bare Pt surface depended on the consumption of surface hydroxide in the reaction with the CO(sol’n). The lower consumption at a lower rotation rate of 400 rpm showed a slowest decay of the current after the plateau (Fig. 3.14) and it is more clear while the voltammetry window opening only to 1.15V (Fig. 3.15).

3.1.2 The Chloride Anion Effects.

In order to further test this mechanism, the chloride anion was used in the electrolyte to inhibit the oxide film formation on the Pt surface. The original perchloric acid assumed to contain less than 10⁻⁵ M Cl⁻ from the impurity assay (see chapter 2). Chloride concentrations of 10⁻⁴ M and 10⁻³ M Cl⁻ in perchloric acid were used in potential hold experiments. A retardation of the CO oxidation peak was observed in Figs 17-19. In the case of the 0.15 V holding potential, the oxidation peak moved from 725 mV to 750 mV for 10⁻⁴M Cl⁻, and to 800 mV for 10⁻³M Cl⁻. For a holding potential of 0.45 V, the oxidation peaks became sharper and shifted from 800
Fig. 3.17 Voltammetry curves of polycrystalline Pt electrode in [a] 0.1 M HClO₄ and [b] 0.1 M HClO₄ + 10⁻⁴ M Cl⁻ and [c] 0.1 M HClO₄ + 10⁻³ M Cl⁻ saturated with mixture of 1% CO in N₂ [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 3 min.
Fig. 3.13 Voltammetry curves of polycrystalline Pt electrode in (b) 0.1 M HClO₄ + 10⁻⁴ M Cl⁻ saturated with mixture of 1% CO in N₂ (dash line). Sweep rate = 50 mV/s. Holding potential= 150mV [dash-point line], 450mV [solid line]. Holding time= 3 min.
Fig. 3.19 Voltammetry curves of polycrystalline Pt electrode in [c] 0.1 M HClO₄ + 10⁻³ M Cl⁻ saturated with mixture of 1% CO in N₂ [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 3 min.
to 850 mV for $10^{-4} \text{ Cl}^-$, and to 900 mV for $10^{-3}\text{M Cl}^-$. The inhibition of surface oxide formation can be observed in the decrease of the Pt oxide reduction peak current at $\approx 0.77\text{V}$ for the dashed line background curve. This result may indicate an involvement of the oxidation of the Pt surface with the oxidation of the adsorbed CO. The shift of the CO oxidation peak to more positive potential may be caused by the shortage of surface hydroxide, which is one of the possible oxygen donors. The sharp oxidation peak can be attributed to interaction between $\text{Cl}^-(\text{ads})$, $\text{CO(ads)}$, $\text{PtOH}$. For holding potential of hydrogen adsorption(150 mV), the adsorbed Cl$^-$ is not involved so that the sharp oxidation peak was not observed.

Rotating disk-potential hold experiments were used to examine further this Cl$^-$ anion effect. A rotation rate of 400 rpm was used and holding potentials of 0.15 and 0.45 V were held for 1 min for CO adsorption. The retardation of the CO oxidation peaks was observed and the potentials shifted from 875 to 900 mV for $10^{-4}\text{M Cl}^-$ and to 925 mV for $10^{-3}\text{M Cl}^-$ (Figs. 20-22). Due to the shortage of oxygen donors from surface hydroxide, the CO oxidation peaks were retarded. The inhibition of the surface oxide formation was increased by rotation, which was evidenced by a greater CO oxidation peak retardation. The rotating disk experiment, there may be an increase in
Fig. 3.20 Voltammetry curves of polycrystalline Pt electrode in [a] 0.1 M HClO₄ and [b] 0.1 M HClO₄ + 10⁻⁴ M Cl⁻ and [c] 0.1 M HClO₄ + 10⁻³ M Cl⁻ saturated with mixture of 1% CO in N₂ at 400 rpm [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 1 min.
Fig. 3.21 Voltammetry curves of polycrystalline Pt electrode in (b) 0.1 M HClO₄ + 10⁻⁴ M Cl⁻ saturated with mixture of 1% CO in N₂ at rotation rate= 400 rpm [dash line]. Sweep rate = 50 mV/s. Holding potential= 150mV [dash-point line], 450mV [solid line]. Holding time= 1 min.
Fig. 3.22 Voltammetry curves of polycrystalline Pt electrode in [c] 0.1 M HClO$_4$ + $10^{-3}$ M Cl$^-$ saturated with mixture of 1% CO in N$_2$ at rotation rate = 400 rpm [dash line]. Sweep rate = 50 mV/s. Holding potential = 150mV [dash-point line], 450mV [solid line]. Holding time = 1 min.
the chloride adsorption on the Pt surface but not for holding potential in the hydrogen adsorption region.

3.1.3 Infrared Spectroscopic Studies of Carbon Monoxide Oxidation on the Polycrystalline Pt Surface.

The coupling of external reflection infrared methods with conventional electrochemical methods can provide molecular-level information on the adsorbate-electrode interactions, including the nature of binding to the surface and the orientation of the adsorbate on the electrode surface. The single potential step method and linear sweep cyclic voltammetry have been used with in situ infrared spectral acquisition for holding potential studies of CO electrochemical oxidation on polycrystalline Pt electrode. All of the experimental techniques are described in Chapter 2 EXPERIMENTS & METHODS. After the electrode potential was held at a potential in the hydrogen adsorption/desorption region (0.15 V vs. RHE) or a potential in the double layer region (0.45 V) for periods of 1, 3, and 5 min, the electrode was pushed against the infrared window, forming a thin layer spectroelectrochemical cell. At this point, the electrode potential was set at $E_r$, the potential used as a reference. Either 0.15 V or 0.45 V was used for $E_r$, then 200 interferometer scans were collected before the electrode potential was stepped to the sample potential, $E_s=1.0$ V, for another
200 interferometer scans. These two sets of data were appropriately ratioed to give the SNIFTIRS spectrum (described in Chapter 2). In these SNIFTIRS spectra, the positive peaks indicate an increase in the concentration or coverage of the species and the negative peaks indicate a decrease.

The series of spectra plotted in Figs. 3.23 & 3.24 were obtained for a CO concentration of $10^{-5}$M in the electrolyte using the potential step method as previously described. The band observed at 2026–2068 cm$^{-1}$ is assigned to the stretching mode of linearly adsorbed CO (Fig. 3.23) at the adsorption potential of 150 mV. Carbon monoxide is bound to the electrode surface through a single Pt–C bond which is colinear with the C–O bond axis. The peak shifts to higher frequencies as the electrode surface coverage increases during longer holding periods. This coverage-dependent frequency shift has been observed by many authors [55-64]. The linearly adsorbed CO for the adsorption potential of 0.45 V was observed over the 2025–2075 cm$^{-1}$ frequency range, with the frequency increasing with increasing coverage (Fig. 3.24). The peak with a frequency of 2350 cm$^{-1}$ is assigned to the asymmetric stretching vibration mode of carbon dioxide in the solution phase which results from CO oxidation.
Fig. 3.23 FTIR spectra of CO adsorption on polycrystalline Pt in different adsorption periods. 0.1 M HClO₄ + 10⁻⁵ M CO. Holding at 150 mV vs RHE for 1, 3, 5 min. Single step at reference 450 mV & sample 1000 mV. NSS= 200. RES= 8 cm⁻¹. SMF= 0. Incident angle with CaF₂ prism= 60°.
Fig. 3.24 FTIR spectra of CO adsorption on polycrystalline Pt in different adsorption periods. 0.1 M HClO₄ + 10⁻⁵ M CO. Holding at 450 mV vs RHE for 1, 3, 5 min. Single step at reference 450 mV & sample 1000 mV. NSS= 200. RES= 8 cm⁻¹. SMF= 0. Incident angle with CaF₂ prism= 60°.
The coupling of cyclic voltammetry with infrared spectroscopy was used to obtain chemically specific information concerning the spectral responsible for the oxidation peak features for the voltammetry curves. The reference spectra were taken with 200 scans interferograms at potentials of either 0.15 or 0.45 V, where the CO was adsorbed. The potential then was slowly swept positively at a rate of 1 mV/s while a series of sample spectra were collected with each spectrum corresponding to 200 scans collected over a 100 mV range. In Figs. 3.25 and 3.26, the electrode potentials given corresponding to the midrange points. After the potential was held at 0.15 V for 5 min, it was stepped to 0.45 V and the potential sweep was initiated from that point. In the 150 mV holding potential case, it can be seen that the CO oxidation has already started for the midpoint potential of 0.50 V (Fig. 3.25). The 0.45 V holding experiment shows the oxidation starting for the midpoint potential of 0.58 V (Fig. 3.26). These results are consistent with the oxidation current-potential features in the voltammograms in Figs. 3.3 & 3.4. Both series of spectra indicate the consumption of CO by the decrease of the 2050 cm⁻¹ band and the production of CO₂ by the increase of the 2350 cm⁻¹ band. The linear bonded CO observed here and in most in situ infrared studies on the polycrystalline Pt surface is consistent with the island formation explanation for the potential shifts for the CO oxidation.
Fig. 3.25 FTIR spectra of CO adsorption on polycrystalline Pt vs electrode potentials. 0.1 M HClO$_4$ + 10$^{-5}$ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans). Holding at 150 mV vs RHE for 5 min. NSS = 200. RES = 8 cm$^{-1}$. SMF = 0. Incident angle with CaF$_2$ prism = 60°.
Fig. 3.26 FTIR spectra of CO adsorption on polycrystalline Pt vs electrode potentials. 0.1 M HClO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans) Holding at 450 mV vs RHE for 5 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.
peaks. The binding structure of CO to Pt surface is changed insignificantly by the co-adsorbed hydrogen and increases in CO coverage.

The 2155 cm\(^{-1}\) frequency for free CO gas is shifted to lower frequencies for the terminal bonded CO (M-CO) in carbonyl metal complexes (ca. 2100-1800 cm\(^{-1}\)). The 1860-1700 cm\(^{-1}\) frequency range for bridge bonding of CO to two metals sites (M-CO-M) is lower (2125-1850 cm\(^{-1}\)) [133-134]. This information can be used to identify bridged and linear forms of CO on surfaces. It should be noted that another type of bridged form of CO can exist (M-C-O-M). The IR band corresponding to this type of bonding is observed at frequency of ca. 1300 cm\(^{-1}\) [135-136].

The infrared absorption bands resulting from the chemisorption of CO on metals, particularly the bands associated with CO stretching modes, can be interpreted in terms of the chemical state of the CO and the types of metal sites involved in the bonding. Often the CO absorption band for CO adsorbed on Pt has been observed in this work in the intermediate wavenumber range, 2050-1900 cm\(^{-1}\). This also includes the measurements with Pt single crystals, described in sections 3.2-3.4. The assignment of higher frequency bands in the range to linear bonding and lower frequency bands to bridge bonding cannot be
judged solely by comparison with IR frequencies for metal carbonyl complexes. The bonding to metal atoms in a solid metal surface should be much different from that to isolated metal atoms. In addition CO adsorbed on sites at the edges or corners of metal crystallites, which would have higher electron density available for back-donation from the metal site to CO, results in lower IR frequencies. A greater degree of back-donation of d-electrons from the Pt metal into anti-bonding orbitals of the CO molecule leads to a structure more like Pt≡C≡O than Pt-C≡O⁺ for linearly bound CO. A CO having greater double bond character should exhibit a lower frequency band. As described in sections 3.2 and 3.3, various CO coverages, surface geometric structures and applied potentials exhibit frequencies and bonding structures between these extremes.

3.2 Carbon Monoxide Oxidation on the Three Low Index Pt(111), Pt(100) and Pt(110) Surfaces in 0.1 M Perchloric Acid.

A major objective of research in electrocatalysis to understand the relationship of the geometric structure of the surface to the catalytic activity. Even on high area Pt catalysts supports such as carbon, the platinum may consist of single crystal particles with specific low index planes exposed [1]. Thus kinetic studies with
massive single crystal are important to the understanding of the highly dispersed catalyst. In this work, the low Miller indices planes, namely Pt(111), Pt(100), and Pt(110) were used to study the CO electro-oxidation. The experimental conditions were the same as in the polycrystalline Pt experiments in Section 3.1 of this chapter. In the voltammetry studies, the upper potential limit was chosen to be sufficiently positive to electrooxidize CO entirely but avoiding or at least minimizing irreversible oxide formation, which would result in surface reconstruction and disordering. The upper potential limits were 0.80 V for Pt(100), 0.90 V for Pt(111) and 1.0 V for Pt(110), respectively.

Voltammograms of low index single crystals were recorded without CO present in order to check for the possibility of any impurities adsorbing on the crystal surface from the electrolyte during the holding period. This was done as previously described by holding the potential in the hydrogen adsorption/ desorption and double layer regions and then recording a cyclic voltamogram(Fig. 3.27). The voltammetry curves were retracted themselves after the first sweep and indicated negligible impurities adsorbed on surfaces during the holding period.
Fig. 3.27 Voltammetry curves of Pt(111) and Pt(100) electrode in 0.1 M HClO₄ saturated with N₂ (Full line). The dash line and dash-point line show the negative sweep curves after 3 min holding time starting at holding potential 0.15 V and 0.45 V.
After the electrolyte was saturated with $10^{-5}$ M CO, the potentials were then held at 0.15 V and 0.45 V, for the three low index surfaces for 3 min periods. The voltammogram for Pt(111) shows a single peak centered at 0.75 V (Fig. 3.28). The peak potential was found to be independent of the holding potential as well as the coverage. The voltammogram for Pt(100) shows a shoulder starting at 0.65 V as well as a peak at 0.75 V (Fig. 3.29). The peak potential was also found to be independent of the holding potential and the coverage.

The voltammetry curve for Pt(110) indicates that the peak potential change and the structure of the CO oxidation peak are all dependent on the holding potential. The largest peak shifts from 675 mV to 775 mV when the holding potential is changed from 0.15 to 0.45 V (Figs. 3.30 & 3.31). A clearer picture of the origin of the peaks can be seen in the voltammetry of Pt(110) by holding the CO adsorption potential at 0.1, 0.2 and 0.3 V for 3 min. After the holding period, the potential was swept either in the positive or negative direction for comparison(Figs.32-34). A single peak appeared at 675 mV with a holding potential of 0.1 V regardless of the sweep direction(Fig.3.32). For the holding potential of 0.2 V, the peak structures obtained in the two sweep directions changed. When the potential was swept negatively to the
Fig. 3.28 Voltammetry curves of Pt(111) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 150, 450 mV. Negative sweep.
Fig. 3.29 Voltammetry curves of Pt(100) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 150, 450 mV. Negative sweep.
Fig. 3.30 Voltammetry curves of Pt(110) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. Holding time = 3, 5, 7, 10 min. Holding potential = 450 mV. Negative sweep.
Fig. 3.31 Voltammetry curves of Pt(110) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. Holding time = 3, 5, 7, 10 min. Holding potential = 150 mV. Negative sweep.
Fig. 3.32 Voltammetry curves of Pt(110) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 100 mV. Negative[dash-point line] and positive[solid line] sweep.
Fig. 3.33 Voltammetry curves of Pt(110) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 200 mV. Negative [dash-point line] and positive [solid line] sweep.
Fig. 3.34 Voltammetry curves of Pt(110) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. Holding time = 3 min. Holding potential = 300 mV. Negative [dash-point line] and positive [solid line] sweep.
hydrogen region before the positive sweep, the single peak feature was maintained at 675 mV(Fig.3.33). For a holding potential of 0.3 V, the multiple peak structure appeared at the potential of 775mV. When the potential was swept negatively to the hydrogen region, a single peak feature remained predominant(Fig.3.34).

3.2.1 Infrared Spectroscopy Studies of Carbon Monoxide Oxidation on the Single Crystal Pt Surfaces.

Combined use was made of infrared spectroscopy and the potential step method to study the behavior of CO on Pt single crystal surfaces. The potential difference spectra obtained for the three low index planes are shown in Figs.3.35-38 for the frequency region 1900-2500 cm⁻¹. The electrode was first polarized either at a potential in the hydrogen adsorption region or in the double layer region in the bulk electrolyte (several mm from the optical window) for 10 min to allow the CO adsorption to take place. The electrode was then pushed close to the optical window at the same potential and a reference spectrum was collected. The sample spectrum was collected after the potential was stepped to a more positive value (ca. 1.0 V) corresponding to CO oxidation. The infrared spectra for Pt(111) exhibit bands at 2059 cm⁻¹ and 2052 cm⁻¹ for linearly bonded CO adsorbed at 408 mV and 135 mV respectively. The production of CO₂ is evi-
Fig. 3.35 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 0.1 M HClO₄ + 10⁻⁵ M CO. Holding at 135, 408 mV vs RHE for 10 min. Single step at reference 450 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm⁻¹. SMF = 0. Incident angle (air/ CaF₂) = 50°.
Fig. 3.36 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 0.1 M HClO$_4$ + 10$^{-5}$ M CO. Holding at 200, 400 mV vs RHE for 10 min. Single step at reference 450 mV and sample 1000 mV vs RHE. NSS= 400. RES= 8 cm$^{-1}$. SMF= 0. Incident angle (air/ CaF$_2$ )= 50°.
Fig. 3.37 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 0.1 M HClO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans) Holding at 400 mV vs RHE for 10 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle (air/ CaF₂) = 50°. First spectrum is the reduction of in situ generation CO₂ at 950 mV.
Fig. 3.38 FTIR spectra of CO adsorption on Pt(110) vs electrode potentials. 0.1 M HClO₄ + 10⁻⁵ M CO. Holding at 150, 450 mV vs RHE for 10 min. Single step at reference 450 mV & sample 1000 mV vs RHE. NSS= 400. RES= 8 cm⁻¹. SMF= 0. Incident angle (air/ CaF₂ )= 50°.
enced by the appearance of the 2343 cm\(^{-1}\) band. Holding potential experiments were also performed for the Pt(100) and Pt(110) surfaces for 3 min holding periods in the hydrogen and double layer regions. The spectra for Pt(100) show a bridge bonded CO band at 1820 cm\(^{-1}\) for the 200 mV holding potential experiment case. There were only slight difference in the spectra for the 200 mV and 400 mV holding potential experiments (Fig. 3.36). In the spectra for Pt(110), the CO bands show a potential dependent frequency shift from 2070 to 2080 cm\(^{-1}\) and a CO\(_2\) band appears at 2368 cm\(^{-1}\) (Fig. 3.38).

The coupled cyclic voltammetry in situ infrared experiment was carried out in similar manner to that described for the polycrystalline Pt. The only difference was one additional potential step to the hydrogen adsorption region (ca. 0.10 V) after the potential was stepped at 1.0 V for the CO oxidation. This was done in order to study the reduction of in situ generated CO\(_2\). The potential was stepped to 0.110 V for 3 min without changing the electrode position against the CaF\(_2\) infrared window (Fig. 3.37). The spectrum at the bottom of Fig. 3.26 shows the decrease of the 2343 cm\(^{-1}\) band, indicating the consumption of CO\(_2\). The remaining spectra show the decrease of the CO band at 2047 cm\(^{-1}\) for the 705 mV midpoint potential, which is close to the CO oxidation peak observed in the voltammetry for Pt(100) shown in
As mentioned earlier in a preliminary discussion (Section 3.1), in order to understand the infrared spectral features of adsorbed CO on Pt surfaces, it is necessary to further consider the topography of Pt surface planes. The adsorption of CO on single atom or multiple atom-Pt sites on low index single crystal planes has been described in Section 1.5. The assignment of IR frequencies and interpretation of absorption bands for CO adsorption on the low index surface will be discussed in terms of linear bonding, bridge bonding and multiple bonding. The blue-shift or red-shift of the IR frequencies for adsorbed CO as compared with CO in given coordination environments in metal-carbonyl complexes is a function of CO coverage, surface electric field, co-adsorbed species (e.g. electrolyte) and different resonance molecular structures for the adsorbed CO. The infrared spectra for adsorbed CO on Pt single crystal surfaces in more strongly adsorbed electrolytes such as phosphoric acid can provide more insight for this matter, as discussed in the next section.

3.3 Carbon Monoxide Oxidation on the Three Low Index Pt Surfaces (111), (100), and (110) in Phosphoric Acid Electrolyte.
Phosphoric acid is the electrolyte which is used in low temperature (≈200°C) H₂-O₂ fuel cells. Organic fuels may also be used in acid-type fuel cells, the performance of such cell tends to degrade due to strongly adsorbed species such as CO on the surface of the catalyst. Thus the studies of CO on single crystal Pt surfaces in phosphoric acid will contribute directly to the understanding of the degradation process of noble metal electrocatalyst. Such experiments have been carried out with H₃PO₄ in concentrations of 85%, 10 M, 5 M, 1 M, 0.01 M for the three low index Pt single crystals.

3.3.1 ¹³C NMR Measurement.

In order to understand the chemistry of CO in H₃PO₄ solution, including the nature of dissolved CO as well as any other species in solution, ¹³C NMR studies were carried out. Isotopic ¹³CO in deuterated phosphoric acid (D₃PO₄ diluted by deuterium oxide) was used in ¹³C NMR (Brucker 400 MHz) measurements. The chemical shift at 184.9 ppm for deuterium oxide was found for ¹³CO dissolved in pure water(Fig. 3.39). The chemical shift decreased slightly for 5 M and 10 M deuterated phosphoric acid at 184.0 ppm and 182.2 ppm respectively(Fig. 3.40). The nature of the CO dissolved in phosphoric acid, even at concentrations of H₃PO₄ as high as 10 M, is evidenced
Fig. 3.39 $^{13}\text{C}$ NMR (400 MHz) chemical shift at 184.887 ppm show $^{13}\text{C}$O presence in D$_2$O.
Fig. 3.40 $^{13}$C NMR (400 MHz) chemical shift at 182.225 ppm (in 4, 8, 12, and 16 hrs accumulating periods) show $^{13}$CO presence in 10 M $D_3$PO$_4$ in $D_2$O.
by the appearance of a single peak. No indication was obtained for other species such as might be present due to chemical reaction of CO in solution. In 10 M deuterated phosphoric acid, the NMR measurements were also accumulated for longer times, 4, 8, 12, and 16 h in order to increase signal/noise ratio over the chemical shift range, there was only a single detectable peak. For the deuterated 85% phosphoric acid, the NMR measurement under the same conditions of instrumental sensitivity, showed no chemical shift signal even after 24 h of accumulation, indicating the absence of dissolved carbon monoxide. The detection limit for this measurement was estimated to be $10^{-6}$M.

3.3.2 Water Effect.

The water molecule is one of the possible oxygen donors for CO electrooxidation to CO$_2$. The variation of water activity in aqueous phosphoric acid and the use of nonaqueous aprotic solvents were employed to examine the effect of water in CO electrooxidation. The voltammetric measurements in CO-saturated 85% phosphoric acid [(The water vapor over a 85% (14.7M) H$_3$PO$_4$ at 129.65°C was estimated to be 350.90 Mm of Hg ($\approx$0.17 atm).] showed no CO oxidation peak and no decrease of the hydrogen adsorption/desorption area. Hydrogen adsorption area started
Fig. 3.41 Voltammetry curves of (a) Pt(111), (b) Pt(100) and (c) Pt(110) electrode in 10 M H₃PO₄ saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. Holding time = 6 min. Holding potential = 400 mV. Negative sweep [full line] following the holding.
to be blocked by CO in 10 M phosphoric acid after holding the potential at 0.40 V for 6 min and then sweeping negatively. It is clear that no significant CO oxidation peak is present except appearance of a slight shoulder (Fig. 3.41). Evidence for the presence of CO dissolved in 10 M $D_3PO_4$ was obtained in the NMR measurements, and evidence for adsorbed CO on the Pt surface was indicated by the shrinkage of the hydrogen adsorption area. Thus the absence of a clear CO oxidation peak in the voltammetry is not due to the absence of either solution or adsorbed CO. A possible explanation for this result may be a lower water activity for the 10 M $H_3PO_4$ solution compared with more dilute electrolyte.

In order to examine the effect of very low water content, the aprotic solvent acetonitrile was used with tetrabutylammonium perchlorate as the supporting electrolyte. The experiment was carried out inside a dry box, with a water level less than 1 ppm. The preparation of the solvent and supporting electrolyte are described in Chapter 2, "Experiments and Methods", in this thesis. Inside the dry box during a 15 min holding period at -1.0 V vs. a pseudo-reference silver electrode, CO was not oxidized on polycrystalline Pt (Fig. 3.42). On the other hand, when the solution was placed in contact with humid ambient air, the electrooxidation of CO was found to
occur (Fig. 3.42).

The surface oxide of Pt is another possible oxygen donor which provides adsorbed hydroxyl to take place in the oxidation of adsorbed CO. The oxidation peak for CO on polycrystalline Pt in 0.1 M perchloric acid occurs at a potential of 0.70 to 0.75 V, which coincides with the onset of Pt surface oxide formation. In protic nonaqueous solvent of trifluoromethane sulfonic acid (with less than $10^{-5}$ M water), the CO oxidation peak is inhibited, occurring at a potential of 0.90 V, which coincides with surface oxide formation. For 10 M $\text{H}_3\text{PO}_4$ experiments on low index single crystal Pt surfaces, the positive potential limits were chosen to electrooxidize CO at a minimum potential so as to avoid irreversible oxide formation while still oxidizing the CO completely. Therefore, the oxygen donor in this case may not be surface oxide but instead maybe the adsorbed water. Due to the low water activity in 10 M phosphoric acid, the electrooxidation of CO may be inhibited due to shortage of adsorbed water. In contrast, for the 5 M concentration, which has two water molecules to every phosphate anion, a clear CO oxidation peak was observed (Fig 3.44).

3.3.3 Anions and Hydrogen co-adsorption Effect.

Phosphoric acid, although it has several advantages
Fig. 3.42 Voltammetry curves of polycrystalline Pt in Acetonitrile w/TEAP saturated with mixture of 1% CO in N₂. Sweep rate = 50 mV/s. Holding potential = -1.0 V vs Ag/Ag⁺. Holding time = 15 min. In dry box (≤1 ppm water) and in the air.
Fig. 3.43 Voltammetry curves of Pt(111) electrode in 5 M H₃PO₄ saturated with mixture of 1% CO in N₂[dashed line]. Sweep rate = 50 mV/s. Holding time= 6 min. Holding potential= 300, 450 mV. Negative sweep [full line] following the holding.
for use as a fuel cell electrolyte, has disadvantage of adsorbing strongly on Pt surfaces and thus inhibiting the electrocatalysis. Phosphoric acid is moderately dissociated (pK_a=2.15), and thus both molecular H_3PO_4 and the conjugate anion exist in the solution. These molecules and anion can adsorb on the Pt surface therefore affect the oxidation of CO. The voltammetry for Pt(111) in 5 M phosphoric acid with 10^{-5} M CO shows no dependence of the holding potential (0.30 V and 0.45 V) in CO oxidation peak structure (Fig.3.43). The Pt(110) surface also showed no holding potential dependence. The voltammetry for the Pt(100) surface in 5 M phosphoric acid is shown in Fig.3.44(a) and with and without 10^{-5} M CO. Three potential regions can be distinguished and can be assigned to weakly-adsorbed, strongly-adsorbed hydrogen, and hydrogen adsorption coupled with phosphate adsorption. Holding potential dependence of the CO oxidation peak structure was observed for Pt(100) (Fig.3.44(b)). The potentials were held at 0.15, 0.25, and 0.35 V, and the resulting CO oxidation peaks occurred at 875, 900, and 925 mV, respectively. Although the peak height varies with the holding potential, the coverage only changes slightly. When the several potentials in the double layer region were used in 5 M H_3PO_4, the oxidation peak potentials did not change but the coverage varied. This was also true for 1 M H_3PO_4 (Fig.3.45(a)). The same CO oxidation peak poten-
Fig. 3.44 Voltammetry curves of Pt(100) electrode in 5 M H₃PO₄ (a) nitrogen saturated [full line] and saturated with mixture of 1% CO in N₂ [dashed line]. Sweep rate = 50 mV/s. (b) Holding time= 6 min. Holding potential= 150, 250, 350 mV. Positive sweep [full line] following the holding.
tial (880mV) was observed with the holding potential set at 0.45, 0.50, and 0.55 V. At a much lower H₃PO₄ concentration (0.01 M), the CO oxidation peak did not shift significantly even using holding potentials in the hydrogen adsorption and anions coadsorption regions as well as the double layer region [Fig. 3.45(b)].

For the Pt(111) surface in 1 M phosphoric acid, CO was adsorbed by holding the potential at 0.15 V and 0.50 V in the hydrogen adsorption and the anions coadsorption regions respectively. The CO adsorbed at 150 mV produces a broad oxidation peak from 650 to 750 mV [Fig. 3.46(b)]. The CO adsorbed at 0.50 V produces multiple peak structure with dominant peak shifted a slightly more positive potential [Fig. 3.46(b)]. More detailed studies were carried out [Fig. 3.47(a)] to determine how the CO oxidation peak structure changes depending on the adsorption potentials, which were 0.15, 0.20, 0.25 and 0.30 V. For 1 M solution, as the holding potential was made more positive, the CO peak structure became increasingly dominated by two peaks. With more dilute H₃PO₄ (0.01M), the effect of adsorbed hydrogen vs. coadsorbed anion on the CO oxidation peak structure was not as pronounced as in the 1 M solution. For the Pt(110) surface [Fig. 3.48], the CO adsorption potentials were held at 0.125, 0.25, and 0.40 V for 1 M phosphoric acid and at 0.125, 0.225, and 0.40 V for 0.01 M phosphoric acid. For the 1 M concentration,
Fig. 3.45 Voltammetry curves of Pt(100) electrode
(a) in 1 M H₃PO₄ saturated with mixture of 1% CO in N₂[dashed line]. Sweep rate = 50 mV/s. Holding time = 6 min. Holding potential = 450, 500, 550 mV. Positive sweep [full line] following the holding.
(b) in 0.01 M H₃PO₄ saturated with mixture of 1% CO in N₂[full line]. Sweep rate = 50 mV/s. Holding time = 1 min. Holding potential = 150, 300, 350, 400, 450 mV. Positive sweep following the holding.
Fig. 3.46 Voltammetry curves of Pt(111) electrode in 1 M H$_3$PO$_4$ (a) nitrogen saturation [full line] and saturated with mixture of 1% CO in N$_2$ [dashed line]. Sweep rate = 50 mV/s. (b) Holding time = 6 min. Holding potential = 150, 450 mV. Positive sweep following the holding.
Fig. 3.47 Voltammetry curves of Pt(111) electrode in 0.01 M H₃PO₄ saturated with mixture of 1% CO in N₂ [full line]. Sweep rate = 50 mV/s. (a) Holding time = 1 min. Holding potential = 150, 200, 250, 300 mV. Positive sweep [full line] following the holding. (b) Holding time = 3 min. Holding potential = 150, 500 mV. Positive sweep [full line] following the holding.
CO oxidation peak structure also shifted to more positive potentials as the CO adsorption potential was shifted from the hydrogen adsorption (0.125 V) and anion coadsorption region (0.25 V) and finally to the double layer region (0.40 V).

3.3.4 Infrared Spectroscopy Studies of Carbon Monoxide Oxidation in Phosphoric Acid Electrolyte.

In situ FTIR techniques were applied to examine the surface adsorbed species on three low index single crystal surfaces in 1 M phosphoric acid. Various CO adsorption potentials were used for the potential step study. The electrode was first polarized at a potential at which CO adsorption took place for 5 to 15 min. The electrode was then pushed close to the optical window while holding the same potential, and a reference spectrum was collected. A sample spectrum was collected after the potential was stepped to a more positive value (1.0 V) corresponding to the CO oxidation peaks in the voltammetry. The coupling of slow linear sweep voltammetry and infrared spectral acquisition was used to examine in more detail the correspondence between the surface adsorbed species as well as products (e.g. CO₂) and the applied potential.

The potential difference spectra obtained for the
three planes are shown for the frequency range 1790-2500 cm\(^{-1}\). The spectra in Fig.3.49 show band for the linearly adsorbed CO at 2081 cm\(^{-1}\) and 2087 cm\(^{-1}\) for adsorption potentials of 146, and 410 mV, respectively, on Pt(111). The series of spectra plotted in Figs.3.50 and 3.51 are for slow linear sweep voltammetry on the Pt(111) surface for CO adsorption potentials of 146 and 400 mV respectively. These spectra indicate that the oxidation of CO indicated by a negative-going band, starts at 609 mV for CO adsorbed at 146 mV and at 652 mV for CO adsorbed at 400 V. These onset potentials agree well with the appearance of CO oxidation peak in the voltammetry of Pt(111) shown in Fig.3.47.

The CO\(_2\) generated by CO oxidation in the thin electrolyte layer between the electrode and the window can be reduced back to CO in situ. A difference spectrum was obtained with a reference spectrum recorded during the CO adsorption at 146 mV, and a sample spectrum recorded during the CO oxidation at 1.0 V(Fig.3.52). The sample spectrum was then used as a reference spectrum for the next difference spectrum, in which the potentials was set to a value at which the CO\(_2\) would be reduced(e.g. 91 mV) without moving the electrode. A sample spectrum was collected at this potential after current was allowed to decay to a steady state. The top spectrum in Fig. 3.52
Fig. 3.48 Voltammetry curves of Pt(110) electrode (a) in 1 M H_3PO_4 saturated with mixture of 1% CO in N_2 [dashed line]. Sweep rate = 50 mV/s. Holding time = 1 min. Holding potential = 125, 250, 400 mV. Positive sweep [full line] following the holding. (b) in 0.01 M H_3PO_4 saturated with mixture of 1% CO in N_2 [full line]. Sweep rate = 50 mV/s. Holding time = 1 min. Holding potential = 125, 225, 400 mV. Positive sweep following the holding.
Fig. 3.49 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Holding at 146, 410 mV vs RHE for 15 min. Single step at reference 146 mV, 410 mV & sample 1000 mV vs RHE. NSS= 400. RES= 8 cm⁻¹. SMF= 0. Incident angle (air/ CaF₂ )= 50°.
Fig. 3.50 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans). Holding at 146 mV vs RHE for 5 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.
Fig. 3.51 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 1 M H$_3$PO$_4$ + 10$^{-5}$ M CO. Linear sweep cyclic voltammetry at sweep rate= 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans) Holding at 400 mV vs RHE for 5 min. NSS= 200. RES=8 cm$^{-1}$. SMF= 0. Incident angle with CaF$_2$ prism= 60°.
shows the oxidation of CO by the negative-going 2081 cm\(^{-1}\) band. The bottom spectrum shows the reduction of CO\(_2\) by positive-going 2010 cm\(^{-1}\) band. A comparison experiment was carried out by holding the potential in the double layer region, in which the reduction of CO\(_2\) will not occur. The spectrum shows a negative-going CO\(_2\) band but no positive-going CO band, indicating that no CO from the infrared thin electrolyte layer was generated. It also shows that negligible CO diffuses into the thin layer from the bulk electrolyte.

CO oxidation and CO\(_2\) reduction experiments were also carried out on Pt(100) surface. FTIR spectra were obtained for CO adsorbed at the two holding potentials, 270 and 470 mV, in the hydrogen adsorption and double layer region, respectively (Fig. 3.53). The spectra show bands indicating the linearly adsorbed CO at both potentials. No indication of bridge bonded CO was found in this case. The series of spectra plotted in Figs. 3.54 and 3.55 were obtained by slow linear sweep voltammetry on the Pt(100) surface for CO adsorption potentials of 132 and 411 mV, respectively. Those spectra show that the oxidation of CO, indicated by the appearance of a negative-going band, starts at 709 mV for CO adsorbed at 132 mV and at 748 mV for CO adsorbed at 411 mV. These potentials agree well with the CO oxidation peak potentials in the voltammetry for Pt(100).
Fig. 3.52 FTIR spectra of CO adsorption on Pt(111) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Holding at 146 mV vs RHE for 15 min and reduction of in situ generation CO₂ at 91 mV for 5 min. Single step at reference 146 mV, 91 mV & sample 1000 mV vs RHE. NSS= 400. RES= 8 cm⁻¹. SMF= 0. Incident angle( air/ CaF₂ )= 50°.
Fig. 3.53 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M H$_3$PO$_4$ + 10$^{-5}$ M CO. Holding at 270, 400 mV vs RHE for 10 min. Single step at reference 270 mV, 400 mV & sample 1000 mV vs RHE. NSS= 400. RES= 8 cm$^{-1}$. SMF= 0. Incident angle(air/CaF$_2$) = 50°.
Fig. 3.54 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M H₃PO₄ + 10⁻⁵ M CO. Linear sweep cyclic voltammetry at sweep rate = 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans) Holding at 132 mV vs RHE for 10 min. NSS = 200. RES = 8 cm⁻¹. SMF = 0. Incident angle with CaF₂ prism = 60°.
Fig. 3.55 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M H$_3$PO$_4$ + 10$^{-5}$ M CO. Linear sweep cyclic voltammetry at sweep rate= 1 mV/sec. Potential recorded halfway through each spectral collection (at 101th scan of 200 scans) Holding at 411 mV vs RHE for 10 min. NSS= 200. RES= 8 cm$^{-1}$. SMF= 0. Incident angle with CaF$_2$ prism= 60°.
For CO adsorbed at 270 mV and 336 mV, after the potential was stepped to 1.0 V to produce CO$_2$, the potential was stepped back to potentials, at which CO$_2$ is reduced, at 90 mV and 86 mV respectively. The reduction of in situ generated CO$_2$ can determine the possibility of reversibly generating CO on the Pt(100) surface. The spectra in Fig. 3.56 show the oxidation of CO by the presence of a negative-going band at 2042 cm$^{-1}$ and the reduction of CO$_2$ by the presence of a positive-going band at 2009 cm$^{-1}$ band. The spectra in Fig. 3.57 show the oxidation of CO by the negative-going of 2038 cm$^{-1}$ band and the reduction of CO$_2$ by positive-going of a complex structure consisting of peaks 2023 cm$^{-1}$ and 1987 cm$^{-1}$. The spectra in Fig. 3.58 indicate that the CO bands shift from at 2045 cm$^{-1}$ to 2063 cm$^{-1}$ to 2071 cm$^{-1}$ following CO adsorption at 180 mV, 289 mV, and 441 mV, respectively. For the Pt(110) surface, these was negligible reduction of in situ generated CO$_2$, as verified in the infrared spectra (Fig. 3.59).
Fig. 3.56 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M $\text{H}_3\text{PO}_4 + 10^{-5}$ M CO. Holding at 270 mV vs RHE for 10 min and reduction of in situ generation CO$_2$ at 90 mV for 5 min. Single step at reference 270 mV, 90 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm$^{-1}$. SMF = 0. Incident angle (air/ CaF$_2$) = 50°.

Fig. 3.57 FTIR spectra of CO adsorption on Pt(100) vs electrode potentials. 1 M $\text{H}_3\text{PO}_4 + 10^{-5}$ M CO. Holding at 336 mV vs RHE for 10 min and reduction of in situ generation CO$_2$ at 86 mV for 5 min. Single step at reference 336 mV, 86 mV & sample 1000 mV vs RHE. NSS = 400. RES = 8 cm$^{-1}$. SMF = 0. Incident angle (air/ CaF$_2$) = 50°.
Fig. 3.58 FTIR spectra of CO adsorption on Pt(110) vs electrode potentials. 1 M \( \text{H}_3\text{PO}_4 \) + \( 10^{-5} \) M CO. Holding at 180, 289, 440 mV vs RHE for 15 min. Single step at reference 180 mV, 289, 441 mV & sample 1000 mV vs RHE. NSS= 400. RES= 8 cm\(^{-1}\). SMF= 0. Incident angle( air/\text{CaF}_2 )= 50^\circ.

Fig. 3.59 FTIR spectra of CO adsorption on Pt(110) vs electrode potentials. 1 M \( \text{H}_3\text{PO}_4 \) + \( 10^{-5} \) M CO. Holding at 289 mV vs RHE for 10 min and reduction of in situ generation CO\(_2\) at 90 mV for 5 min. Single step at reference 289 mV, 90 mV & sample 1000 mV vs RHE. NSS= 400. RES= 8 cm\(^{-1}\). SMF= 0. Incident angle( air/\text{CaF}_2 )= 50^\circ.
3.4 Summary of Infrared Spectroscopy Studies.

Summarizing the IR difference spectra for adsorbed CO before and after oxidation on polycrystalline (Section 3.1) and single crystal (Sections 3.2 & 3.3) Pt surfaces, most of the IR absorption bands observed for adsorbed CO fell in the 2020-2090 cm\(^{-1}\) range. According to comparison with metal-carbonyl coordination compounds, the preferred assignment of these bands was linearly bonded adsorbed CO. For the IR absorption bands in the 2000-1800 cm\(^{-1}\) range observed on the Pt(100) surface, particularly for the reduction product of CO\(_2\) (Sections 3.3 & 3.4), the assignment was to bridge bonded adsorbed CO. Reduction of solution phase CO\(_2\) is a convenient way to produce relatively low adsorbed CO coverage, and it appears that these low coverages favor the bridge-bonded structure on Pt(100) to some extent.
Table 3.1. Summary of Infrared Stretching Frequencies in Difference Spectra for Adsorbed CO on Polycrystalline and Single Crystal Pt Surfaces.

<table>
<thead>
<tr>
<th>SURFACES</th>
<th>Eads(V vs. RHE)</th>
<th>CONDITIONS</th>
<th>wavenumber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycrystalline</td>
<td>0.15</td>
<td>HClO₄</td>
<td>2026-2068</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td></td>
<td>2025-2075</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>Hads/DL region</td>
<td></td>
<td>2052, 2059</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>Hads region</td>
<td></td>
<td>1827 and 2039</td>
</tr>
<tr>
<td></td>
<td>DL region</td>
<td></td>
<td>2047</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>Hads/DL region</td>
<td></td>
<td>2077, 2083</td>
</tr>
</tbody>
</table>

Pt(100) 0.15 (Reduction product) 1842, 1823 and (will be discussed in Section 3.4) 2017, 2014
Pt(110) 0.15 (Reduction product) 2044, 2048

| Pt(111)      | Hads/DL region  | H₃PO₄      | 2078, 2085      |
| Pt(100)      | Hads/DL region  |            | 2041, 2043      |
| Pt(110)      | Hads/DL region  |            | 2045, 2071      |

(Reduction product of these surfaces) 2010, 2009, 1987

Note: These IR wavenumbers for adsorbed CO were summarized from Sections 3.1-3.4.
3.4.1 Comparison in the Oxidation of Reduction Product of Carbon Dioxide and Carbon Monoxide Oxidation on Three Low Index Pt Surfaces.

The multiplicity of oxidation peaks (Table 3.2) in the cyclic voltammetry may not be interpreted completely in terms of the bonding structure of the adsorbed CO. Linear bonding was assigned for the adsorbed CO on polycrystalline Pt and Pt(110) surfaces on the basis of the IR spectra. Multiple CO oxidation peaks were observed in the voltammetry curves in both cases, however. On the other hand, the simultaneous presence of linearly and bridge-bonded CO on Pt(100) was assigned on the basis of the IR spectra for the oxidation of adsorbed CO and the oxidation of the reduction product of CO$_2$ (Section 3.4), but a single peak was observed in both cases.

Arvia et al. [141] proposed that the multiple voltammetric peaks resulted from ensembles of Pt surface hydroxide and adsorbed CO. Their extended Hückel molecular orbital calculation indicated that only linearly bonded adsorbed CO was involved in the oxidation reaction. The IR spectra obtained for adsorbed CO in the present in situ studies confirms that linearly bonded adsorbed CO appears to be a dominant species on Pt surfaces. Moreover, according to ASED-MO calculation of Anderson and coworkers [142], CO adsorbed at more posi-
tive potentials could result in favoring the linear form of adsorbed CO on Pt(111) and Pt(100). The stabilization of single coordination is due to relative lowering of the metal d-band and resulting strengthening of the CO $5\sigma$ back-donation to the Pt.

Thus instead of being related to the CO-Pt bonding structure, the multiple peak structure for CO oxidation is proposed to depend on the following: adlayer structure of adsorbed CO; the interaction between oxygen donors and adsorbed CO; the CO coverages and the reaction mechanism. These factors will be discussed further in Section 3.6.

3.5 Carbon Dioxide Reduction on the Three Low Index Pt(111), (100), and (110) Surfaces in 0.1 M Perchloric Acid.

The reduction of CO$_2$ on Pt surfaces in acid solution, takes place at hydrogen adsorption potentials. This indicates that adsorbed hydrogen may play a role in the reaction. The reduction of CO$_2$ on the platinum surface has been studied in the three low index surfaces of Pt in 0.1 M HClO$_4$ by holding at hydrogen adsorption potentials.

Cyclic voltammetry measurements were carried out for the three Pt low index surfaces in the presence and
absence of CO$_2$. The solution was saturated with nitrogen until a typical cyclic voltammogram under aerobic condition was obtained and then the solution was saturated with CO$_2$(99.99%, Matheson). The voltammetry curves for Pt(100) and Pt(110) without a holding potential show only small changes in the curves comparing the absence and the presence of CO$_2$(Figs. 3.60 and 3.61). These changes were caused by the reduction of a small amount of CO$_2$ during the potential sweep in the hydrogen adsorption region followed by oxidation of the reduced species at more positive potential. On the other hand, holding the potential in the hydrogen adsorption region caused the reduction of substantial amount of CO$_2$. For the (100) surface, the potential was held at 130 mV for 5 min (Fig. 3.60). The negative-going sweep shows a shrinkage of the hydrogen adsorption charge probably caused by the adsorption of reduction products. A single sharp peak for the oxidation of the adsorbed reduced species occurs at 680 mV. For Pt(110), the potential was held at 110 mV for 5 min (Fig. 3.61). The subsequent anodic oxidation current at 500 mV is due to the oxidation of the reduced species. The charge associated with these two broad merged peaks which occur at 600 mV and 720 mV is much larger than for Pt(100).

The comparison of voltammetry curves for the oxida-
Fig. 3.60 Voltammetry curves for Pt(100) in a CO₂-saturated solution without [dashed line] and with [full line] holding at 130 mV for 5 min. Sweep rate = 50 mV/s.
Fig. 3.61 Voltammetry curves for Pt(110) in a CO₂-saturated solution without [dash line] and with [full line] holding at 110 mV for 5 min. Sweep rate = 50 mV/s.
tion of the product of CO\textsubscript{2} reduction and the oxidation of CO should be noticed from Figs. 3.28-3.34. The multiplicity of CO oxidation peaks feature for Pt(110) (Figs. 3.30 & 3.31) was similar to these two broad merged peaks in Fig. 3.62. The potential of CO oxidation peak for Pt(100) (Fig. 3.29) was identical to the oxidation peak for the reduction product of CO\textsubscript{2} in Fig. 3.60. This may indicate that the reduction product of CO\textsubscript{2} could be CO.

For the Pt(111) surface, the CO\textsubscript{2} reduction behavior was quite different from that on the (100) and (110) surfaces. The pair of sharp anodic-cathodic peaks observed at 800mV for the N\textsubscript{2}-saturated solution was suppressed and shifted to more negative potential in the presence of CO\textsubscript{2} in solution (Fig. 3.62). Holding the potential for 5 min at 110 mV resulted in only a small coverage of reduced species as evidenced by the very small decrease in the hydrogen adsorption and desorption charge. The charge due to reduction of CO\textsubscript{2} on Pt(111) was very small.

The reaction equilibria for the dissolution of CO\textsubscript{2} in H\textsubscript{2}O at 25 °C can be represented as follows [140]:

1) \[ \text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) ; \quad 0.0345 \text{ moles/Kg H}_2\text{O (1 atm)} \]
2) \[ \text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 ; \quad K_{\text{hydrolysis}} = 0.00258 \]
3) \[ \text{CO}_2(aq) \leftrightarrow \text{HCO}_3^- + \text{H}^+ ; \quad p\text{K}_a_1 = 6.25 \]
4) \[ \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+ ; \quad p\text{K}_a_2 = 10.32 \]
Fig. 3.62 Voltammetry curves for Pt(111) in the absence [dash line] and presence of CO₂-saturated solution without [dash point line] and with [full line] holding at 130 mV for 5 min. Sweep rate = 50 mV/s.
Considering the $pK_a$ values, it appears that in 0.1 M HClO$_4$ solution the predominant species would be dissolved CO$_2$. Species such as $H_2CO_3$ and $HCO_3^-$ could possibly adsorb on Pt, but both of these would be at low concentration in the perchloric acid solution. The pronounced effect of these small concentrations (=$10^{-3}$M) of species on the voltammetry of Pt(III) is unexpected. In order to check for any CO impurity present in the CO$_2$ gas, the potential was held in the double layer region, where infrared measurements do not show any evidence for the generation of adsorbed CO by electrochemical reduction of CO$_2$, then the potential was swept positively from this holding potential. There was no oxidation peak for adsorbed CO, however.

The electroreduction of gas phase CO$_2$ to CO is as follows:

$$CO_2(g) + 2H^+ + 2e^- \rightarrow CO(g) + H_2O(l) \quad E^0 = -0.106V$$

From this $E^0$ value, the equilibrium CO partial pressure in the CO$_2$ saturated solution at 0.10 V is estimated to be very low (=$10^{-8.8}$ atm). The solubility of CO in 0.1M HClO$_4$ is estimated to be $10^{-3}$ M at $P$(CO$_2$) = 1 atm, then the highest concentration of CO in the solution phase at $E = +0.10$ V is estimated to be $10^{-11.8}$ M (=$10^{-8.8}$ atm x
10^{-3} \text{ M/atm}). This value is so low that pure diffusion control with a boundary layer concentration in mild bubbling agitation(δ = 0.005 cm), approximately a 1000 s could be required to from a monolayer of adsorbed CO on Pt. At less cathodic potential than 0.10 V, even longer period could be required. Thus, the formation of adsorbed CO layer must come directly from simultaneous adsorptive reduction of the CO_2(solution).

3.5.1 Infrared Spectroscopy Studies of Reduction of Carbon Dioxide on the Single Crystal Pt Surfaces.

As described in the chapter on experimental methods, the single crystals were prepared by flame annealing. Following the flame annealing, the crystal was protected by a drop of ultrapure water which remained on the surface during the assembly of the IR cell. IR measurements were carried out in two ways. In the procedure 1, the CO_2 reduction was performed in the electrolyte with the electrode pulled back several mm from the optical window, the electrode was then moved close to the window and the spectra recorded. In procedure 2, the CO_2 was reduced to CO with the electrode position close to the window. The FTIR spectra was subsequently recorded. Both of the procedures involve substantial IR drop in the thin film of electrolyte and leave in non-uniform current distribution. Since the IR spectra are recorded at
steady state, however this is negligible current flow when the spectra recorded and IR drop is no longer a problem. Procedure 1 was normally used obtained information on the adsorbed product of the reduction reaction. Procedure 2 is needed to be performed because the optical system, particularly the thin layer of the optical cell is undisturbed.

Procedure 1

Potential cycling → holding 5 min → E_{ref} → E_{sample}

at 100 mV at 100 mV at 900 mV

Procedure 2

Potential cycling → E_{ref} → E_{sample}

at 500 mV at 100 mV

Time domain

----------------------------------------------

Thin layer cell [open] → [close]

The potential difference IR spectra obtained using procedure 1 for three surfaces are shown in Fig. 3.63 in the frequency region 1700-2500 cm\(^{-1}\). The electrode was first polarized at a potential in the hydrogen adsorption region, 0.10 V, in the bulk electrolyte for 2 to 10 min to allow the reaction to take place. The electrode was then pushed close to the optical window at the same potential and a reference spectrum collected. The sample spectrum was collected after the potential was stepped to
Fig. 3.63 Potential difference FTIRRAAS spectra obtained in a CO$_2$-saturated 0.1 M HClO$_4$ solution with reference potential at 0.10 V and sample potentials at 0.60, 0.70, and 0.90 V for Pt(100), Pt(111), and Pt(110), respectively. The electrode was pushed close to the optical window at 0.10 V after holding this value for 2 to 10 min.
a more positive value corresponding to the anodic CO oxidation peaks in the voltammetry (0.60, 0.70 and 0.90 V for Pt(100), (111) and (110), respectively). For the Pt(110) surface, one negative-going peak at 2044 cm\(^{-1}\) with a negligible shoulder around 1805 cm\(^{-1}\), and one positive-going peak at 2343 cm\(^{-1}\) can be identified. For the Pt(100) surface, the peak for the bridged CO at 1842 cm\(^{-1}\) is larger than that for the linear CO at 2017 cm\(^{-1}\), indicating that the bridge-bonded CO is predominant. On the Pt(111) surface no adsorbed species corresponding to CO were detected at 100 mV even with holding times of 20 min, which is consistent with voltammetry in Fig. 3.48. A negative-going peak for Pt(111) can be observed at 2343 cm\(^{-1}\) for the solution phase, indicating a decrease of CO\(_2\) concentration in the solution of thin layer. An explanation for the consumption of CO\(_2\) may be caused by a higher oxidation state (such as C\(_2\)O\(_4\)^{2-}\) during the positive potential step. An alternative explanation for the decreasing of CO\(_2\) was the diffusion of higher concentration of CO\(_2\) from thin layer electrolyte to the bulk electrolyte during the potential step.

In procedure 2, the electrode was first polarized at a potential in the double layer region (0.50 V) at which no CO\(_2\) reduction occurs. Then it was pushed close to the optical window and a reference spectrum collected. Then the potential was shifted stepwise to more negative
Fig. 3.64 Potential difference FTIRRAS spectra obtained in a CO₂-saturated 0.1 M HClO₄ solution with reference potential at 0.50 V and sample potential at 0.10 V. The electrode was pushed close to the optical window at 0.50 V and a reference spectrum collected; the potential was then shifted to 0.10 V without moving the electrode.
values without moving the electrode. A sample spectrum was collected at each potential after current was allowed to decay to a steady state. Fig. 3.64 shows the difference spectra for the Pt(111), (100), (110) surfaces with a sample potential of 0.10 V. The result for the (100) and (110) surfaces are similar to those shown in Fig. 3.64. No other bands were found for these two surfaces in the frequency region 1100-3000 cm⁻¹ indicating absence of species other than adsorbed CO as the reduction product. The featureless spectrum of Pt(111) indicates the low activity of this surface for CO₂ reduction.

3.6 Carbon Monoxide Oxidation on the Three High Index Pt surfaces(311), (332), and (755) in 0.1 M Perchloric Acid.

That the high Miller index surfaces are composed of low Miller index surface by monatomic steps was evidenced by the spot separation and variation of spot intensity in LEED studies. The periodicity of steps and/or kinks was introduced by Kossel and Stranski [138] as the terrace-ledge-kink(TLK) model and can represent a given stepped surface using the following notation: n(hₜ,kₜ,lₜ)-(hₛ,kₛ,lₛ), where (hₜ,kₜ,lₜ) represents the crystallographic orientation of the terraces, (hₛ,kₛ,lₛ) represents the orientation of the step face, and n denotes the width of the terraces in number of atoms. The three high index surfaces that have been used this
work can be represented as follows:

\[
\begin{align*}
(311) &= 2(111)-(100) = 2(100)-(111) \\
(332) &= 6(111)-(111) \\
(755) &= 6(111)-(100)
\end{align*}
\]

Although those three high index surfaces were not verified with LEED, these crystals were handled carefully by the procedures described in Chapter 2 and typical symmetrical voltammetry curves were obtained in the hydrogen adsorption/desorption region (Fig. 3.65). The potential was held either in the hydrogen adsorption/desorption region or in the double layer region in nitrogen-saturated electrolyte. A subsequent potential sweep in the positive direction showed the recovery of the original shape of the voltammetry curve within one cyclic sweep, indicating the absence of significant amounts of impurities. The holding potential experimental procedures were the same as those described in Section 3.2 for low index single crystals.

For the Pt(311) surface, there was no dependence of CO oxidation peak structure in the holding potential or the coverage (Fig. 3.66). The potentials were held at 0.20, 0.30, and 0.40 V and in every case the CO oxidation peak occurred at 0.85 V. For the Pt(755) surface, the peak feature changed only very slightly after the holding
Fig. 3.65 Voltammetry curves of Pt(311), (322), (755) electrode in 0.1 M HClO₄ saturated with nitrogen. Sweep rate = 50 mV/s.
Fig. 3.67 Voltammetry curves of Pt(755) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential= 100, 400 mV. Holding time= 6 min.

Fig. 3.66 Voltammetry curves of Pt(311) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential= 200, 300, 400 mV. Holding time= 3 min.
Fig. 3.69 Voltammetry curves of Pt(322) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 100, 400 mV. Holding time = 9 min.

Fig. 3.68 Voltammetry curves of Pt(755) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential = 100 or 400 mV. Holding time = 3[dash-point], 9[solid line] min.
Fig. 3.71 Voltammetry curves of Pt(322) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential= 100 mV. Holding time= 3, 6, 9 min.

Fig. 3.70 Voltammetry curves of Pt(322) electrode in 0.1 M HClO₄ saturated with mixture of 1% CO in N₂ gas at 1 atm [dash line]. Sweep rate = 50 mV/s. Holding potential= 400 mV. Holding time= 3, 6, 9 min.
potential was held at 0.10 and 0.40 V for 6 min (Fig. 3.67). The same type of coverage dependence was found regardless of the adsorption potential whether it was in the hydrogen adsorption region or in the double layer region. In Fig. 3.68, the potential is held at 0.40 V for 3 min and 9 min and the CO oxidation peaks shift to more positive potential for higher coverage. For the Pt(332) surface, the CO oxidation peak structure dependence on the adsorption potential and the coverage was found to be pronounced. Comparing in Fig 3.69, CO adsorption potentials of 0.10 mV and 0.40 V, the oxidation peak at 0.70 V was lower at the latter potential, while 0.80 V peak was larger for the same holding times. For given adsorption potential, the increase of coverage (longer holding times) caused an increase of the current for the first peak in the multiple peak structure (Figs. 3.70 & 3.71).

Clavilier et al.[139] provided some interpretation of such multiple peaks structures. They proposed that the strongly adsorbed intermediate formed on stepped Pt surfaces as a result of methanol dissociation was CO. They suggested that the multiplicity of peaks in the voltammetry curves was connected to the various types of adsorption sites on the surfaces. This multiplicity of the oxidation peaks may not necessarily be interpreted only in term of the simultaneous presence of linearly or
bridge bonded CO.

3.7 Overall Discussions.

A summary table (Table 3.2) is presented as follows for the comparison of CO oxidation peaks potentials.

In order to estimate the number of electrons transfer during the CO oxidation reaction, the decrease in the integrated charge in the hydrogen adsorption/desorption region was interpreted as being due to the occupancy of CO on the surface, and the ratio between the charge for the CO oxidation peaks to the decrease of the charge in the hydrogen adsorption/desorption region was calculated. Based on the present experimental results, the electrical charge for the desorption of hydrogen (corrected for the double layer charge) was 194 \( \mu \text{C cm}^{-2} \) for Pt(100), 182 \( \mu \text{C cm}^{-2} \) for Pt(110) and 148 \( \mu \text{C cm}^{-2} \) for Pt(111) [corrected for the "butterfly region" charge].
Table 3.2 Potentials for the CO Oxidation on Pt Surface from Voltammetry Curves.

Note: 1. $E_p$ are range of multiple (M) peaks potentials or peak potential for single peak (S).
2. $E_{ads}$ is holding potential for CO adsorption, and cycling means continual potential sweep. If there is no adsorption potential dependence for $E_p$, then it is marked "no dep."

<table>
<thead>
<tr>
<th>CONDITIONS (rotation speed)</th>
<th>$E_p$(V vs. RHE) (S. or M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>Electrolyte</td>
</tr>
<tr>
<td>Poly. Pt</td>
<td>0.1M HClO$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(400 rpm)</td>
<td>0.1M</td>
</tr>
<tr>
<td>(400 rpm)</td>
<td>0.1M</td>
</tr>
<tr>
<td>(400-3600 rpm)</td>
<td>0.1M Cycling</td>
</tr>
<tr>
<td>(400-3600 rpm)</td>
<td>0.001M Cycling</td>
</tr>
<tr>
<td>(400-3600 rpm)</td>
<td>0.1M Cycling</td>
</tr>
<tr>
<td>(400 rpm)</td>
<td>$+10^{-4}$M Cl$^-$</td>
</tr>
<tr>
<td></td>
<td>$+10^{-3}$M Cl$^-$</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>0.1M HClO$_4$</td>
</tr>
<tr>
<td>Pt(100)</td>
<td></td>
</tr>
<tr>
<td>Pt(110)</td>
<td>0.150 V</td>
</tr>
<tr>
<td></td>
<td>0.450 V</td>
</tr>
</tbody>
</table>
Table 3.2 (Cont.)

Oxidation of the Product of CO\textsubscript{2} Reduction

(IR spectra indicating that CO is the reduction product)

<table>
<thead>
<tr>
<th>Surface</th>
<th>Solution</th>
<th>Potential (V)</th>
<th>Current Density (mA cm\textsuperscript{-2})</th>
<th>E (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>no reduction reaction observed in IR spectra</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(100)</td>
<td>0.1 M HClO\textsubscript{4}</td>
<td>0.150</td>
<td>*</td>
<td>0.680 (S)</td>
</tr>
<tr>
<td>Pt(110)</td>
<td></td>
<td>0.150</td>
<td>*</td>
<td>0.60-0.72 (M)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface</th>
<th>Solution</th>
<th>Potential (V)</th>
<th>Current Density (mA cm\textsuperscript{-2})</th>
<th>E (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(100)</td>
<td>5 M H\textsubscript{3}PO\textsubscript{4}</td>
<td>0.15-0.35</td>
<td>1%</td>
<td>0.875-0.925 (M)</td>
</tr>
<tr>
<td></td>
<td>1 M</td>
<td>0.45-0.55</td>
<td>1%</td>
<td>0.88 (S)</td>
</tr>
<tr>
<td></td>
<td>0.01 M</td>
<td>NO</td>
<td>1%</td>
<td>0.80 (S)</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>1 M</td>
<td>0.15-0.45</td>
<td>1%</td>
<td>0.70-0.80 (M)</td>
</tr>
<tr>
<td></td>
<td>0.01 M</td>
<td>NO</td>
<td>1%</td>
<td>0.80 (S)</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>1 M</td>
<td>0.125-0.40</td>
<td>1%</td>
<td>0.75-0.85 (M)</td>
</tr>
<tr>
<td></td>
<td>0.01 M</td>
<td>0.125-0.40</td>
<td>1%</td>
<td>0.75-0.90 (M)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface</th>
<th>Solution</th>
<th>Potential (V)</th>
<th>Current Density (mA cm\textsuperscript{-2})</th>
<th>E (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(311)</td>
<td>0.1 M HClO\textsubscript{4}</td>
<td>no dep.\textsuperscript{2}</td>
<td>1%</td>
<td>0.850 (S)</td>
</tr>
<tr>
<td>Pt(755)</td>
<td></td>
<td>no dep.\textsuperscript{2}</td>
<td>1%</td>
<td>0.70-0.85 (M)</td>
</tr>
<tr>
<td>Pt(332)</td>
<td></td>
<td>0.15-0.45</td>
<td>1%</td>
<td>0.70-0.85 (M)</td>
</tr>
</tbody>
</table>
The electrochemical reactions on Pt in the absence of O₂ is expressed as followings:

1) Adsorption of CO(sol’n):

\[ \text{CO(sol’n)} \rightarrow \text{CO(ads)} \]

2) Surface hydroxide:

\[ \text{OH}_2 \rightarrow \text{OH(ads)} + \text{H}^+ + \text{e}^- \]

3) Surface oxide:

\[ \text{OH(ads)} \rightarrow \text{O(ads)} + \text{H}^+ + \text{e}^- \]

4) Chemical oxidative desorption:

\[ 2 \text{OH(ads)} + \text{CO(ads)} \rightarrow \text{CO}_2(\text{sol’n}) + \text{H}_2\text{O} \]

5) Electrochemical oxidative desorption:

\[ \text{OH(ads)} + \text{CO(ads)} \rightarrow \text{CO}_2(\text{sol’n}) + \text{H}^+ + \text{e}^- \]

6) Chemical oxidation:

\[ 2 \text{OH(ads)} + \text{CO(sol’n)} \rightarrow \text{CO}_2(\text{sol’n}) + \text{H}_2\text{O} \]

7) Electrochemical oxidation:

\[ \text{OH(ads)} + \text{CO(sol’n)} \rightarrow \text{CO}_2(\text{sol’n}) + \text{H}^+ + \text{e}^- \]

8) Chemical oxidative desorption:

\[ \text{O(ads)} + \text{CO(ads)} \rightarrow \text{CO}_2(\text{sol’n}) \]

9) Chemical oxidative desorption:

\[ \text{O(ads)} + \text{CO(sol’n)} \rightarrow \text{CO}_2(\text{sol’n}) \]
The electrical charge for the CO oxidation peaks on single crystals and polycrystalline Pt surfaces were calculated as following:

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Hads/des charge (μC cm⁻²)</th>
<th>CO peaks charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>98.7</td>
<td>84.8</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>95.3</td>
<td>75.0</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>96.8</td>
<td>82.5</td>
</tr>
<tr>
<td></td>
<td>120.0</td>
<td>111.2</td>
</tr>
<tr>
<td>Polycrystalline</td>
<td>36.0</td>
<td>28.6</td>
</tr>
<tr>
<td>Pt</td>
<td>75.6</td>
<td>60.0</td>
</tr>
<tr>
<td></td>
<td>117.0</td>
<td>79.6</td>
</tr>
<tr>
<td></td>
<td>153.2</td>
<td>120.0</td>
</tr>
</tbody>
</table>

The theoretical calculated charge for adsorbed hydrogen on Pt(111) and Pt(100) are 240 μC cm⁻² and 208 μC cm⁻², respectively. Depending on the experimentally calculated values, the ratio of the CO oxidation charge to the decrease of charge in the hydrogen adsorption/desorption region was estimated to be somewhat smaller than 1. This is evidence of a one electron transfer process for CO(ads) oxidation with surface Pt hydroxide OH(ads)
[reaction 5]. Based on the HMRDE data (Fig. 3.16) and previous discussion (p.80), the oxidation of solution phase CO with surface hydroxide OH(ads) [reaction 7] provided evidence for a one electron transfer process. If the diffusion coefficient of CO in the aqueous solution was assumed to be $2.03 \times 10^{-5}$ cm²/s, then the n value (number of electrons transferred) was calculated to be 1.15. An alternative reaction mechanism for one electron transfer process is proposed as follows:

\[
2 \left[ CO_{(bulk)} \rightarrow CO \text{ (outer Helmholtz plane)} \right] \\
2 \left[ CO \text{ (OH}) \rightarrow CO^{\cdot+} + e \right] \\
2 CO^{\cdot+} + H_2O \rightarrow CO_2 + CO + 2 H^+ \\
\]

Overall reaction:

\[
CO + H_2O \rightarrow CO_2 + 2 H^+ + 2 e 
\]
CHAPTER 4
SUMMARY AND CONCLUSIONS

**Electrolyte Effects:**

CO electrooxidation experiments involving various electrolytes have indicated that the type of anions has definite effects on the CO oxidation potentials. Strongly adsorbed phosphate anions may create replacement between surface hydroxide and adsorbed CO, resulting in an inhibition of the reaction. The formation of the adsorbed PtOH film can be involved by competition for surface sites with anions (e.g. Cl\(^{-1}\)) and also by suppression of the low water activity such as concentrated H\(_3\)PO\(_4\) and or greater suppression in nonaqueous solvent (e.g. CH\(_3\)CN). Such impediment of the adsorbed PtOH film formation results either in suppression of the reaction, or in retardation of the CO oxidation voltammetry peaks (to more positive potentials).

**Surface Structure Sensitivity:**

The catalytic activity for CO electrooxidation was found to be strongly dependent on the surface geometric structure. Both CO oxidation and the oxidation of the reduction product of CO\(_2\) on low index Pt surfaces showed
decreasing catalytic activity in the following order: 
(100) > (110) > (111). The activity for CO oxidation on high index Pt surfaces showed some dependence on the particular surfaces, but not enough different stepped surfaces were examined to draw any firm conclusions.

Island Mechanism:

The CO adsorption potentials and coverages have influence on the structure of adsorbed CO adlayers. Either for CO adsorbed at potentials in the double layer region or for higher coverage CO adlayers, irrespective of the adsorption potential, a less easily oxidizable adlayer structure results. It is proposed that the reason for this behavior is that relatively large CO adlayer islands are formed, which are more difficult to oxidize. Different adlayer domain sizes create different accessibilities for the surface Pt hydroxide, which was found to be the principal oxygen donor, resulting in the multiplicity of CO oxidation peaks. The in situ FTIRRAS technique revealed the predominance of the linear bonding structure of adsorbed CO on polycrystalline Pt surfaces. This implies that the multiple CO oxidation peak features in the voltammetry curves are caused by energy barrier differences associated with the interaction of the PtOH and the CO in various adlayer structures, without much
contribution from different bonding structures. The lack of effect of the bonding structure can be supported from the results of single crystal studies. On one hand, while linear bonding was assigned for CO adsorbed on the Pt(110) surface on the basis of the IR spectra, multiple CO oxidation peaks were observed in the voltammetry curves for Pt(110). On the other hand, the simultaneous presence of linearly and bridge-bonded CO was observed in the IR spectra for Pt(100), but only a single oxidation peak was observed in the voltammetry curve. This was also true for the oxidation of the CO₂ reduction product, which was found to be adsorbed CO, on the Pt(110) and (100) surfaces.

Reaction Mechanism:

The \textit{in situ} FTIRRAS studies showed that the reaction product of CO electrooxidation is CO₂, and the electrochemical reduction of CO₂ can produce adsorbed CO on the Pt(100) and (110) surfaces. The oxidation of adsorbed CO was found to be an apparent one electron transfer process, involving surface hydroxide, on the basis of CO oxidation charge as compared with hydrogen adsorption/desorption charge. The oxidation of solution-phase CO with surface hydroxide was also found to be an apparent one electron transfer process based on the HMRDE studies. The corresponding electrochemical sequence of reactions
was proposed as follows:

1) Adsorption of CO(sol’n):

\[ \text{CO(sol’n)} \rightarrow \text{CO(ads)} \quad \text{[rate determining step]} \]

The adsorption of CO is a slow process (rate determining step) under both kinetic and diffusion control at the holding potentials (e.g. 0.15 V and 0.45 V vs. RHE). Various adsorbed CO adlayer structures may be formed. During potential sweeping or potential holding, the CO adsorption process can continue until the potential reaches that at which CO\(_2\) oxidative desorption, which is \(\approx 0.7 \text{ V (vs. RHE)}\), or \(\approx 0.95 \text{V for HMRDE studies}\). (Such retardation of the oxidation peak in voltammetry for HMRDE studies was explained on the basis of the inhibition of surface PtOH film formation and proposed island mechanism.)

2) Electrochemical oxidative desorption for CO(ads):

\[ \text{OH(ads)} + \text{CO(ads)} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- \]

The adsorption step was followed by oxidative desorption at much more positive potential (e.g. 0.85 V vs. RHE) and those oxidation step was irreversible. The oxidation of the adsorbed CO may occur at a less positive potential
(e.g. 0.6V vs. RHE) due to CO having greater accessibility to OH(ads) as for example CO in small islands, while a more positive potential (0.85V vs. RHE) is required to overcome the energy barrier in order to turn on the interaction of OH(ads) and CO(ads) in larger islands. A shortage of surface hydroxide (e.g. in 85% H₃PO₄) can impede the reaction or an inhibition of surface oxide formation can cause retardation of the CO oxidation peak (e.g. in the presence of Cl⁻ or trifluoromethanesulfonic acid)

3) Electrochemical oxidation of CO(sol’n):

\[ \text{OH(ads)} + \text{CO(sol’n)} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- \]

or

\[ \text{CO(sol’n)} \rightarrow \text{CO(OHP)} \rightarrow \text{CO}^* + \text{e} \]

The oxidation of solution-phase CO was easily detectable under forced convection conditions (e.g. HMRDE) in the potential region of surface Pt hydroxide formation.
REFERENCES


19. B. Beden; K. Bewick; K. Kunimatsu and C. Lamy, J.


92. M. Steinberg and Vi-Duong Dang, Energy Convers., 17 (1977) 97.


114. A. Patterson and R. Ettinger, Zeitschrift fur Electrochemie, Bd.64 Nr.1 (1960) 98.


140. A. Patterson, Jr. and R. Ettinger, Z. Elektrochem. 64 (1960) 98.


