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**Characterization of Electrochemically Modified
Polycrystalline Platinum Surfaces**

by

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MASTER

**Characterization of Electrochemically Modified
Polycrystalline Platinum Surfaces**

A Thesis Presented

by

Leonard Carl Krebs

to

The Graduate School

in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

in

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State University of New York

at

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The Graduate School

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Abstract of the Thesis

**Characterization of Electrochemically Modified
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The characterization of electrochemically modified polycrystalline platinum surfaces has been accomplished through the use of four major electrochemical techniques. These were chronoamperometry, chronopotentiometry, cyclic voltammetry, and linear sweep voltammetry. A systematic study on the underpotential deposition of several transition metals has been performed. The most interesting of these were: Ag, Cu, Cd, and Pb. It was determined, by subjecting the platinum electrode surface to a single potential scan between -0.24 and $+1.25$ V_{SCE}, while stirring the solution, that the electrocatalytic activity

would be regenerated. As a consequence of this study, a much simpler method for producing ultra high purity water from acidic permanganate has been developed. This method results in water that surpasses the water produced by pyrocatalytic distillation. It has also been seen that the wettability of polycrystalline platinum surfaces is greatly dependent on the quantity of oxide present. Oxide-free platinum is hydrophobic and gives a contact angle in the range of 55 to 62 degrees. We have also modified polycrystalline platinum surface with the electrically conducting polymer poly- ρ -phenylene. This polymer is very stable in dilute sulfuric acid solutions, even under applied oxidative potentials. It is also highly resistant to electrochemical hydrogenation. The wettability of the polymer modified platinum surface is severely dependent on the choice of supporting electrolyte chosen for the electrochemical polymerization. Tetraethylammonium tetrafluoroborate produces a film that is as hydrophobic as Teflon, whereas tetraethylammonium perchlorate produces a film that is more hydrophilic than oxide-free platinum.

I dedicate this thesis to my family and friends.
Without their support, encouragement, and enthusiasm
this would never have been possible.

Table of Contents

	Page
Abstract	iii
Dedication	v
List of Figures	vii
List of Tables	ix
Acknowledgments	x
Chapter	
1 INTRODUCTION	1
References	7
2 POISONING AND REGENERATION OF PLATINUM ELECTRODE SURFACES	11
Experimental	15
Results and Discussion	26
Conclusion	53
References	54
3 INFLUENCE OF SURFACE OXIDE ON CONTACT ANGLE MEASUREMENTS OF WATER ON CLEAN PLATINUM	59
Experimental	62
Results and Discussion	71
Conclusion	77
References	78
4 POLY- ρ -PHENYLENE MODIFIED PLATINUM ELECTRODES	80
Experimental	84
Results and Discussion	94
Conclusion	123
References	125
APPENDIX	128
References	136

List of Figures

	Page
2-1. Pt-wire electrode with Teflon sleeve	17
2-2. Pyrocatalytic distillation apparatus	22
2-3. Acid-permanganate distillation apparatus	24
2-4. Cyclic voltammogram of polycrystalline platinum	27
2-5. Comparison of HER-current decay for various poisons .	31
2-6. Decay-recovery cycles for Cadmium poisoning	33
2-7. Recovery of polycrystalline Pt from Ag poisoning	35
2-8. Recovery of polycrystalline Pt from Cu poisoning	37
2-9. Recovery of polycrystalline Pt from Cd poisoning	39
2-10. Recovery of polycrystalline Pt from Pb poisoning	40
2-11. Recovery of polycrystalline Pt from SO ₂ poisoning ...	42
2-12. Decay-recovery cycles for Bisulfite poisoning	43
2-13. Recovery of polycrystalline Pt from Cr poisoning	46
2-14. Recovery of polycrystalline Pt from Mn poisoning	47
2-15. Recovery of polycrystalline Pt from Fe poisoning	48
2-16. Recovery of polycrystalline Pt from Co poisoning	49
2-17. Recovery of polycrystalline Pt from Ni poisoning	50
2-18. Recovery of polycrystalline Pt from Al poisoning	51
2-19. Recovery of polycrystalline Pt from Zn poisoning	52
3-1. Platinum disk electrode with Teflon sleeve	64
3-2. Specimen polishing mount	65

	Page
3-3. Illustration of sessile drop method	68
3-4. Graph of contact angle and EOC as a function of applied potential	73
4-1. Ag/Ag ⁺ reference electrode with Pt-glass junction ...	85
4-2. CV of Ferrocene-Ferrocenium couple	87
4-3. Acetonitrile distillation apparatus	91
4-4. Illustration of external input signal	95
4-5. Polymerization series in TEAP solution	96
4-6. Polymerization scheme for <i>p</i> -terphenyl	99
4-7. Chronopotentiogram for poly- <i>p</i> -phenylene	101
4-8. Plot of Log [($\tau^{1/2} - t^{1/2}$) / $t^{1/2}$] against potential .	103
4-9. CV of poly- <i>p</i> -phenylene	105
4-10. Plot of i_p vs $\nu^{1/2}$ for peak at +1.0 V _{Ag/Ag⁺}	107
4-11. Plot of i_p vs ν for peak at +0.4 V _{Ag/Ag⁺}	109
4-12. Comparison of polymerization currents	113
4-13. CVs of different polymer films	114
4-14. CVs of polymer coated Pt-wire in 0.05 M H ₂ SO ₄	117
4-15. CVs of polymer coated Pt-wire in 0.1 M TEATFB	118
4-16. Polymer CVs in 0.1 M TEAP	122
A-1. Polymerization potential cycles for poly-thiophene ..	132
A-2. Cyclic voltammogram of poly-thiophene	134

List of Tables

	Page
3-1. Effect of applied potential (oxide generation) on surface wettability	72
3-2. Effect of surface oxide reduction on surface wettability	75
4-1. Accessible potential range and relative solubility of supporting electrolyte in acetonitrile	111
4-2. Contact angle measurements on poly- ρ -phenylene	123

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CHAPTER 1

INTRODUCTION

In the past, numerous methods for the production of heavy water have been studied,¹⁻⁶ but for all practical purposes only three methods have been adopted for large scale production. These methods employ the following isotope exchange reactions.

At the temperatures used in these industrial plants, deuterium enriches in the liquid phase, i.e., the single stage separation factor (α) is greater than unity.⁷ The exchange reactions take place in packed columns, through which the gas and liquid reactants flow counter-currently (i.e., the gas bubbles up through the liquid which travels down the column). The greater the number of separation stages per column, the higher the level of enrichment.

The Girdler-Sulfide process based on Reaction (1) does not require a catalyst and has been used in Canada, India, and the

United States (e.g., the Savannah River plant in Georgia). Reactions (2) and (3), however, require catalysts. Except for the need for catalysis, the hydrogen/water pair of Reaction (3) has long been recognized as the best possible isotope exchange pair for the purpose of heavy water production.^{3,9,10} It has the highest α among all known exchange pairs.

A major problem associated with heterogeneous catalysts is chemical poisoning and crystallographic surface deterioration. In systems involving Reactions (2) and (3), another problem arises when using conventional heterogeneous catalysts containing group VIII metals. The highly nucleophilic ammonia and water molecules tend to preempt the catalyst surfaces, excluding hydrogen molecules from the active sites and resulting in the retardation of the surface reactions.¹¹⁻¹⁶

Canadian scientists, in order to minimize this second problem for the HD/H₂O system, developed two types of hydrophobic catalyst. The two catalysts are platinum dispersed on poly(tetrafluoroethylene)¹⁴⁻¹⁶ and platinum-impregnated porous supports which are coated with poly(tetrafluoroethylene).^{15,16} These catalysts still have the potential of suffering a loss in catalytic activity due to surface deterioration and chemical poisoning.

It has been proposed¹⁷ that the general design of these hydrophobic catalysts may be altered so as to provide some active control over the degree of hydrophobicity and afford the ability

to regenerate the catalyst's activity in-situ. The proposed change in design consists of essentially two parts, (i) constructing the catalyst bed using an electrically conducting porous support material and (ii) a coating made of an electrically conducting organic film, instead of using poly(tetrafluoroethylene). The basis for this design is the new developments in the area of electrochemistry, especially those pertaining to chemically modified electrodes.

There has been a tremendous increase in the number of studies involving chemically modified electrodes¹⁸⁻²⁰ since Murray's 1975 pioneering work on the derivatization of tin oxide electrodes.²¹ Surfaces of metals, metal oxides, semiconductors and carbonaceous materials have been chemically modified by coverage with monomers,²¹ polymers with anchor molecules,²² and polymers without anchors. The derivatization without anchors has been accomplished by electrochemical,^{20,23} thermal,^{20,24,25} and plasma^{22,26} polymerizations of monomers directly on the substrate surfaces.

Of particular interest for our purpose were the following developments:

- (1) The wettability of electroactive modifiers, which appears to be adjustable through electrochemical control of the average redox state of the modifier molecule.^{27,28}

- (2) Fine aggregates of metals can be electrochemically imbedded in a polymer film formed on a substrate electrode.^{24,25,29,30}

These facts suggest that if an electroactive chemically modified electrode is used as a support for a catalyst metal (e.g., Pt), one may be able to electrochemically control the hydrophobicity of the catalyst. An important requirement is that the electroactive modifier must have a high level of hydrophobicity, similar to that of poly(tetrafluoroethylene), in its neutral or non-cationic state. In addition, any significant dependence of wettability and other properties of such a modifier substance on its oxidation state can be applied to an in-situ control of the catalyst activity and, hopefully, its selectivity.

This new design for gas-liquid reactions could allow for the efficiency and selectivity of the catalyst to be controlled by the application of an electric potential to the catalyst bed. This is neither electrolysis nor conventional electrocatalysis in that no significant flow of electric current is due to the reaction of interest.

Another advantage, as a result of the catalyst being an electrode, is the possibility of in-situ regeneration of the catalytic activity by periodic potential excursions. It is well-known that the catalytic activities of platinized platinum electrodes can be restored by repeated cycling of the potential

between cathodic and anodic voltages.³¹⁻³³ This is at least partially due to regeneration of the active sites during the potential cycling.³²⁻³⁴ In addition, some claim that the restoration of catalytic activity is also due to elimination of chemical poisons from the surfaces.^{32,33,35} Underpotential deposition and stripping voltammetry studies performed on Pt surfaces have shown that the deposition of metals is in general reversible with a few exceptions, e.g., mercury and lead.^{36,37}

Thus, the proposed use of an electrode as a catalyst support, besides allowing the possibility of controlling the wettability of the catalyst surface, would also provide the means for in-situ catalyst regeneration.

The research that will now be presented was conducted in the pursuit of designing, constructing, and testing of this new catalyst. Essentially, this research constitutes the ground work necessary for further investigation into the use of a chemically modified electrode as a catalyst for the hydrogen isotope exchange reaction between liquid water and hydrogen gas. The presentation is divided into three major chapters. Data on the systematic study of poisoning, by various compounds and metals, and the effective regeneration of clean platinum electrode surfaces is presented in Chapter 1. This chapter also contains a comparison of two methods for the preparation of ultra-high purity water. One method is based on Conway's pyrocatalytic distillation process.³⁸ The subject of Chapter 2 is the

measurement of contact angle data for "clean" platinum surfaces. The method by which the "clean" platinum surface is prepared greatly influences the interaction between water and the surface. The wettability appears to be directly related to the quantity of oxide present. Chapter 3 details the modification of platinum electrode surfaces by films of poly(paraphenylene). The physical properties and electrochemistry of this electrode modifier are presented in light of the methods and solutions used for its preparation. Discussions of data and results obtained using pyrrole, thiophene, and 3-methylthiophene monomers as electrode modifiers are presented in the appendix.

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CHAPTER 2

POISONING AND REGENERATION OF PLATINUM

ELECTRODE SURFACES

One of the primary problems associated with the use of a heterogeneous catalyst is its chemical poisoning and the deterioration of its crystallographic surfaces. Reactivation of a heterogeneous catalyst is usually achieved through its reformation, which can be a costly and, most of all, time consuming process. The catalytic activity of a platinized platinum electrode can be restored by repeated cycling of its potential between cathodic and anodic potentials.¹⁻³ It has been well established that this reactivation is due, at least in part, to surface structural changes³⁻¹² such as those in surface morphology^{4-6,10-12} and crystallographic faceting^{3,6-10,12} and an overall increase in the real surface area.^{3-6,12}

Activation, due to surface restructuring, requires an extensive anodization prior to a cathodic potential swing. This process involves partial dissolution of the absorbed and phase oxides and hydroxides of platinum.^{4-6,13-17} The efficiency of the potential cycling process for the activation and restructuring depends on the waveform of the potential program,

in particular, on the potential and duration of the anodization and the rate of ensuing electro-reduction.^{4,6-10,12} The relative population of low-index crystallographic planes of a treated polycrystalline platinum surface can be correlated to various parameters of the input waveform^{6,8-11} imposed on the appropriately annealed and quenched piece of platinum.¹⁸

In addition, some claim that the restoration of the catalytic activity is also due to elimination of chemical poisons from the platinum surfaces.^{2,3,19,20} Common chemical poisons of platinum are nucleophiles: (1) inorganic and organic compounds of Group Va and Group VIa elements, which includes water and hydroxyl compounds, ammonia, pyridine, sulfides and thiophenes, (2) complex ions of transition metals with their outermost d-shells more than half-filled, and (3) unsaturated compounds.²¹ The reactivation due to the removal of these poisons by potential cycling has not attracted as much attention as the surface-restructuring. This is probably because most chemical adsorbates, from ordinary laboratory water used for electrochemistry, are presumably removed with relative ease by a small number of anodic excursions.^{13,22}

The importance of careful attention to every aspect in the preparation of high purity aqueous solutions has been emphasized by many authors (e.g., 3,5,13,22). Consequently, several laboratory procedures for ultra-pure water have been prescribed.

Most noted of these are pyrocatalytic distillation²³ and pre-electrolysis. Preparatory procedures for polycrystalline platinum electrodes, for reproducible results, have also been recommended.²⁴

These having been done, studies of adsorbates as surface poisons have generally centered around problems related to organic intermediates in electrocatalytic synthesis reactions.^{20,25} The emphases, in studies on the effects of underpotential deposition of metals and other adatoms on platinum surfaces, have been on the characterization of platinum surfaces (e.g., 26), adatom structures (e.g., 27-35) and the enhancement of catalytic activity in the catalyses of fuel cells and electrosynthetic reactions (e.g., 36-42), but not on poisoning as a problem. However, the problem of catalyst poisoning still exists, especially in industrial environments where the purity of the process water is difficult to control. The problem is particularly acute in processes where the electrode must be kept at a cathodic potential such as that for hydrogen evolution.

This chapter reports on a systematic study of the chemical poisoning of polycrystalline platinum electrodes in sulfuric acid media by metal cations, e.g., Ag(I), Cu(II), Cd(II), Pb(II), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Al(III), Zn(II), and bisulfite, and the de-poisoning of the affected surfaces by means of anodic-cathodic potential cycling. This study was undertaken for the purpose of determining whether an occasional, in-situ,

superimposition of relatively short bursts of such potential cycles, during an industrial electrocatalytic process, would help to minimize the effects of the catalyst poisons. In preparation for this study, we have re-examined the purification processes for water.

EXPERIMENTAL

In this study, the hydrogen evolution reaction (HER) current was followed as a function of time while potentiostating the platinum working electrode at -0.280 V (relative to SCE). The supporting electrolyte solution contained a controlled concentration of one of the metallic ions or bisulfite ion. The effects of the triangular wave potential cycles on the removal of the adsorbates were examined by observing the recovery of the HER current and reappearance of the clean platinum cyclic voltammogram (CV). The potentiostating and CV scans were carried out using an IBM Instruments Model EC/225 Voltammetric Analyzer and the data were recorded using a Data Translation AD/DA data acquisition board Model DT2805 (13.7 KHz) and an IBM-AT with a math-coprocessor.

Electrochemical Set-up

A standard electrochemical cell with electrodes separated by Vycor disk partitions was used. The set-up consisted of a platinum working electrode (1.0 mm dia. x 3 mm long AESAR/Johnson Matthey Puratronic wire, 99.9985%, fed through a Teflon sleeve), a platinum spiral auxiliary electrode (1.0 mm dia. x 24

cm long, AESAR Puratronic wire), and a KCl saturated calomel reference electrode. The volume of electrolyte solution in the main compartment was approximately 20 ml. Nitrogen gas (99.999%) was further purified by passing it through columns of: activated charcoal; warm concentrated sulfuric acid; and warm permanganate (10^{-3} M)-sulfuric acid solution. Entrained mists were trapped in a column packed with coarsely crushed quartz. This purified nitrogen was used to stir and purge the electrolyte solutions in both the working and counter electrode compartments and to provide an inert atmosphere for the experiments in quiescent solutions. The typical flow rate of the stirring gas was 500 ml/min. All potentials reported are relative to the SCE.

Platinum Working Electrode

The platinum working electrode was constructed from a new piece of platinum wire mounted to a 10 cm length of 1/16 inch diameter, type 304, stainless steel rod, see Figure 2-1a. This platinum electrode was then prepared in the following manner:

- (1) polished with 0.5 μ m alumina on green felt cloth using distilled water;

FIGURE 2-1: Pt-WIRE ELECTRODE WITH TEFLON SLEEVE

- (2) washed repeatedly with ultra-pure water (see below)
in an ultrasonic cleaner;
- (3) inserted through a Teflon sleeve (cf: Figure 2-1b)
until approximately 3 mm of the wire protruded from
the tip of the sleeve, and rinsed using ultra-pure
water;
- (4) conditioned by potentiostating at 1.35 V in a fresh
portion of 0.5 M H_2SO_4 , while stirring magnetically
and bubbling nitrogen, until the current density
dropped to about $2 \mu\text{A}/\text{cm}^2$;
- (5) potentiostated for an additional 15 minutes, with
stirring as before after replacement of the
sulfuric acid with new solution, keeping as much
solution hanging on the electrode as possible
during the transfer under open circuit conditions;
and finally,
- (6) potential cycled in a series of 2 or 3 fresh
portions of 0.05 M H_2SO_4 between the switching
potentials of -0.24 V and +1.25 V, at a scan rate
of 1.00 V/s, until a reproducible CV was obtained
(10-20 min).

After each poisoning experiment, the working electrode was taken out of the Teflon sleeve and cleaned by subjecting it to Steps (1)-(3) and (6), while skipping Steps (4) and (5). The electrode prepared in this manner, used in sulfuric acid solution made from the acid permanganate-distilled water (see below) and the AESAR/Johnson Matthey sulfuric acid, passed all of the Conway tests^{23,24} for a clean Pt surface and pure water. In addition, it passed a similar test of potentiostating at near-HER potential, which is more stringent than Conway's. The geometric area of the electrode was approximately $0.10 \pm 0.01 \text{ cm}^2$ which varied from run to run depending on the extruded length. The roughness factor was always close to 2.0 (basis; $210 \mu\text{C}/\text{cm}^2$). The platinum wire used for the auxiliary electrode was cleaned in hot chromic acid solution, followed by thorough washing and electrochemical polishing.

Aqueous Solution Preparation

We have tested the following preparations of water in combination with two sources of sulfuric acid, i.e., AESAR (Johnson Matthey) and ULTREX (Baker), and one source of perchloric acid, i.e., AESAR. All water purification was started with $18 \text{ M}\Omega\cdot\text{cm}$ water from a Barnstead NANOpure system.

(1) Pyrocatalytically distilled water was prepared using an apparatus built according to Conway's design²³, except that it has been improved and also scaled down, such that the flow/distillation/purification rates in ours, Figure 2-2, are one quarter of Conway's. The improvements are that all greased stopcocks and greased standard-taper joints were replaced with Teflon-barreled stopcocks and Teflon-sleeved taper joints. In addition, the gas outlet has been equipped with an all-Teflon relief valve with a differential opening pressure of 0.07 bar to maintain a positive pressure throughout the distillation system. We ran the system for a total of 480 hours and produced 1.8 liters of pyrocatalytically distilled water. The distillation procedure is as follows: A charge of water (e.g., 500 ml) is distilled with a stream of ultra-high purity oxygen through a quartz column packed with pieces of 90% Pt-10% Rh gauze heated to 750-800 °C. The distillate is periodically returned to the still through a Soxhlet-type syphon. This process runs continuously for 24 hours, after which the water (ca 450 ml) is removed from the distillate receiver. The procedure is primarily aimed at removing organic impurities, especially the volatile ones. This water will be referred to as PCD water.

FIGURE 2-2: PYROCATALYTIC DISTILLATION APPARATUS

All parts are Pyrex except for those
whose code starts with Q (quartz).

AC	Allihn condenser
DR	Distillate receiver
FD	Fritted disk
QD	Perforated quartz disk fused on the I.D. of Q1
QJ	Quartz standard-taper 24/40 joint
Q1	25 mm x 70 cm quartz tubing packed with crushed quartz chips
Q2(CAT)	10 mm x 30 cm quartz tubing packed with 90% Pt-10% Rh gauze (Johnson Matthey)
Q3	25 mm x 30 cm quartz tubing
Q4	20 mm quartz connecting tubing
RP	Return path for water
RV	Relief valve (Teflon)
SC	Sample collector flask (100 ml capacity)
VC	Vigreux-like condenser, with wedge shape indentations instead of rods
2WS	2-Way stopcock with Teflon barrel
3WS	3-Way stopcock with Teflon barrel

(2) Water was distilled from $1 \times 10^{-3} \text{ M}$ permanganate solution in 0.01 M sulfuric acid using the apparatus shown in Figure 2-3 and a procedure as follows: A solution (typically 2.5 liter) was prepared from a permanganate stock solution, $18 \text{ M}\Omega\cdot\text{cm}$ water and AESAR sulfuric acid. After letting the solution stand for 48 hours or longer at room temperature under a purging flow of the purified nitrogen (see above), the water was distilled at a rate of 150 ml/h for at least 24 hours, during which the distillate was continuously fed back to the still by gravity. It is important that the refluxing water not be directly exposed to the vapor rising from the still. This was then followed by a period of withdrawal of product water at a rate of 150 ml/h. The system was continuously purged by a stream of ultra-pure nitrogen gas (flow rate, 50 ml/min). A Teflon check valve (0.07 bar differential) provides an exit for the gas and keeps the system under positive pressure. This water will be called APD water.

(3) Other water preparations studied were; triple distillation, triple distillation with the last step from alkaline permanganate, triple distillation with the last distillation from acid permanganate (but without the 2-day digestion period prior to distillation), and single distillation as in (2) but without the 2-day digestion period.

FIGURE 2-3: ACID-PERMANGANATE DISTILLATION APPARATUS

Overall height is 1 m. A, still, 5 liter flask, with electric heating mantle; B, purge gas inlet, Teflon-barrel stopcock; C, purge gas outlet, Teflon check valve; D, APD water outlet; E, Teflon-barrel stopcock; F, water recycle path, 3 mm I.D. tubing; G, 1 l flask; H, height difference between bottom of receiver flask and branching point for gas inlet is 20 cm; J1, O-ring joint, No. 40; J2, standard-taper joint, 24/40.

All electrolyte solutions prepared from the water obtained by the purification methods described above were used without pre-electrolysis. Except where otherwise noted, all electrolyte solutions were prepared by diluting the AESAR sulfuric acid with the APD water. Approximately 20 ml of $1.0 \times 10^{-6} \text{ M}$ "poison" in $0.05 \text{ M H}_2\text{SO}_4$ was used as the electrolyte solution for each poisoning run. The total amount of poisoning species present in the solutions is about 40 times the amount needed for a monolayer coverage of the Pt working electrode's surface used in this study. All Pt-surface recovery runs were conducted in the mother solution, which still contained a large remaining excess of the poison species.

RESULTS AND DISCUSSION

Purity of The Acid-Permanganate-Distilled Water

To test the purity of the APD water, the polycrystalline platinum working electrode (prepared as described above) was subjected to 2.5 hours of potentiostating (PS) at -0.28 V, accompanied by bubbling nitrogen, in 0.5 M H_2SO_4 . Figure 2-4 compares the CVs taken in the same (quiescent) solution, immediately following the PS period, with that of a newly prepared Pt electrode in a fresh portion of 0.5 M H_2SO_4 . The Figure also shows a significant recovery (c) of the potentiostated surface after three cycles (PCs) between -0.225 V and $+1.25$ V.

In Figure 2-4, Curve a contains all the peaks and other features of a clean polycrystalline Pt CV in an impurity-free sulfuric acid solution. The anodic hydrogen peaks at -0.14 V, -0.07 V, and -0.02 V are primarily due to hydrogen adsorbed on the (111) sites^{43,44}, (110) sites⁴⁴, and (100) sites^{43,45-48}, respectively. There are no peaks in the double layer (DL) region, and three anodic peaks in the oxygen adsorption region: a shoulder at 0.62 V and two peaks at 0.68 V and 0.77 V. The cathodic oxygen peak is at 0.50 V at this scan rate of 0.1 V/s,

FIGURE 2-4: CYCLIC VOLTAMMOGRAM OF POLYCRYSTALLINE PLATINUM

Solution is 0.5 M H_2SO_4 prepared from APD water and AESAR sulfuric acid. Sweep rate is 100 mV/s. (a) freshly prepared and conditioned Pt, (b) after PS at -0.28 V with N_2 -stirring for 2.5 hrs, (c) after 2 potential cycles at 100 mV/s between -0.225 and 1.25 volts.

and the two peaks in the hydrogen adsorption region are at -0.02 V and -0.15 V. Stirring did not affect the features in the oxygen region, and slower scan rates did not yield any peaks in the DL region.

Curve b of Figure 2-4, taken immediately after stopping the nitrogen flow following 2.5 hours of PS at -0.28 V with nitrogen bubbling, shows (i) blocking of the H-desorption processes, (ii) a higher charging current, but no peaks in the DL region, (iii) partially suppressed oxygen deposition, which was expected, (iv) a significantly larger anodic current near the oxygen evolution potential, (v) a small change in the oxygen desorption peak, and (vi) an enhancement of H adsorption. Since the CV was started at the cathodic end immediately following the PS at the HER potential, observation (i) is not a consequence of the blocking of H adsorption during the anodic sweep⁴⁹, but rather due to poisons deposited from the solution during the HER period. Hydrogen generated by HER would have made a positive contribution to the H oxidation current.⁴⁹ The suppression of the anodic hydrogen peaks proceeds slowly during the HER period. These peaks were reduced to the level indicated by Curve b after 2.5 hours at as cathodic a potential as -0.28 V. The characteristic peaks for a clean Pt surface were restored after only 3 potential cycles (Curve c) in the same mother solution. These observations are indicative of the high purity of the electrolyte solution. If the increase in the anodic current in the oxygen region was

all due to impurities from the solution, it would correspond to 1.1×10^{-8} equivalents per liter, or 11 equivalent-parts per trillion.

A similar experimental run at -0.28 V for 2.5 hours, but in 0.5 M H_2SO_4 prepared from our pyrocatalytically distilled water and AESAR sulfuric acid, yielded a small but distinct anodic peak with its maximum at 1.0 V. Based on the estimations made above, this additional peak would correspond to an impurity level of about 30 equivalent-parts per trillion.

The sulfuric acid solutions prepared with the waters produced by the other distillation procedures, when tested, gave a distinct broad peak with varying peak positions ranging from 0.75 V to 1.0 V. Baker's ULTREX sulfuric acid, diluted to 0.5 M using the APD water, produced a CV in which the anodic oxygen peaks were completely suppressed and a broad peak centered at 0.9 V was observed after 5 minutes of PS at 0.57 V, with nitrogen bubbling. The peak generally increased with the duration of PS, when the PS-potential was lower than 0.58 V. The impurity level in the ULTREX sulfuric acid was estimated from the data to be several equivalent-parts per million.

It was found that the other water preparations (cf: Experimental) are far inferior to the APD and PCD preparations. We note, in particular, that the 2-day digestion period prior to the APD distillation, the low concentration of the permanganate, the slow distillation rate and the separate reflux path for the

distillate water are essential for obtaining high purity water. The APD apparatus shown in Figure 2-3 is much simpler and less expensive to construct than the PCD apparatus. It is also less tedious to operate and the APD water purity is at least that of the PCD water.

Poisoning-Depoisoning Processes

Figure 2-5 illustrates relative rates of decay of the HER current when a platinum electrode is potentiostated at near HER potential. Among those tested, sulfite is by far the quickest poison and the transition metals, which have their Nernst potentials far anodic to the HER potential, produced only small effects.

In each experiment, the Pt working electrode was first potentiostated at -0.28 V for 15 minutes in the N₂-stirred solution containing 1.0×10^{-6} M of the specific poison. At the end of the HER period, the N₂ bubbling was stopped, and the first CV was taken immediately in the same mother solution from which the poison had been deposited. The mother solution contained a large excess of the poison species during all the recovery runs. The indicated number of cleaning potential scans were taken at a sweep rate of 0.1 V/s prior to the next CV scan. The process of

FIGURE 2-5: COMPARISON OF HER-CURRENT DECAY FOR VARIOUS POISONS

Initial poison concentrations are $1.0 \mu\text{M}$ in $0.05 \text{ M H}_2\text{SO}_4$ solution for all poisons. Pt electrode was potentiostated at $-0.28 \text{ V}_{\text{SCE}}$. All solutions were stirred by bubbling N_2 . NOTE: The curves for Cr, Mn, Al, and Zn fall between the curves for Fe and Co. The curve for Pb was taken in 0.10 M HClO_4 .

cleaning-scans/CV-scan was repeated several times successively. All CVs were taken at 1.0 V/s. Both cleaning and CV scans were carried out in quiescent solutions. Generally, when the solution was stirred during the cleaning scan, one scan was found sufficient to restore the clean Pt surface. Figure 2-6 illustrates the response of HER current to the poisoning-depoisoning cycles in the Cd(II) solution. Figures 2-7 through 2-11 show the recoveries of polycrystalline Pt electrode surfaces from poisoning by Ag(I), Cu(II), Cd(II), Pb(II) and bisulfite, respectively. All were done in 0.05 M H_2SO_4 , except Pb(II) which was done in 0.10 M HClO_4 .

On the first CV for Ag (Fig. 2-7), the anodic peaks at 0.44 V and 0.89 V are, respectively, due to the stripping of bulk Ag from Ag layers and monolayer Ag from Pt.³⁰ It is noted that the area, sectioned off the supposed monolayer Ag peak on the first CV and the oxygen region peaks of the fourth CV, corresponds to about two Ag atoms per H-site. Although the peak contains a slight shoulder on its cathodic side, which makes it resemble the features called by Stucki³⁰ Sites I and II, the large excess in the stoichiometry in this work cannot be explained either by his adsorbate-adsorbate interaction postulate or by Arvia's AD-NG model of Ag deposition on Pt.³⁵ The fact that this study has used an unannealed polycrystalline Pt electrode suggests that this may be a possible cause of the phenomenon, or perhaps a

FIGURE 2-6: DECAY-RECOVERY CYCLES FOR CADMIUM POISONING

Solution is $1 \mu\text{M}$ CdSO_4 in 0.05 M H_2SO_4 . Potentiostating was at -0.28 V and each recovery was achieved by one cleaning cycle at 0.1 V/s between -0.28 V and $+1.25 \text{ V}$ in the N_2 -stirred mother solution.

FIGURE 2-7: RECOVERY OF POLYCRYSTALLINE Pt FROM Ag POISONING

Initially poisoned by potentiostating for 15 min at -0.28 V in N_2 -stirred solution of $0.5 \mu M Ag_2SO_4$ in $0.05 M H_2SO_4$. Both cleaning and CV cycles (switching potentials were -0.24 V and +1.25 V; sweep rates were 0.1 V/s and 1.0 V/s, respectively) were taken under quiescent conditions.

----- 1st CV immediately after HER

-.-.-.- 2nd CV after 2 cleaning cycles following
the 1st CV

..... 3rd CV after 5 more cleaning cycles following
the 2nd CV

———— 4th CV after 9 more cleaning cycles following
the 3rd CV

portion of the Ag peak may be due to the adsorption of oxygen on Ag prior to Ag dissolution. This still remains to be understood.

The CV also shows that (i) the bulk Ag is removed within two cleaning scans, (ii) it takes more than 10 cleaning scans to remove the monolayer Ag in the quiescent solution, and (iii) Pt oxidation is inhibited as long as the monolayer of Ag atoms remains on the Pt surface.^{28a,35} If the solution is stirred, all features of a clean Pt surface, including those in the oxygen region, return after only two cycles. This indicates that some Ag(I) generated during the anodic scan, in the unstirred solution, is redeposited when the sweep rate is 0.1 V/s.

Similar observations can be made concerning the poisoning by Cu (Fig. 2-8). The bulk Cu (Cu on Cu) peak^{27,30} at 0.04 V disappears after one cleaning scan, while the monolayer/submonolayer Cu peak^{27,30} at 0.52 V remains after 9 cleaning and 2 CV scans. It takes more than 10 cleaning scans to remove the remaining submonolayer Cu in quiescent solution, but only one in stirred solutions. The broadness of the monolayer/submonolayer peak may be due to contributions from various Pt surfaces.^{26a,b,d} Referring to the first CV for Cu, the remnants of weakly adsorbed hydrogen and the slight shoulder seen on the cathodic side of the bulk Cu peak may be due to bare Pt surfaces resulting from the restructuring of the Cu monolayer. These deposits can undergo restructuring to form islands of Cu

FIGURE 2-8: RECOVERY OF POLYCRYSTALLINE Pt FROM Cu POISONING

Poisoning solution was $1.0 \mu\text{M}$ CuSO_4 in 0.05 M H_2SO_4 .

All other parameters are the same as for Figure 2-7.

clusters, as has been discussed by Arvia.³⁴

Cadmium (Fig. 2-9) gives a shoulder at 0.18 V and a peak at 0.27 V on the first CV. These observations are in good agreement with similar anodic scan features obtained by Adzic⁵⁰ in 1 M HClO₄. The area of the peak (48 μ C) in the DL region, above the current baseline, corresponds to a 1:1 Cd coverage for every hydrogen site. The amount of Cd deposited is one percent of the total cadmium available. The exact nature of the double Cd peaks remains to be determined. Cadmium does not affect the oxygen region, but suppresses the anodic hydrogen peaks. Even the more strongly held Cd is removed after 10 cleaning scans in unstirred solution, while both are eliminated by one scan when the solution is stirred.

The recovery of the HER current after one such scan in the stirred Cd(II) solution is illustrated in Figure 2-6 (initial concentration of Cd(II) is 1.0×10^{-6} M). The current recorded here is almost entirely due to HER; the Cd deposition current is negligible, as is evident from the above discussion. The amount of Cd deposited during the 10 minute decay period corresponds to a monolayer covering 75% of the total Pt surface area, while the HER activity (current) is reduced by 50%.

Lead adsorbate (Fig. 2-10) inhibits both weakly and strongly bound hydrogen at all coverages. The slight shoulder at 0.34 V, on the first CV of Figure 2-10, can also be seen in

FIGURE 2-9: RECOVERY OF POLYCRYSTALLINE Pt FROM Cd POISONING

Poisoning solution was $1.0 \mu\text{M}$ CdSO_4 in 0.05 M H_2SO_4 .

All other parameters are the same as for Figure 2-7.

FIGURE 2-10: RECOVERY OF POLYCRYSTALLINE Pt FROM Pb POISONING

Poisoning solution was $1.0 \mu\text{M}$ $\text{Pb}(\text{ClO}_4)_2$ in 0.10 M HClO_4 . All other parameters are the same as for Figure 2-7.

Bruckenstein's data at high coverage²⁷ and appears as a more pronounced shoulder in Adzic's work.⁵⁰ The peak at 0.52 V is in agreement with Adzic⁵⁰, who however, also observed a smaller peak at 0.6 V.

Poisoning by bisulfite is easily resolved (Figure 2-11). The ease with which it can be eliminated is independent of whether the solution is stirred or not. The characteristics of the major peak at 1.02 V on the first CV are independent of scan rate, and so, the peak is due to the oxidation of surface adsorbate.

In Figure 2-12, we see that the rate of decay of the HER current decreases after each regeneration cycle. This observation leads us to believe that the "bisulfite", on the surface, is being oxidized to a species that does not poison the Pt surface. We can say this, because of the lack of new additional peaks in the subsequent CVs taken after each of the cleaning cycles (cf: Figure 2-11). We conclude that the oxidation product is the sulfate anion. This interpretation is in agreement with the literature.^{19,51}

Appleby and Pichon observed another anodic peak⁵¹ at 0.5 V, which we did not. This additional peak reportedly changed its height as a function of sweep rate.⁵¹ We believe that this peak was probably due to an impurity in their sulfuric acid solution. It is also noted that the first CV in Figure 2-11 shows a

FIGURE 2-11: RECOVERY OF POLYCRYSTALLINE Pt FROM SO_2 POISONING

Poisoning solution was $1.0 \mu\text{M}$ NaHSO_3 in 0.05 M H_2SO_4 .

All other parameters are the same as for Figure 2-7.

FIGURE 2-12: DECAY-RECOVERY CYCLES FOR BISULFITE POISONING

Solution is $1.0 \mu\text{M}$ NaHSO_3 in 0.05 M H_2SO_4 . Potentiostating was at -0.28 V with N_2 -stirring. Each recovery was by one cleaning cycle at 0.1 V/s between -0.28 V and $+1.25 \text{ V}$ without N_2 -stirring.

significant amount of adsorbed hydrogen in spite of the fact that bisulfite is the quickest of all the poisons we have tested (Fig. 2-5). The loss of HER catalytic activity and the presence of a significant amount of adsorbed hydrogen at the same time can be explained as being due to the blockage of dihydrogen formation by adsorbed sulfur species at the HER potential.

Figures 2-13 through 2-19 illustrate the effects of potentiostating at the HER potential in solutions containing other metal ions: Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Al(III), and Zn(II). It is noted that (i) none of these yield distinctive adsorbate peaks, which was to be expected, and (ii) Cr(III) and Mn(II) enhance the strongly bound hydrogen peak while suppressing the weakly bound one. The relatively small effects of these ions on the HER and CVs of the platinum electrode (Figures 2-5, and 2-13 through 2-19), however, may not be negligible with considerably longer exposure periods.

FIGURE 2-13: RECOVERY OF POLYCRYSTALLINE Pt FROM Cr POISONING

Initially poisoned by potentiostating for 15 min at -0.28 V in N_2 -stirred solution of $0.5 \mu M Cr_2(SO_4)_3$ in $0.05 M H_2SO_4$. Both cleaning and CV cycles (switching potentials were -0.24 and 1.25 volts; sweep rates were 0.1 V/s and 1.0 V/s, respectively) were taken under quiescent conditions.

----- 1st CV immediately after HER

----- 2nd CV after 2 cleaning cycles following the
1st CV

FIGURE 2-14: RECOVERY OF POLYCRYSTALLINE Pt FROM Mn POISONING

Poisoning solution was $1.0 \mu\text{M}$ MnSO_4 in 0.05 M H_2SO_4 . All other parameters are the same as for Figure 2-13.

FIGURE 2-15: RECOVERY OF POLYCRYSTALLINE Pt FROM Fe POISONING

Poisoning solution was $1.0 \mu\text{M}$ FeSO_4 in 0.05 M H_2SO_4 . All other parameters are the same as for Figure 2-13.

FIGURE 2-16: RECOVERY OF POLYCRYSTALLINE Pt FROM Co POISONING

Poisoning solution was $1.0 \mu\text{M}$ CoSO_4 in 0.05 M H_2SO_4 . All other parameters are the same as for Figure 2-13.

FIGURE 2-17: RECOVERY OF POLYCRYSTALLINE Pt FROM Ni POISONING

Poisoning solution was $1.0 \mu\text{M}$ NiSO_4 in 0.05 M H_2SO_4 . All other parameters are the same as for Figure 2-13.

FIGURE 2-18: RECOVERY OF POLYCRYSTALLINE Pt FROM Al POISONING

Poisoning solution was $0.5 \mu\text{M Al}_2(\text{SO}_4)_3$ in $0.05 \text{ M H}_2\text{SO}_4$. All other parameters are the same as for Figure 2-13.

FIGURE 2-19: RECOVERY OF POLYCRYSTALLINE Pt FROM Zn POISONING

Poisoning solution was $1.0 \mu\text{M}$ ZnSO_4 in 0.05 M H_2SO_4 . All other parameters are the same as for Figure 2-13.

CONCLUSION

An exemplary platinum surface and cyclic voltammogram can be obtained by following the platinum preparation procedure presented in the Experimental section in conjunction with solutions prepared using AESAR sulfuric acid and water produced by slow distillation from dilute acidic permanganate solution. The water produced using our method has at least as high a purity as the pyrocatalytically distilled water. Our sulfuric acid solutions passed our purity test (potentiostating at $-0.28 \text{ V}_{\text{SCE}}$ for 2.5 hours), which is more stringent than Conway's test. Metal-ion and bisulfite impurities affect the HER catalytic activity of polycrystalline platinum surfaces in many ways, both qualitatively and quantitatively. In general, the cathodic deposits can be removed and the catalytic activity regenerated repeatedly while the electrode is still immersed in the poison-bearing solution. The regeneration is accomplished by having the electrode undergo one to several linear potential scans between $-0.24 \text{ V}_{\text{SCE}}$ and $1.25 \text{ V}_{\text{SCE}}$. Poison removal is achieved by one such scan if the solution is well stirred.

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CHAPTER 3

INFLUENCE OF SURFACE OXIDE ON CONTACT ANGLE MEASUREMENTS OF WATER ON CLEAN PLATINUM

In order to discuss the wettability of a platinum surface modified by an electrically conducting polymer film, it is first necessary to know the wettability of a clean platinum surface. Upon inspection of the literature, it was found that there exists a large range of values for the contact angle formed between water and clean platinum surfaces. These values range from 0° (complete wetting) to an upper limit of about 61° . Values differing from 0° are assumed to be due to the presence of organic contaminants.

Many studies on the wettability of clean metal surfaces by water have established the fact that the presence of hydrophobic organic contaminants on these surfaces results in an increase in the measured contact angle. These contaminants are most often small amounts of grease or oil that are present in the air and readily adsorbed onto the metal surfaces. Several investigators developed elaborate procedures to reduce or eliminate this kind of contamination, but there still arose discrepancies in the wettability results.

It was the consensus, until the late 1950's, that all clean metal surfaces were completely wetted by water and most organic liquids.¹ Reviews by Sutherland and Wark² and Gaudin³ regarding the field of ore flotation revealed that truly clean surfaces of nearly all minerals, including oxides, gave zero or small contact angles. Extensive investigation by Fox, Hare, and Zisman⁴ on the wetting of surfaces (e.g., platinum) also concluded that "all pure liquids" will spread spontaneously if the surface is free of adsorbed organic films. This line of thought resulted in establishing the criterion that a clean metal surface was one that was completely wetted by water.

As a consequence of this criterion, several methods for the reproducible "cleaning" of metal surfaces were developed. These methods included mechanical abrasion, heat treatments,^{4,5} electropolishing,⁶ wet oxidation using hot 30% hydrogen peroxide,^{7,8} aqua regia,^{8,9} hot concentrated nitric acid,¹⁰ or hot dichromate-sulfuric acid.⁶ Early work using mechanical polishing alone resulted in surfaces that were completely wetted by water, but these results appear to be erroneous.^{11,12}

White¹³ reports that the presence of hydrophilic inorganic contaminants (residual abrasives) on the sample surface can affect wettabilities as seriously, but in the opposite direction, as the commonly discussed contamination by hydrophobic organic material. The methods using vigorous chemical and electrochemical oxidation treatments result in metal surfaces

containing some degree of oxide coverage.^{6,8} These metal oxides behave, in essence, no differently than residual abrasives and would also give incorrect contact angle values for "clean" metal surfaces.

When we prepared our platinum surfaces in a manner similar to the method used by White,¹³ the contact angles measured had values of 55 to 62 degrees. We believe that these values represent clean oxide-free platinum surfaces. We also believe that surfaces giving very small angles (complete wetting) are almost, if not entirely, covered with oxide. We have attempted to substantiate these claims using electrochemical methods in combination with contact angle measurements.

EXPERIMENTAL

Chemicals

High purity water (APD) was obtained by redistilling distilled water from acidic permanganate solution (cf: Chapter 2, Experimental) under an atmosphere of ultra high purity (UHP) nitrogen (Linde, 99.999%). The APD water was used throughout all stages of this study. The 0.5 M sulfuric acid solutions were prepared with 99.999% H_2SO_4 (AESAR, Johnson-Matthey) and used as supporting electrolyte. The UHP nitrogen used was further purified by: (i) passing through a column of activated coconut charcoal, (ii) bubbling through hot (80 °C) concentrated 99.999% H_2SO_4 , followed by (iii) bubbling through warm (60 °C) acidic potassium permanganate solution (0.5 M H_2SO_4 and 0.02 M KMnO_4), and finally (iv) bubbling through APD water. Entrained mists were removed by a column packed with crushed quartz. This nitrogen gas was used to deoxygenated the supporting electrolyte in the electrochemical cell, blanket the solution in the cell, and provide an inert atmosphere during the contact angle measurements.

Platinum Disk Electrode

The surface used for the contact angle measurements is the cross-sectional surface of a platinum rod which has been fashioned into a platinum disk electrode with the following configuration. A rod of 99.99% Pt (AESAR, Johnson Matthey) 0.250 inch in diameter and 5/16 inch in length is attached at one end to a 1/2 inch long piece of 0.250 inch diameter stainless steel (SS), type 304, rod with silver solder (Figure 3-1a). This Pt/SS unit is a manageable size for polishing of the platinum surface and for contact angle measurements, but not for electrochemical study. In order to accommodate the electrochemical cell, an extension rod of 1/8 inch diameter SS, type 304, and 4 inches long is screwed into the SS end of the Pt/SS unit. The entire electrode assembly is then covered with a Teflon sleeve (Figure 3-1b). This Teflon sleeve fits tightly over the Pt rod and allows only for the exposure of the cross-sectional end of the Pt.

Mechanical polishing of the platinum surface is accomplished via the use of a specimen mount designed in our laboratory and a Leco Corp. model GP-20 Grinder/Polisher. The mount (Figure 3-2) is constructed of optical pyrex, SS (type 304), Nylon, and Teflon and is equipped with a micrometer. To polish the Pt surface, the Pt/SS unit is pressed into the tight fitting teflon guide of the

FIGURE 3-1: PLATINUM DISK ELECTRODE WITH TEFLON SLEEVE

FIGURE 3-2: SPECIMEN POLISHING MOUNT

mount from the bottom with the micrometer retracted. The mount is then placed against another disk of optical pyrex and the micrometer adjusted until the platinum surface makes contact with the disk. The micrometer is then adjusted further so that 0.001 inch of the Pt is exposed for polishing.

In order to obtain a Pt surface that is perpendicular to the axis of the Pt/SS unit, it was first necessary to level the surface. This was accomplished using 17 μm garnet powder (Harrick Scientific Corp.), distilled water and the GP-20 equipped with a Pellon cloth (Leco Corp.). The final polishing, and the polishing between experimental runs, were done with an aqueous suspension of either 1-1/2 μm or 1/2-1/4 μm diamond powder (Kay Industrial Diamond Corp.) using a Leco Technotron Red polishing cloth on the GP-20. When a relatively scratch-free and mirror smooth surface was obtained, the specimen was held against an abrasive-free piece of the technotron red cloth while it was flushed with distilled water so that the polished surface was scrubbed free of any platinum/diamond powder residues. The platinum surface was then rinsed with APD water and allowed to dry under nitrogen. The contact angle obtained on a platinum surface prepared in this manner falls within the range of 55-62 degrees.

Instrumentation

All electrochemical experiments were conducted with an IBM Instruments EC/225 Voltammetric Analyzer and a standard three electrode electrochemical cell (cf: Chapter 2, Experimental). Potentials reported were measured with respect to a standard KCl saturated calomel reference electrode (SCE). A platinum spiral wire, with a surface area of 6.4 sq cm, was used as the auxiliary electrode.

Contact angle measurements were taken using a contact angle goniometer (Rame-Hart, Inc.; Model 100-00) equipped with a micro-syringe attachment (Model 100-10) and an environmental chamber (Model 100-07). The environmental chamber was continuously purged with UHP nitrogen saturated with APD water. The contact angles were measured using the sessile drop method¹⁴ (Figure 3-3). After the Pt/SS unit has been in the chamber for approximately 10 minutes, a 2 μ l droplet of APD water was placed in the center of the platinum surface. Readings were taken at multiple positions around the droplet and the average calculated. A green filter was used with the light source.

Young's Equation

$$\gamma_1 - \gamma_2 = \gamma_{12} \cos \theta$$

FIGURE 3-3: ILLUSTRATION OF SESSILE DROP METHOD

Interfacial tensions between
 γ^1 : solid and vapor phases.
 γ^2 : solid and liquid phases.
 γ^{12} : liquid and vapor phases.

Experimental Procedure

There were basically two types of experiment. The first consisted of measuring the contact angle formed by water on a platinum surface at each step of a step-wise oxidation of the surface. The platinum disk electrode (after an initial contact angle measurement) was assembled, rinsed with supporting electrolyte, and placed in the electrochemical cell. Nitrogen was bubbled through the electrolyte solution for 10 minutes. The disk electrode was potentiostated at a potential within the range of -0.30 V (hydrogen evolution) to $+1.70$ V (oxygen evolution) for 15 minutes. The disk electrode was then removed, rinsed thoroughly with APD water and disassembled. The Pt/SS unit was then placed in the goniometer and the contact angle measured. The electrode was reassembled, rinsed with supporting electrolyte and returned to the cell containing fresh solution. It was now potentiostated at a potential 200 mV more anodic than the previous potential and the process repeated. All runs started with a potential of -0.30 V and ended with $+1.70$ V.

The second was the monitoring of the wettability of a platinum surface during the reduction of an electrochemically generated oxide film. The disk electrode (after measurement of initial contact angle) was assembled, rinsed, and placed into the cell. The electrode was potentiostated at $+1.70$ V for 15 minutes. It was then removed, rinsed thoroughly with APD water,

disassembled, and the contact angle measured. The disk electrode was now reassembled, rinsed, and returned to the cell (filled with fresh solution). A potential of -0.30 V was now applied for a series of 15 minute periods. After each period of reduction, the electrode was again removed from the cell, rinsed with APD water, the contact angle measurement taken, and then returned to the cell. In both experiments, the electrode open circuit (EOC) potential was measured after the contact angle measurement had been taken.

RESULTS AND DISCUSSION

Table 3-1 and Figure 3-4 contain experimental results for the step-wise oxidation of a clean platinum surface. The electrode open circuit potential, the third column in Table 3-1, is the measurement of the working electrode (i.e., the platinum disk) potential relative to the SCE reference electrode at open circuit (i.e., without imposing a current). This measurement provides a means of gauging the state of oxidation/reduction of the metal-solution interface.¹⁵

Upon inspection of the data in Figure 3-4, we see that both the wettability and oxidation state of the platinum surface remains relatively constant until an applied potential between +0.90 V and +1.10 V is reached. This potential range is located at the foot of the oxygen reduction wave on a clean platinum cyclic voltammogram (cf: Chapter 2, Figure 2-4). It is near these potentials and above that surface oxide begins to accumulate. As the degree of surface oxidation increases, indicated by the rise in the EOC, the wettability of the surface also increases. After potentiostating at +1.70 V for 15 minutes, the surface has been oxidized sufficiently to result in complete wetting.

APPLIED POTENTIAL (volts)	CONTACT ANGLE (degrees)	EOC POTENTIAL (volts)
polished	56	+0.54
-0.30	56	+0.55
-0.10	50	+0.56
+0.10	54	+0.58
+0.30	51	+0.60
+0.50	52	+0.58
+0.70	52	+0.59
+0.90	54	+0.67
+1.10	45	+0.75
+1.30	40	+0.80
+1.50	30	+0.90
+1.70	completely wetted	+0.94

**TABLE 3-1: EFFECT OF APPLIED POTENTIAL (OXIDE GENERATION)
ON SURFACE WETTABILITY**

FIGURE 3-4: GRAPH OF CONTACT ANGLE AND EOC AS
A FUNCTION OF APPLIED POTENTIAL

The increase in wettability is not due to surface roughening.¹⁶ The reason is that these anodic potentials (+1 V and higher in the case of platinum) are the same as those used in the process of electropolishing of metals. During this process, anodic dissolution takes place and a smoothing action occurs. This smoothing phenomenon has been confirmed by electron microscopy.⁶

As stated in the beginning of this chapter, it is believed that the presence of hydrophobic agents on platinum will produce a non-wetting surface. Upon removal of these agents, the surface will be completely wetted. We couldn't rule out this possibility based on the data in Table 3-1 alone, so a second type of experiment was conducted. Here, the electrode surface is subjected to a potential of +1.70 V for 15 minutes. This gives a surface that is free of organic contaminants and wets completely. The surface is now electrochemically reduced at the hydrogen evolution potential of -0.30 V for a period of 15 minutes in a fresh volume of supporting electrolyte. If the presence of surface oxide doesn't affect the wettability, then its absence shouldn't either. The experimental data appear in Table 3-2.

The data show that the EOC has decreased and the contact angle has greatly increased after only the first 15 minutes of electro-reduction. The successive electro-reductions afforded comparably small changes in the EOC and contact angle. This is

REDUCTION*	CONTACT	EOC
PERIOD	ANGLE	POTENTIAL
(15 min)	(degrees)	(volts)
polished	57	+0.53
0 [†]	completely wetted	+0.93
1	45	+0.62
2	44	+0.59
3	46	+0.56
4	48	+0.54
5	47	+0.52
6	51	+0.48
7	50	+0.45

* Reduction potential was -0.30 V.

† Polished surface was oxidized at +1.70 V for 15 minutes.

**TABLE 3-2: EFFECT OF SURFACE OXIDE REDUCTION
ON SURFACE WETTABILITY**

due to the difficulty in reducing Pt-oxide that has been generated at potentials between +1.55 V and +1.95 V.¹⁷

The decrease in the hydrophilicity, after only the first reduction period, supports the theory that it is the presence of an oxide film that results in the complete wetting. If the hydrophobic nature of the surface was due to organic contaminants, then the electro-reduction would not have regenerated the hydrophobicity of the surface. Several studies agree that it is this presence of an oxide film that gives rise to small contact angles or complete wetting.^{6,8,13,18}

CONCLUSION

We have shown that a clean polished oxide-free platinum surface is hydrophobic giving contact angles with water of 55 to 62 degrees. The presence of various amounts of oxide on a platinum surface affects its wettability. An increase in the amount of oxide present increases the wettability. The amount or coverage of surface oxide necessary for complete wetting is unknown, but we suspect it is close to that of a monolayer.

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CHAPTER 4

POLY-*p*-PHENYLENE MODIFIED PLATINUM ELECTRODES

As stated in Chapter 1, it was proposed that we would design and construct a new catalyst that would afford, in-situ, both the ability to regenerate its catalytic activity and control over its wettability. The work presented in Chapter 2 illustrated that it is possible to regenerate platinum catalytic activity in-situ. Our next objective is to control the hydrophobicity of a platinum surface. We propose to accomplish this via the implementation of an electrically conducting organic film coating.

There has been a great number of studies involving chemically modified electrodes.¹⁻⁵ The surfaces of metals, metal oxides, semiconductors, and carbonaceous materials have been electrochemically modified by coverage with monomers⁶ and polymers.^{3,7} Of particular interest for our purpose is that the wettability of electroactive modifiers appears to be adjustable through electrochemical control of the average redox state of the modifier molecules.^{8,9} There have also been studies showing that fine aggregates of metals (e.g., Pt) can be electrochemically imbedded in a polymer film^{10,11} and that hydrogen gas can be generated on these aggregates.¹¹

The chemical modifier suitable for the present purpose has to satisfy the following requirements:

- (1) Electrochemical polymerization. This could allow control over the formation and uniformity of the modifier film.
- (2) Large potential range. The potential range for the electrochemical redox reactions of the modifier film should be wide enough to accommodate various potential excursions (e.g., -0.24 to +1.25 V_{SCE}).
- (3) Stability. The film should possess chemical, electrochemical, and mechanical stabilities in various aqueous solutions, upon exposure to air, and with respect to repeated potential excursions.
- (4) High hydrophobicity. Contact angles between water or dilute aqueous solutions and the non-cationic film of more than 90° are preferred. Teflon and water give a contact angle of about 112 degrees.¹² In addition, a strong dependence of the hydrophobicity on applied potential would make its use more flexible.

(5) High electrical conductivity. Under ideal conditions a high conductivity, in its reduced form, would not be required for a steady state operation of the isotope exchange columns. However, in order to implement an in-situ catalyst regeneration (cf: Chapter 2) while the columns are in operation, it would be necessary that the film have some degree of electrical conductivity in its reduced form.

Based on the above list of criteria, four chemical modifiers were chosen for this study. These were poly-pyrrole, poly-thiophene, poly-3-methylthiophene, and poly- ρ -phenylene. Preliminary experiments were conducted on these four. As a result of the information obtained, it was decided that poly- ρ -phenylene held the most promise for our purpose. A discussion of the experimental results for poly-pyrrole, poly-thiophene, and poly-3-methylthiophene can be found in the appendix.

The study of poly- ρ -phenylene has produced many interesting results. Presented in this chapter will be the following: A mechanism for the polymerization of ρ -terphenyl based on literature and observations made in the laboratory. The evaluation of η for the electropolymerization of ρ -terphenyl. Investigation into the nature of the polymer's cyclic voltammogram. The effects of supporting electrolyte on the

polymerization reaction and the resulting cyclic voltammogram. The stability of the polymer film toward potential excursions in sulfuric acid media. The wettability of poly- ρ -phenylene films characterized as a function of both the polymerization reaction duration (e.g., film thickness) and supporting electrolyte.

EXPERIMENTAL

Electrochemical Set-up

In the experiments where the supporting electrolyte solution was dilute sulfuric acid, a standard electrochemical cell with the electrodes separated by Vycor disk partitions was used. This set-up included a KCl saturated calomel reference electrode and a platinum spiral wire auxiliary electrode (1.0 mm dia. x 24 cm, AESAR (Johnson Matthey) Puratronic wire, 99.9985%). Volume of electrolyte solution in the main compartment was approximately 20 ml.

The experiments conducted in acetonitrile solutions were performed in an undivided electrochemical cell, where both the working and auxiliary electrodes were contained in the same compartment. The volume of solution necessary to fill the cell was approximately 25 ml. The auxiliary electrode was constructed from platinum gauze (25 mm x 50 mm, 52 mesh woven from 0.1 mm dia. wire, AESAR, 99.9%) folded into a square (ca 1 cm on edge) and spot welded to a Pt/W lead sealed in pyrex. This electrode was positioned in the center of, parallel to, and near the bottom of the cell.

The reference electrode (Figure 4-1) was a silver wire (0.5 mm dia. x 15 cm, AESAR Puratronic wire, 99.9985%) in a solution

FIGURE 4-1: Ag/Ag⁺ REFERENCE ELECTRODE WITH Pt-GLASS JUNCTION

of 0.1 M AgNO_3 in acetonitrile (Koslow Scientific Corp). The electrode junction was a platinum wire (0.1 mm dia. x 1 cm, AESAR Puratronic, 99.9985%) sealed into the end of a 2 mm O.D. pyrex tube.¹³ The potential of this electrode (that will now be referred to as the Ag/Ag⁺ electrode) versus the SCE was determined to be approximately +0.35 volts. The stability and reliability of the Ag/Ag⁺ electrode was checked periodically by recording and examining the cyclic voltammogram (CV) of ferrocene in an acetonitrile solution of tetraethylammonium tetrafluoroborate (TEATFB) with the platinum wire working electrode (cf: Chapter 2, Experimental). A representative CV for ferrocene appears in Figure 4-2. The redox potential for the ferrocene-ferrocenium couple, using this Ag/Ag⁺ reference electrode, was determined to be +0.072 volts. All data taken in acetonitrile solution have been corrected using this value as a standard.

Platinum Working Electrodes

Two platinum working electrodes were used in this study. These were the platinum wire (Pt-wire) electrode (cf: Chapter 2, Experimental) and the platinum disk (Pt-disk) electrode (cf: Chapter 3, Experimental). Prior to each experiment, the electrode surfaces were cleaned in hot (95 °C) chromic acid

FIGURE 4-2: CV OF FERROCENE-FERROCENIUM COUPLE

The solution is $1 \times 10^{-3} \text{ M}$ Ferrocene with 0.1 M tetraethylammonium tetrafluoroborate in acetonitrile. The sweep rate was 25 mV/sec and the Ag/Ag^+ reference and Pt-wire electrodes were used.

solution for 15 minutes followed by mechanical polishing with a diamond powder suspension in acidic permanganate (APD) distilled water (cf: Chapter 2 & 3, Experimental sections). Electrochemical pretreatments of the electrodes were not performed in order to eliminate the electrochemical formation of platinum oxide on the surfaces.

Reagents

The 0.05 M H_2SO_4 solutions were prepared with concentrated sulfuric acid (AESAR, 99.999%) and APD water (cf: Chapter 2, Experimental). APD water was used any time distilled water was required. Ultra high purity (UHP) nitrogen (Linde, 99.999%) was further treated by two different methods depending on its final use. If the UHP nitrogen was to be used for electrochemical experiments in sulfuric acid solution or contact angle measurements, then it was treated in the manner presented in Chapter 3. If it was to be used with the acetonitrile still or acetonitrile based electrochemical experiments, then it was further treated by: (i) passing through a column of activated coconut charcoal, (ii) bubbling through concentrated 99.999% H_2SO_4 , and (iii) passing through a column of indicating silica gel. When the UHP nitrogen was used to deoxygenate or provide an

inert atmosphere over an acetonitrile solution, it was saturated with acetonitrile stored over CaH_2 .

Acetonitrile (Aldrich, HPLC) was dried prior to use by slow distillation (100 ml/hr) over CaH_2 (J.T. Baker, Practical) in an all Teflon and pyrex still (Figure 4-3). The still is continually purged with UHP nitrogen (25 ml/min). The initial distillate is collected until the temperature rises to 82 °C. This fraction is then discarded and the distillate receiver rinsed with the second fraction, which is also discarded. At this time, acetonitrile may be collected for use in the preparation of electrolyte solutions and the rinsing of cells and electrodes. During this study, acetonitrile had also been distilled from phosphorus pentoxide.¹⁴ Results obtained using this method appeared the same as those using the CaH_2 distillation previously described.

The tetraethylammonium *p*-toluenesulfonate (TEA-tos, Kodak), when received, was very wet. The water was removed by azeotropic dehydration with benzene.¹⁵ Five grams of TEA-tos and about 125 ml of benzene were placed in a 250 ml round-bottom flask fitted with a Dean-Stark trap, Friedrichs condenser, a drying tube packed with indicating CaSO_4 , and the solution stirred by magnetic stirrer. The solvent was reduced to about 20 ml by slow distillation. The remainder of the benzene was removed on a rotary evaporator fitted with a column packed with indicating

FIGURE 4-3: ACETONITRILE DISTILLATION APPARATUS

All parts are pyrex and Teflon.

CP: Column packed with 1/4" pyrex helices
DR: Distillate receiver
FC: Friedrichs condenser
RV: Relief valve (Teflon) 6
SP: Syringe port, ACE fitting #7
TC: Thermocouple well (copper-constantan)
TS: Teflon Swagelok
TT: Teflon tubing, 1/4" O.D.
2WS: 2-Way stopcock with Teflon plug
3WS: 3-Way stopcock with Teflon plug

CaSO_4 in the aspirator line. The salt was then attached to a vacuum system at 150 millitorr for 2 days.

The following chemicals were used as received: tetraethylammonium chloride (TEAC, Fluka), tetraethylammonium tetrafluoroborate (TEATFB, AESAR), tetraethylammonium perchlorate (TEAP, Fluka, Kodak), tetraethylammonium trifluoromethanesulfonate (TEA-triflate, Fluka), tetrabutylammonium tetraphenylborate (TBATPB, Aldrich), *p*-terphenyl (Aldrich), and ferrocene (Aldrich).

Instrumentation

The chronoamperometry, cyclic voltammetry, and linear sweep voltammetry experiments were performed using an IBM Instruments EC/225 Voltammetric Analyzer. The chronopotentiometry experiments were conducted with an EG&G (PAR) Model 371 Potentiostat-Galvanostat. All electrochemical instrumentation control and data acquisition, with the exception of the linear sweep voltammetry data, was accomplished using an IBM-AT (Model 339) equipped with a math-coprocessor and a Data Translation AD/DA data acquisition board Model DT2805 (13.7 kHz). The software program used for instrument control and data acquisition and analysis was ASYSTANT+ (Macmillan Software Company). Linear sweep voltammetry data were acquired on an XY recorder (Houston Instruments, Model 200).

Contact angle measurements were taken using a Rame-Hart contact angle goniometer with the proper attachments. The experimental procedure was the same as that given in the experimental section in Chapter 3.

RESULTS AND DISCUSSION

Polymerization of *p*-Terphenyl

Polymerization Procedure

The electrochemical method of polymerization used during this study was potentiostatic (chronoamperometry). The polymerization solution consisted of 0.1 M supporting electrolyte and 2 mM *p*-terphenyl in acetonitrile. The solution was deoxygenated with acetonitrile saturated nitrogen for about 15 minutes. After this 15 minute period, the nitrogen was used to blanket the solution. The platinum working electrode, after polishing and rinsing with APD water and acetonitrile, was then potentiostated in this solution at the polymerization potential.

The polymerization was controlled by generating an external input signal for the potentiostat using the ASYSTANT+ software and the IBM-AT. An example of this signal is given in Figure 4-4. The duration of the applied potential is adjusted by changing the width of the pulse. The results obtained using this method were very reproducible (cf: Figure 4-5).

The applied polymerization potential was different depending on the platinum working electrode. Polymerizations conducted on

FIGURE 4-4: ILLUSTRATION OF EXTERNAL INPUT SIGNAL

Generation rate is 25 points per second.

FIGURE 4-5: POLYMERIZATION SERIES IN TEAP SOLUTION

Solution is 2 mM ρ -terphenyl with 0.1 M TEAP in acetonitrile.

The electrode is the Pt-disk and the potential is +1.40 V.

The polymerization durations are 2, 4, 6, 8, and 10 seconds.

the Pt-wire electrode were performed at a potential of +1.30 $V_{Ag/Ag+}$. The potential employed for polymerizations with the Pt-disk electrode were +1.40 $V_{Ag/Ag+}$. These potentials were determined by recording CVs in the monomer containing solution with both working electrodes. The potentials where monomer oxidation commenced were obtained from the CVs and used for the polymerization potentials. Polymerization on the Pt-disk electrode actually commences around +1.35 volts, but +1.40 V appears to give better results. It is believed that the difference in potential for the Pt-wire versus the Pt-disk may be due to the difference in their respective potential field gradients.

Polymerization Mechanism

The product of the electrooxidation of an aromatic compound is believed to be its radical cation.⁴ If the radical cation is very unstable, it can rapidly undergo indiscriminate reactions with either solvent or anions to form low molecular weight, and thus soluble products. On the other hand, if the radical cation is very stable, it can diffuse from the electrode surface and undergo reactions that also form low molecular weight soluble products. When the stability of the radical cation falls between these two extremes, it can then undergo dimerization reactions.

These reactions are thought to proceed by the coupling of two radical cations.⁴ An electropolymerization reaction is regarded as an extension of the dimerization reaction, i.e., it represents a sequence of dimerization reactions involving radical cation coupling.

Evidence for such a reaction pathway, in which chain propagation is dependent on the presence of the radical cation (as opposed to the neutral monomer), is reflected in the finding that in order to sustain film growth the electrode potential must be maintained at the electrochemical oxidation potential of the monomer.¹⁶ This has also been observed in this study for *p*-terphenyl. The electropolymerization reaction scheme is depicted in Figure 4-6. Note that the polymerization reaction proceeds via an intermediate "dihydro-oligomer dication"⁵ that loses two protons to form the neutral oligomer. Street¹⁷ has observed that during the electropolymerization of pyrrole the solution became increasingly acidic, which is consistent with proton elimination.

Determination of $\bar{n}$ for the Polymerization Reaction

The electropolymerization reaction consumes 2 electrons for every pair of monomer/oligomer coupled (cf: Figure 4-6). The total charge spent during the polymerization reaction is not due

FIGURE 4-6: POLYMERIZATION SCHEME FOR *p*-TERPHENYL

to bond formation alone. During polymerization, the polymer film undergoes further electrooxidation. This is accompanied by the incorporation (i.e., intercalation) of supporting electrolyte anions (counter-ions). The combination of these two processes (electropolymerization and intercalation) results in n values that are usually in the range between 2.0 and 2.7,⁵ where the charge in excess of 2.0 is consumed by the intercalation process.

If the value of n for the polymerization of p -terphenyl were known, then the amount of monomer deposited could be determined from the quantity of charge spent during the polymerization reaction. The film thickness may then be approximated using the rule-of-thumb coverage value of 10^{14} units/cm²⁴ and bond length data. Since it is known that the contribution to n by the coupling of radical cations is 2, then all that is required is the contribution due to the intercalation process.

During this study, the value of n for the intercalation of BF_4^- has been determined using chronopotentiometry. The polymer film was grown, rinsed with supporting electrolyte, and placed into a cell containing only supporting electrolyte. An oxidizing current of 100 μA was then applied to the polymer coated electrode and the resulting potential (vs. Ag/Ag^+) was recorded as a function of time. An example of the chronopotentiogram produced by poly- p -phenylene can be seen in Figure 4-7.

FIGURE 4-7: CHRONOPOTENTIOTAGRAM FOR POLY- ρ -PHENYLENE

Applied current of $100\mu\text{A}$. Solution was 0.1 M TEATFB in acetonitrile. The polymer film was grown over a period of 40 seconds on the Pt-disk electrode at $+1.40\text{ V}_{\text{Ag/Ag}^+}$ in a solution of 2 mM ρ -terphenyl with 0.1 M TEATFB in acetonitrile. $\tau = 91\text{ seconds}$.

For a particular system, there is a one-to-one correlation between the number of plateaus in the chronopotentiogram and the number of peaks in the corresponding half of the CV. In the case of poly-*p*-phenylene oxidation, there should be two plateaus (cf: Figure 4-9, below). The first plateau is difficult to discern in Figure 4-7, but it is the second plateau (beginning around +1.05 V) that is of interest here. This plateau corresponds to the intercalation process (The validity of this statement will be addressed in the next section.).

According to Delahay and Mattax,¹⁸ a plot of $\log [(r^{1/2} - t^{1/2}) / t^{1/2}]$, where r is the transition time for the plateau, against potential should yield a line of slope $-nF/2.3RT$ for an oxidation. The potential where the logarithmic term equals zero is $E_{1/2}$ for the reaction. The method used for determining r was that of Reinmuth.¹⁹ Tangent lines are drawn to the linear portions of the wave preceding and following the potential pause (plateau) and to the linear part of the wave near its inflection. A line is then drawn, parallel to the time axis, from the line drawn to the preceding linear portion to the point of intersection of the lines drawn to the linear part and the following linear portions of the potential pause. The length of this parallel line gives the transition time (r).

The plot of $\log [(r^{1/2} - t^{1/2}) / t^{1/2}]$ against E , for the data in Figure 4-7, is shown in Figure 4-8. The value of n for

FIGURE 4-8: PLOT OF $\log [(\tau^{1/2} - t^{1/2}) / t^{1/2}]$ AGAINST POTENTIAL

The time and potential data are taken from Figure 4-7. The value for τ is 91 seconds. The value of the slope is -3.587 and the value for $E_{1/2}$ is +1.37 V_{Ag/Ag+}.

the intercalation process involving BF_4^- , determined using this method, is 0.2 ± 0.04 . Combining this with the value of 2 for the coupling process gives $n \approx 2.2$ for the polymerization of p -terphenyl in TEATFB supporting electrolyte.

Nature of Poly- p -Phenylene CV Peaks

Figure 4-9 is a CV of poly- p -phenylene taken in 0.1 M TEATFB acetonitrile solution. The CV gives two oxidation-reduction couples. The first centered about $+0.55 \text{ V}_{\text{Ag}/\text{Ag}^+}$ and the other at about $+1.10 \text{ V}_{\text{Ag}/\text{Ag}^+}$. Very little attention has been addressed to the nature of the reactions or species comprising these peaks. It is thought that the peaks centered around $+0.55 \text{ V}$ are the result of triphenylenic moieties generated during polymerization.²⁰ The peaks at $+1.10 \text{ V}$ are generally accepted as the oxidation/reduction of the polymer (i.e., intercalation/de-intercalation).

We felt that a linear sweep voltammetric study examining the response of the peak current as a function of sweep rate may give some insight into the processes occurring. If an electroactive molecule is immobilized on an electrode surface, then the peak current (i_p) is proportional to the potential sweep rate. On the other hand, if the electroactive molecule is in solution, then i_p

FIGURE 4-9: CV OF POLY- ρ -PHENYLENE

The solution is 0.1 M TEATFB in acetonitrile. E-range is 0.00 to 1.25 V_{Ag/Ag+} with a sweep rate of 1.00 V/sec. The polymer film was grown on the Pt-disk in a solution of 2 mM ρ -terphenyl with 0.1 M TEATFB over a period of 2 seconds at a potential of +1.40 V_{Ag/Ag+}.

is proportional to the square root of the sweep rate. Since the reduction peaks were better resolved, it was decided that these would be studied.

The procedure was as follows: (i) the polymer film coated electrode (placed in a cell with supporting electrolyte) was potentiostated at $+1.25 \text{ V}_{\text{Ag/Ag}^+}$ for a period of 10 seconds, (ii) the potential was then decreased at a specified rate to a final potential of $-0.30 \text{ V}_{\text{Ag/Ag}^+}$ while recording the current, and (iii) the film was allowed to rest at the final potential for 5 minutes before repeating steps (i) and (ii).

The i_p data for the reduction wave at $+1.0 \text{ V}$ (Figure 4-10) has been presented as a function of the square root of the sweep rate ($\nu^{1/2}$). When fitting the data, it was discovered that the peak current has two components, one proportional to the square root of the sweep rate ($\nu^{1/2}$) and the other proportional to the sweep rate (ν). This implies that the electrochemical process occurring at $+1.0 \text{ V}$ involves both mobile and immobilized species. Note that the contribution of both species are about equal (i.e., 103.8 and 93.6, respectively). This suggests that the net reaction is equally dependent on both. We believe that the immobilized species is the polymer undergoing reduction and the mobile species is counter-ions migrating out of the film during the reduction process. This agrees with the thought that the intercalation/de-intercalation process occurs around $+1.10 \text{ volts}$.

FIGURE 4-10: PLOT OF i_p vs $\nu^{1/2}$ FOR PEAK AT +1.0 V_{Ag/Ag+}

Solution is 0.1 M TEATFB in acetonitrile. The conditions were the same as in Figure 4-9.

$$i_p (\mu A) = 103.8 \nu - 93.6 \nu^{1/2}$$

It was observed that the peak current for the +0.4 V reduction wave is proportional to the sweep rate (Figure 4-11), which indicates that this wave is due to the reduction of an immobilized species. This disproves the theory that the wave is due to the reduction of triphenylenic moieties present in the film, as was suggested earlier.²⁰ If it were, then the reduction process would include movement of counter-ions and this would result in a component showing a dependence on the square root of the sweep rate. We believe that the reaction occurring at this potential is the reduction of the polymer molecules. This reaction (radical cation to neutral polymer chain) would have an n value of one and not involve the movement of counter-ions.

Anson and co-workers²¹ have presented a method of determining n for a surface bound species using the slope of the i_p verses sweep rate data and the charge (any sweep rate) under the voltammogram wave.⁵ The value of n obtained for the reduction wave at +0.4 V is 1.1 ± 0.3 . It was observed, when recording the CVs of films produced using various polymerization times (i.e., 8 to 40 seconds), that the charge consumed by this reduction wave remained relatively constant while that for the wave at +1.0 V increased with the length of polymerization. This consistency suggests that the charge may only depend on electrode area. In addition, the charge and this value for n give a coverage of 2.5×10^{14} units/cm². This value is in excellent

FIGURE 4-11: PLOT OF i_p vs ν FOR PEAK AT $+0.4 V_{Ag/Ag+}$

Solution is 0.1 M TEATFB in acetonitrile. The conditions were the same as in Figure 4-9.

$$i_p (\mu A) = -132.9 \nu$$

agreement with the rule-of-thumb value of 10^{14} units/cm². We conclude that the wave at +0.4 V is the reduction of the polymer radical cation and not triphenylenic moieties.

Effect of Supporting Electrolyte

Early in the study of the polymerization of *p*-terphenyl, there was an attempt to estimate the degree of intercalation by conducting the reaction using supporting electrolytes having anions of different size. The thought was that the larger the anion, the lower the amount of intercalation and, therefore, the smaller the polymerization current. First it was necessary to gather a collection of useful salts. A summary of the possible choices is presented in Table 4-1 with their determined working potential ranges and relative solubilities. Only three of these salts (TEATFB, TEAP, and TEA-triflate) were stable toward oxidation within our potential range of interest (0.00 to +1.40 V_{Ag/Ag+}). The size of the anions (stripped of any solvation sphere) for each of these salts was estimated using covalent bond radii. The calculated sizes are: ClO₄⁻ - 62 Å³, CF₃SO₃⁻ - 57 Å³, and BF₄⁻ - 52 Å³.

SUPPORTING ELECTROLYTE	REDUCTION ^{*†} POTENTIAL (V _{Ag/Ag⁺})	OXIDATION [*] POTENTIAL (V _{Ag/Ag⁺})	RELATIVE SOLUBILITY (vs TEATFB)
TEAC	-2.00	+0.37	soluble
TEA-tos	-2.00	+1.20	v. soluble
TEATFB	-2.00	> +2.00	v. soluble
TEAP	-2.00	> +1.80	v. soluble
TEA-triflate	-2.00	> +1.60	v. soluble
TBATPB	-2.00	+0.30	slightly

* Potentials measured using Pt-disk electrode.

† Lowest potential attempted.

**TABLE 4-1: ACCESSIBLE POTENTIAL RANGE AND RELATIVE SOLUBILITY
OF SUPPORTING ELECTROLYTES IN ACETONITRILE**

The polymerization of *p*-terphenyl was then performed with each salt. The resulting polymerization current curves appear in Figure 4-12. The data show the opposite effect (i.e., the larger anion gave the larger polymerization current). The plausible explanation is that some of the radical cations, produced during the polymerization reaction, are undergoing side-reactions with the anions. Rousseau et al.²³ have suggested that BF_4^- can react with electrochemically generated cations and radical cations. They have seen porphyrin π dications, that were stable in the presence of ClO_4^- , react with BF_4^- . If this were the case, then there would be a lower polymerization current as a consequence of fewer intercalation sites. At this time, the differences in the polymerization currents are believed to result from side-reactions occurring between the radical cations and the anions of the supporting electrolyte.

After the polymerizations, CVs of the polymer films were taken in solutions containing the same supporting electrolyte from which they were grown. Representative CVs in each of the three salts are given in Figure 4-13. Obvious are the differences in the shape of both oxidation/reduction couples, their positions, and their intensities. These differences are most probably due to both the stability of the film towards the particular anion and any effect of anion size on the intercalation/de-intercalation process. Also note that the

FIGURE 4-12: COMPARISON OF POLYMERIZATION CURRENTS

The polymerization reaction was conducted for a period of 10 seconds with the Pt-disk at a potential of $+1.40 \text{ V}_{\text{Ag}/\text{Ag}^+}$. The solution was 0.1 M of the supporting electrolyte indicated and 2 mM p -terphenyl in acetonitrile.

FIGURE 4-13: CVs OF DIFFERENT POLYMER FILMS

Sweep rate is 1.0 V/sec with an E-range of 0.00 to +1.25V_{Ag/Ag+}. The CVs are taken in solutions containing the same supporting electrolyte as the polymerization solutions. The films were grown over a period of 10 sec.

perchlorate polymerization produced a conducting film. This contradicts observations made by others^{24,25} using similar methods of polymerization.

Stability of Poly- ρ -Phenylene Films

Another criterion of the chemical modifier is that it should possess chemical and electrochemical stability in aqueous solution and with respect to repeated potential excursions as well as mechanical stability. The simplest of these to test is the mechanical stability. A film of poly- ρ -phenylene was grown on the Pt-disk as per the procedure above. During the polymerization reaction, the electrode surface is masked by a bright blue-green haze. Upon reduction, this blue-green color disappears and the polymer film turns a bright gold. The thicker the film, the more brownish and dull it becomes. After rinsing with acetonitrile, the film was allowed to dry for about 30 minutes.

The mechanical stability was now examined by the "peel test" method of Wrighton et al.²⁶. A piece of clear adhesive tape (Scotch (3M) Brand 810 Magic Transparent Tape) is applied to the poly- ρ -phenylene film surface and smoothed to remove any air

bubbles; the tape is then peeled off the surface. Visual inspection of both the film surface and the tape did not reveal the removal of any of the polymer. CVs taken before and after the test showed very little change.

Next, the chemical and electrochemical stability of the polymer was examined. These tests were conducted in 0.05 M H_2SO_4 solution under repeated potential cycling (-0.24 to +1.25 V_{SCE}). The CVs in Figure 4-14 were taken before and after 15 hours of continuous potential cycling at a sweep rate of 1.0 V/sec. This corresponds to approximately 1.8×10^4 cycles. The increase in the size of the platinum CV (directly related to the quantity of exposed platinum) is due to dissolution of platinum from exposed areas and the subsequent deposition on or into the polymer film⁹ or the exposed platinum. Inspection of the electrode, after the treatment, presented a surface that no longer was gold, but now a gun-metal gray in color.

A comparison of CVs taken in acetonitrile solution (Figure 4-15) prior-to and following the cycling in sulfuric acid, show that there is a loss in electrochemical activity. This loss may be due to either irreversible electrochemical oxidation of the polymer molecules or interference from the platinum deposition. Suffice to say that the loss in poly- ρ -phenylenic activity is exceptionally small compared to the increase in effective platinum area. The stability of poly- ρ -phenylene is far more

FIGURE 4-14: CVs OF POLYMER COATED Pt-WIRE IN 0.05 M H_2SO_4 .

Sweep rate is 1.0 V/sec, E-range is -0.24 to +1.25 V_{SCE} .

(a) --- before cycling, (b) — after 15 hr of cycling. The polymer film was grown in acetonitrile solution of 2 mM ρ -terphenyl and 0.1 M TEATFB at +1.30 $\text{V}_{\text{Ag}/\text{Ag}^+}$ for 20 seconds.

FIGURE 4-15: CVs OF POLYMER COATED Pt-WIRE IN 0.1 M TEATFB

Sweep rate is 1.0 V/sec, E-range is 0.00 to +1.25 V_{Ag/Ag+}.

(a) --- before H₂SO₄ treatment, (b) — after treatment (cf: Figure 4-14). Polymer film is the same one as in Figure 4-14.

superior, in reference to potential excursions in dilute sulfuric acid, than poly-pyrrole (cf: Appendix).

Wettability of Poly- ρ -Phenylene Films

This last section pertains to the effect the polymer film has on the wettability of platinum surfaces. This is important, since we would like to have a chemically modified surface that mimics the hydrophobicity of the Canadian hydrogen isotope exchange catalyst of platinum impregnated Teflon (cf: Chapter 1). This was the reason for studying electrode modifiers in this research.

Contact angles formed between water (APD) and poly- ρ -phenylene were measured (Table 4-2) for films produced using TEATFB or TEAP supporting electrolyte and different polymerization times. The choice of supporting electrolyte has a definite effect on the wettability of the film. The films produced in TEATFB are increasingly hydrophobic as the thickness increases. The contact angle formed by water and the film grown over a period of 20 seconds (1 μ m thick) is the same as that formed with Teflon (112 degrees)¹⁰. The polymer film grown for 2

POLYMERIZATION TIME (seconds)	BF_4^-		ClO_4^-	
	FILM* THICKNESS (μm)	CONTACT ANGLE (degrees)	FILM* THICKNESS (μm)	CONTACT ANGLE (degrees)
0	—	57	—	57
2	0.13	80	0.11	77
4	0.21	89	0.18	54
6	0.28	100	0.24	52
8	0.36	102	0.28	50
10	0.41	107	0.33	48
20	0.65	112	—	—
30	0.91	114	—	—
40	1.33	117	—	—
50	1.68	115	—	—

* Film thickness was calculated using the experimentally determined coverage of 2.5×10^{14} units/cm² and the $n = 2.2$ value for the polymerization reaction in TEATFB.

TABLE 4-2: CONTACT ANGLE MEASUREMENTS ON POLY- ρ -PHENYLENE

seconds in TEAP gives a contact angle comparable to the 2 second film grown in TEATFB. The films grown for longer times are increasingly more hydrophilic. The interesting thing about this is that the thickness of the polymer films (grown with either electrolyte) are approximately the same for a particular polymerization time.

In the section headed "Nature of Poly- ρ -Phenylene CV Peaks", it was stated that the de-intercalation peak around +1.0 V (in TEATFB solution) increased in intensity as the film thickness increased. Inspection of the CVs (Figure 4-16), recorded for polymer films grown in TEAP for 2 and 10 seconds, reveals that this peak does not increase with film thickness. Actually, both reduction peaks decrease with an increase in thickness. What we believe is that during the polymerization reaction ClO_4^- is incorporated into the polymer as BF_4^- is. During the reduction of the film, after the preset polymerization time, these ClO_4^- anions, being somewhat more sluggish than the BF_4^- anions, become trapped in the film.

This explains the observation concerning the intensity of the peak at +1.0 V. The presence of ClO_4^- anions in the film would give it a greater ionic character. This "ionic" film would interact with the water in a fashion similar to the interaction of water with residual polishing abrasives on a platinum surface (cf: Chapter 3).

FIGURE 4-16: POLYMER CVs IN 0.1 M TEAP

The polymer films were grown in a solution of 0.1 M TEAP and 2 mM ρ -terphenyl at +1.40 V_{Ag/Ag+}. (a) --- polymer grown for 2 seconds, (b) — polymer grown for 10 seconds.

CONCLUSION

Reproducible poly- ρ -phenylene films have been grown successfully from ρ -terphenyl on both the platinum wire and disk electrodes in TEATFB, TEAP, and TEA-triflate supporting electrolyte solutions. These electrolytes give different polymerization current curves, the reason for which is not fully understood at this time. The polymerization reaction has been shown to proceed via the coupling of radical cations. The value of $\bar{n} \approx 2.2$ was determined for the polymerization reaction of ρ -terphenyl in TEATFB/acetonitrile solution. Poly- ρ -phenylene was found to possess mechanical stability as well as chemical and electrochemical stability in dilute sulfuric acid and prolonged exposure to potential excursion (-0.24 to $+1.25$ V_{SCE}).

The species responsible for the oxidation/reduction couples present in a poly- ρ -phenylene CV, were identified. The couple at $+0.55$ V_{Ag/Ag+} is not due to triphenylenic moieties as had been thought, but rather the polymer molecules ($\bar{n} \approx 1$). The process occurring at $+1.10$ V_{Ag/Ag+} was proven to be intercalation/deintercalation of the polymer film by anions from the supporting electrolyte. In the case of ClO₄⁻, this process was found not to be as reversible as that for BF₄⁻. The wettability of poly- ρ -phenylene was observed to be dependent on the choice of supporting electrolyte used for the polymerization solution.

Polymer films produced with TEATFB solution possessed a hydrophobicity comparable to that of Teflon.

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APPENDIX

Early in our studies, we decided to employ electrode modifiers that had already been examined to some extent, since we were new to this type of research (Electrochemical polymerizations). We chose to investigate poly-pyrrole (PP), poly-thiophene (PT), and poly-3-methylthiophene (PMT). Each of these, PP and PT in particular, have been well studied. However, very little was known about their stabilities in aqueous solution with regard to electrochemical oxidation/reduction and extensive potential cycling.

For these early studies, we used a "micro-platinum" electrode and the platinum wire electrode (cf: Chapter 2, Experimental). The micro-platinum electrode was fabricated from a platinum wire (0.1 mm dia., AESAR, Puratronic 99.9985%) sealed through a length of soft glass (ca. 6mm dia.) and connected electrically via mercury sealed in a glass tube extension. After every run the tip was ground and polished with alumina powder (0.5 μm) and deionized water. The surface was then electrochemically treated using the same procedure used for the platinum wire electrode (cf: Chapter 2, Experimental). The electrode area varies from one run to the next, but is on the

order of 1.5×10^{-4} cm². This will be referred to as the micro-electrode. For each run, the platinum wire was prepared in the manner presented in Chapter 2. The amount of surface area for the platinum wire electrode was approximately 0.1 cm².

Experiments in sulfuric acid solution were performed using the electrochemical set-up as per Chapter 2. Those in acetonitrile solution used the electrochemical set-up in Chapter 4, with the exception that the reference electrode was an SCE equipped with a vycor disk partition. The potentiostating and cyclic voltammetry scans were carried out with the IBM Instruments Model EC/225 Voltammetric Analyzer. Data was collected on a XY recorder (Houston Instruments, Model 200).

Poly-Pyrrole

Poly-pyrrole is one of the most studied electrode surface modifiers. However, only a handful of studies on its behavior in aqueous solution have been published. Pyrrole polymerization experiments were carried out by generally following Burgmayer's procedure.¹

The micro-electrode was placed in the electrochemical cell containing 0.01 M - 0.5 M pyrrole (Kodac, used as received) and 0.1 M tetraethylammonium tetrafluoroborate (TEATFB; 99+%, Alfa, used as received) in acetonitrile (HPLC Grade, Aldrich, used as

received). For the polymerization, the electrode was potentiostated at a value ranging from $+0.650 V_{SCE}$ to $+0.850 V_{SCE}$. The current density was on the order of 0.05 mA/cm^2 . It has been generally observed that relatively uniform PP films can be prepared using this procedure (as indicated by a sharp peak near $-0.15 V_{SCE}$ in acetonitrile solution²⁻⁴), and the polymerization process is easily controllable. The thickness of the PP film, thus prepared, ranges between $100 \text{ \AA}$ to $500 \text{ \AA}$.

Each film was then subjected to a few potential scans in $0.1 \text{ M TEATFB/acetonitrile}$ solution, followed by a few in $0.5 \text{ M H}_2\text{SO}_4$ solution, then again in the 0.1 M TEATFB . All scans were performed at a sweep rate of 100 mV/sec . The potential range in acetonitrile solution was $-0.800 V_{SCE}$ to $+0.450 V_{SCE}$. The range for the sulfuric acid solution was $-0.280 V_{SCE}$ to $+1.250 V_{SCE}$. It was observed that the PP films were readily hydrogenated when subjected to the $-0.280 V_{SCE}$ in the acid solution.

In aqueous solutions, the most extreme cathodic potentials to which PP films have been exposed are: (i) the Murray-Burgmayer ion-gate experiments⁵ where a very thick film was subjected to $-0.8 V_{SCE}$ and (ii) the Zinger-Miller timed anion release experiments⁶ in which a thick film, deposited on a glassy carbon electrode, was subjected to a short cathodic pulse of $-1.0 V_{SCE}$. All other studies in aqueous media have had $0.0 V_{SCE}$ as their lower limit. In the Murray-Burgmayer work, the substrate (gold grid) was completely covered by a $1 \text{ }\mu\text{m}$ thick film of PP (cf: 0.01

μm in ours), so there was little possibility of catalysis by the metal surface.

The hydrogenation of our PP films, which occurred with such extreme ease, is an indication of the presence of exposed platinum. Since this type of arrangement (polymer and exposed platinum) would be required to exist in the hydrogen isotope exchange catalyst, poly-pyrrole as a surface modifier is unsuitable for our purposes.

Poly-Thiophene and Poly-3-Methylthiophene

The electropolymerization of thiophene and 3-methylthiophene have been carried out on the platinum wire electrode. Wrighton's potential cycling technique⁷ has been used for the polymerization of these monomers. The polymerization solutions contained 0.05 M of monomer (both: 99+ %, Aldrich, used as received) and 0.1 M TEATFB in acetonitrile. The potential was cycled, for the polymerization, at a rate of 100 mV/sec between 0.000 V_{SCE} and +1.800 V_{SCE} for thiophene and between 0.000 V_{SCE} and +1.600 V_{SCE} for 3-methylthiophene.

Control of the potential to a level of 1 mV or better is necessary, because the minimum polymerization potentials for the thiophenes are evidently very sharply defined. Thus, in Figure A-1 which shows the current traces of successive potential cycles

FIGURE A-1: POLYMERIZATION POTENTIAL CYCLES FOR POLY-THIOPHENE

Polymerization from a solution of 0.01 M thiophene and 0.1 M TEATFB in acetonitrile by potential cycles. Sweep rate = 100 mV/sec, E-range = 0.000 to +1.800 V. (Numbers on the curves are the sequence numbers.)

for a PT polymerization, the current is seen to sharply increase every time the potential of +1.800 volt is approached. This polymerization technique apparently yields an unstable mixture of polymers of various chain lengths.

Figure A-2 presents three successive cyclic voltammograms of a 0.34 μm PT film taken in a 0.1 M TEATFB acetonitrile solution immediately following polymerization. The trend seen in Figure A-2 follows that reported by Diaz,⁸ from a relatively uniform distribution of short chains to a broader distribution containing longer chains (cf: References 3 and 4).

Poly-3-methylthiophene films, prepared by the potential cycling technique, also exhibit a similar tendency for polymer chain rearrangement during potential scanning in the 0.1 M TEATFB acetonitrile solution, again approaching published results.^{9,10}

Both PT and PMT are much more stable, with regard to hydrogenation and electrochemical oxidation in aqueous media, than PP. Of the two polythiophenes, PMT is more oxidation- and reduction-resistant than PT. This observation is in agreement with the results of Garnier and Tourillon.^{9,10} As a consequence of the findings for poly-pyrrole, poly-thiophene, and poly-3-methylthiophene it was decided that a more stable electrically conducting polymer was needed. Preliminary experiments using the monomer p-terphenyl resulted in what appears to be a much more

FIGURE A-2: CYCLIC VOLTAMMOGRAMS OF POLY-THIOPHENE

Solution is 0.1 M TEATFB in acetonitrile. Sweep rate = 100 mV/sec, E-range = -0.400 to 1.200 V. The polymer was grown as in Figure A-1.

stable polymer (i.e., poly-p-phenylene). Several experiments have been conducted on this electrode modifier, the results of which have been presented in Chapter 4 of this thesis.

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