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ELECTROCATALYSIS WITH PLATINUM AND MODIFIED CARBON ELECTRODES

The Ohio State University

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ELECTROCATALYSIS WITH PLATINUM AND
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DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Wen-Hong Kao, B.S.

* * * * *

The Ohio State University
1984

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Spherical Pt Micro-particles Dispersed in Polymeric Electrodes" J. Am.

Wen-Hong Kao and Theodore Kuwana "Electrochemical Oxidation of Arsenious

Major Field: Analytical Chemistry
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<tr>
<td>A</td>
<td>(a) electrode area; (b) ampere</td>
</tr>
<tr>
<td>A'</td>
<td>nucleation rate constant</td>
</tr>
<tr>
<td>Å</td>
<td>angstrom</td>
</tr>
<tr>
<td>a</td>
<td>the first term of the Tafel relationship</td>
</tr>
<tr>
<td>As</td>
<td>arsenic ad-atom</td>
</tr>
<tr>
<td>As(0)</td>
<td>elemental arsenic</td>
</tr>
<tr>
<td>As(III)</td>
<td>arsenious acid</td>
</tr>
<tr>
<td>As(V)</td>
<td>arsenic acid</td>
</tr>
<tr>
<td>b</td>
<td>slope of Tafel relationship</td>
</tr>
<tr>
<td>BE</td>
<td>binding energy</td>
</tr>
<tr>
<td>C_{As}</td>
<td>concentration of arsenious acid</td>
</tr>
<tr>
<td>C_{dl}</td>
<td>double layer capacitance</td>
</tr>
<tr>
<td>C_0</td>
<td>bulk concentration in mole/cm$^3$</td>
</tr>
<tr>
<td>C_{S}</td>
<td>surface concentration in mole/cm$^3$</td>
</tr>
<tr>
<td>compound I</td>
<td>$\alpha,\alpha,\beta,\beta$-tetra(o-N-methyl-4-carbonyl pyridinium phenyl) porphyrithio cobalt(II) tetraperoxalate</td>
</tr>
<tr>
<td>CoT(o-A)PP</td>
<td>cobalt tetra(o-amino)phenyl porphyrin</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry, cyclic voltammogram</td>
</tr>
<tr>
<td>D_{0}</td>
<td>diffusion coefficient in cm$^2$/s</td>
</tr>
<tr>
<td>DPSE</td>
<td>double potential-step electrolysis</td>
</tr>
<tr>
<td>E</td>
<td>potential</td>
</tr>
<tr>
<td>E_{0}</td>
<td>standard potential</td>
</tr>
<tr>
<td>E_{0'}, (a) formal potential; (b) average of redox peak potentials</td>
<td></td>
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<tr>
<td>E_{act}</td>
<td>activation potential for As(III) oxidation</td>
</tr>
<tr>
<td>E_{app}</td>
<td>applied potential</td>
</tr>
<tr>
<td>E_p</td>
<td>peak potential</td>
</tr>
<tr>
<td>\Delta E_p</td>
<td>$</td>
</tr>
<tr>
<td>E_{0.85p}</td>
<td>potential at which current = 85% of a peak</td>
</tr>
<tr>
<td>E_{pa}</td>
<td>anodic peak potential</td>
</tr>
<tr>
<td>E_{pc}</td>
<td>cathodic peak potential</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray analyzer</td>
</tr>
<tr>
<td>F</td>
<td>the faraday</td>
</tr>
<tr>
<td>f</td>
<td>rotating frequency of a RDE</td>
</tr>
<tr>
<td>FeTMPyP</td>
<td>iron tetramethylpyridylporphyrin</td>
</tr>
<tr>
<td>FeT(o-A)PP</td>
<td>iron tetra(o-amino)phenyl porphyrin</td>
</tr>
<tr>
<td>FeT(2-Py)P</td>
<td>iron tetra(2-pyridyl)porphyrin</td>
</tr>
<tr>
<td>GC</td>
<td>glassy carbon</td>
</tr>
<tr>
<td>HMDE</td>
<td>hanging mercury drop electrode</td>
</tr>
<tr>
<td>Hz</td>
<td>frequency unit, herz</td>
</tr>
<tr>
<td>I_0</td>
<td>exchange current density</td>
</tr>
<tr>
<td>i</td>
<td>current</td>
</tr>
<tr>
<td>i_{inst}</td>
<td>growth current for instantaneous nucleation</td>
</tr>
<tr>
<td>i_k</td>
<td>kinetic current</td>
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\( i_t \) Levich limiting current
\( i_p \) peak current
\( i_{pa} \) anodic peak current
\( i_{pc} \) cathodic peak current
\( i_{pro} \) growth current for progressive nucleation
\( \text{Im}(Z) \) imaginary part of complex impedance
\( j \) current density
\( k \) rate constant
\( M \) (a) molarity; (b) molar mass
\( N \) number of nuclei formed
\( n \) electrons per mole of species oxidized or reduced
\( N_0 \) total number of nucleation sites
\( \text{NHE} \) normal hydrogen electrode
\( \text{PAA} \) polyacrylic acid
\( \text{PB} \) Prussian Blue
\( \text{PMMA} \) polymethyl methacrylate
\( \text{PS} \) polystyrene
\( \text{PVAA} \) polyvinyl acetic acid
\( \text{PVS} \) polyvinyl sulfonate
\( Q \) (a) total charge passed for controlled potential oxidation of As(III); (b) charge required for monolayer coverage of PtOH
\( Q_{\text{As}} \) charge due to the dissolution of arsenic ad-atoms
\( Q_H \) charge required for monolayer coverage of hydrogen on platinum
\( Q_{\text{H}}' \) charge due to hydrogen desorption in the presence of As(V)
\( Q_{\text{ox}} \) charge due to the formation of platinum oxides
\( Q_T \) total anodic charge under CV of Pt background in the presence of As(V)
\( R \) gas constant
\( R_{ct} \) charge transfer resistance
\( R_s \) solution resistance
\( R_{\text{DDE}} \) rotating disk electrode
\( \text{rds} \) rate-determining-step
\( \text{Re}(Z) \) real part of complex impedance
\( \text{rpm} \) revolution per minute
\( \text{SAM} \) scanning Auger electron microprobe
\( \text{sat'd} \) saturated
\( \text{SEM} \) scanning electron microscopy
\( \text{SPSE} \) single potential-step electrolysis
\( T \) temperature
\( t \) time
\( t_d \) open-circuit time for As(III) oxidation at a oxide covered platinum electrode
\( t_o \) induction time for progressive nucleation
\( V \) volt
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<th>Definition</th>
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<tr>
<td>$\nu$</td>
<td>scan rate</td>
</tr>
<tr>
<td>VAA</td>
<td>vinyl acetic acid monomer</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>$Z$</td>
<td>(a) Waburg impedance; (b) total impedance</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>transfer coefficient</td>
</tr>
<tr>
<td>$t_c$</td>
<td>thickness of diffusion layer over a RDE</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>extinction coefficient</td>
</tr>
<tr>
<td>$\eta$</td>
<td>overpotential</td>
</tr>
<tr>
<td>$\theta_0$</td>
<td>surface coverage of PtO</td>
</tr>
<tr>
<td>$\theta_{\text{OH}}$</td>
<td>surface coverage of PtOH</td>
</tr>
<tr>
<td>$k$</td>
<td>rate constant</td>
</tr>
<tr>
<td>$\nu$</td>
<td>kinematic viscosity</td>
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<tr>
<td>$\rho$</td>
<td>density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>surface energy</td>
</tr>
<tr>
<td>$\omega$</td>
<td>(a) angular velocity of a RDE; (b) frequency</td>
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CHAPTER I

INTRODUCTION

Activation of an electrode has been crucial to the performance of the electrode. The definition of activation can be, in a thermodynamic term, a small or zero overpotential, or in a kinetic term, a fast charge transfer rate. There are several methods known to be able to activate an electrode [1,2]. These include (a) electrochemically pretreating the electrode surfaces, (b) adsorption of catalysts or mediators on an electrode, (c) covalent linkage of catalysts or mediators via surface functional groups of an electrode, and (d) polymeric modification. Two other methods have been recently discovered [3-6] to effectively activate a glassy carbon electrode. They are (a) dispersion of metal oxide particles on carbon surfaces by polishing, and (b) electrochemical dispersion of spherical metal micro particles on a glassy carbon electrode with or without a coating of polymer. All the activation methods described above involve changes of surface functionalities or introduction of catalytic or mediating species.

Platinum and carbon, in the form of graphite or glassy carbon, are two materials widely used as an electrode substrate for chemical modification. Due to their surface properties, the modification applied on platinum and carbon electrodes can be different. In this work,
several activation methods for platinum and glassy carbon electrodes are applied for electrocatalysis of various chemical systems. The systems studied include (a) oxidation of arsenious acid at a platinum electrode, (b) oxygen reduction at a glassy carbon electrode adsorbed with a metalloporphyrin, covalently bound metalloporphyrin, or polymeric glassy carbon electrode with dispersion of platinum micro particles, and (c) the redox of several transition-metal complexes at polymeric electrodes.

An active platinum electrode is usually short-lived [7]. The deactivation can be the results of oxide formation on platinum surfaces or adsorption of poison such as sulfur, arsenic and organics. This deactivation is particularly pronounced for electrochemical oxidation of arsenious acid [denoted as As(III)] at a platinum electrode. There are several reports published in the literature [8-11] describing the deactivation of a platinum electrode for As(III) oxidation. There appears to be general agreement that the deactivation is the result of the formation of high valent forms of platinum oxide. However, regarding the activation mechanism for As(III) oxidation at platinum, there exists an unresolved controversy about the role of surface oxides [8-14]. This is probably due to unidentified chemical states of the oxides and the mechanism to activate or deactivate a platinum electrode. Furthermore, the formation of arsenic ad-atoms during the oxidation of As(III) [14-16] may have effects on the activation/deactivation of a platinum electrode. A kinetic study is thus conducted to determine the effect of the arsenic ad-atom and the formation of platinum oxides on the As(III) oxidation. The results are incorporated into Chapter II and III for discussions.

Platinum is also known the best electrode material available today
for oxygen reduction. However, due to the cost of platinum and the rare natural resources, there is a tendency recently to use carbon electrodes modified with oxygen catalysts or to use highly dispersed platinum particles in electrode substrates as a cathode in an energy conversion/storage system like a fuel cell. Carbon is chosen simply due to its many surface functional groups [17-19] which can be used to link catalysts.

Many catalysts applied on carbon for $O_2$ reduction are metal macrocyclic compounds such as metallophthalocyanine (MPc) and metallo-porphyrin (MPy) due to their resemblance to the natural oxygen carrier, such as cytochrome C and heme, in biological systems. The methods currently practical for immobilization of these catalysts on carbon include (a) strong adsorption, (b) covalent linkage, and (c) incorporation into a polymeric matrix.

Modified surfaces by adsorption, the simplest modification method, usually do not last as long as covalently modified ones. However, interesting results have been obtained for $O_2$ reduction from this type of modification. For example, Anson adsorbed Fe(II)-tetraphenyl porphyrin [20] on carbon electrodes and found catalytic reduction of $O_2$ to water. Zagal and co-workers [21] modified a basal plane of pyrolytic graphite with adsorbed Cobalt(II) tetrasulphonatephthalocyanine complexes, which reduced $O_2$ in the solution via a first order reaction to $H_2O_2$. Other adsorbates on carbon, include Cobalt tetrapyridyl porphyrins [22] and the "face-to-face" dicobalt porphyrins [23], are reported in the literature. The strength of the adsorption increased usually with an increased size or aromatic characteristics of the modifier. Metal complexes or other mediators which do not adsorb can
also be anchored via a bonding with large aromatic compounds [24,25].

Recently, a cobalt porphyrin with four side chains attached at the meso positions of the porphyrin ring which are asymmetric to the ring plan has been synthesized. These four side chains are speculated to hinder the adsorption of the porphyrin ring due to the stereo effect. However, a strong adsorption of this compound on carbon which catalyze \text{O}_2 \text{ reduction to H}_2\text{O}_2 \text{ has been observed. The results are described in Chapter IV.}

Generally, the covalent linkage method, which needs a functionalyzed surface or a linking compound to react with the catalyst or the redox mediator, involves a complex synthetic procedure. Silanization, first demonstrated by Murray and co-workers [1], is a well-known example of covalent linkage modification. However, an attempt to bind FePy's to silanized SnO\textsubscript{2} using an amidization procedure has been unsuccessful [26]. Another well-known linking agent is cyanuric chloride reported by Kuwana and co-workers [27,28]. These linkers are bonded via the surface hydroxyls. It is also possible to bind the mediators directly to the oxidized [29] and reduced [30] carbon surfaces. Murray [31] has also demonstrated mechanical abrasion of the electrode in an olefinic compound under nitrogen atmosphere to produce an oxide-free glassy carbon surface that is covalently modified by the olefinic compound.

Lennox and Murray [32] reported that the surface carboxylic acid group generated by heating or chemical oxidation could be used to bond porphyrins covalently via an amidization process. Elliott et al. [33] and Rocklin et al. [34] also had success in immobilizing iron and cobalt (o-aminophenyl)porphyrins on pyrolytic graphite and glassy carbon electrodes via the covalent amide bond. Evans and Kuwana [29] created
surface carboxylic acid functional groups on carbon electrode by radio-frequency oxygen-plasma treatment, while Fujihira et al. [35] used air oxidation techniques for the same purposes. On the other hand, Oyama and Anson [30] used radio-frequency argon-plasma treatments to reduce the surface oxides on graphite, thereby allowing amines to anchor themselves to the surfaces. Generally, all of these covalently bonded porphyrins catalyzed oxygen reduction. However, for some reasons, the bonded iron porphyrins showed less stability than the cobalt equivalents. Some of the bonded iron porphyrins lost their activity even after one potential cycle.

Bettelheim and co-workers [36] have successfully immobilized iron porphyrins via covalent amide or ester bonds on polymethacryl chloride coated glassy carbon electrodes. These modified electrodes catalyze the reduction of oxygen in aqueous solutions via an ec mechanism. Other examples of polymeric modification can be found in the literature.

In an attempt of exploring new catalytic polymeric electrodes, a thin polyvinyl acetic acid film has recently been formed on a glassy carbon (PVAA/GC) electrode by refluxing in neat VAA monomer [5]. With iron and cobalt porphyrins bonded on this polymeric electrode via amide bonds, catalytic oxygen reduction has been observed. The other polymer studied in this lab for the same purposes has been the Gulf PA-18 which is spread on carbon surfaces by dip and spin coating methods. The detail of these polymeric modifications and the application of these polymeric electrodes in electrocatalytic reduction of oxygen will also be described in Chapter IV.

Polymers can be used to modify almost any electrode material because of their non-specific adsorption. Besides modifying an
electrode, polymers have been known for a long time the support of metal complexes and metal colloid catalysts [37]. Polyacrylonitrile and polyvinylalcohol [38] have been used as supports for easily reducible metals such as platinum and palladium. Ion exchange resins, in both cationic and anionic exchangeable form, have also been used as supports for platinum group metals [39]. These polymers, however, usually possess reaction sites, coordination sites, ion exchange sites or certain functional groups to interact with or ion exchange the metal or metal complexes. Recently, Pickup and co-workers [40] have electrochemically deposited metal particles or metal films onto poly-[Ru(bpy)$_2$ 4-vinylpyridine$_2$]$^{2+}$ coated platinum electrodes. Again, they have claimed that the ion exchange sites are necessary for the formation of metal particles.

In contrast to the above argument, spherical platinum microparticles had been successfully formed and dispersed in the PVAA/GC electrode by electrochemical methods in this lab before the publication of Pickup's work [40]. Other metals like Pd, Ag, Ni, Cd and metal composites were also able to be dispersed by following the similar procedures [6]. These metal particles dispersed polymeric electrodes possessed catalytic abilities for reactions such as oxygen reduction, As(III) oxidation, etc. Interesting results regarding the charge transfer through the film were also obtained. Details of this research will be given in Chapter V and VI.

Since the inception of the chemically modified electrodes in the mid-seventies, many researches of applying CME's for electrocatalysis have contributed to the current level of technology. However, further understanding of CME's, exploration of new CME's, improvement of the
current technology level, all demand more contribution from the research groups. This is still a challenging field for inputs of new ideas and researches. This gives rise to the motivation of this research.
CHAPTER II

ELECTROCHEMICAL OXIDATION OF ARSENIOUS ACID
AT PLATINUM ELECTRODES

Arsenic compounds have been known insecticides since the fifteenth century [41]. Natural occurring arsenic has two stable forms, as trivalent arsenic, As(III), in the arsenites and as pentavalent arsenic, As(V), in the arsenates. The arsenites, which dominates the arsenic resource, are in general more toxic than the corresponding arsenates and more dangerous and destructive to foliage [42]. Thus, the demand for a method to oxidize arsenites to the less toxic arsenates has appeared since early 1920's.

An electrolytic process was first developed in 1924 by Lloyd and Kennedy [42-44] for producing calcium arsenate from arsenic trioxide in caustic soda solutions using sheet iron electrodes. Several industrial processes were developed later for oxidizing As(III) to As(V) in basic solutions using porous graphite electrodes [45,46].

The first study of electrochemical oxidation of As(III) at a platinum electrode in an acidic electrolytic bath was reported by MacNevin [8a] in 1949. There are now several basic studies of this oxidation at noble metal electrodes published in the literature [8b,9,11-14]. Generally, this oxidation was reported to be
electrochemically irreversible at Pt [8-14] and Au [11,14] electrodes in strongly acidic or basic solutions. However, a controversy regarding the role of surface oxides and a possible arsenic intermediate in this oxidation has remained unresolved.

MacNevin found that the As(III) oxidative current at a platinum electrode was highly dependent on the pretreatment of the electrode [8] and that the current efficiency was a function of the solution pH. At pH less than 3 or greater than 11, a current efficiency of 100% was attained. At intermediate pH values, the current efficiency versus pH followed a volcano curve and reached the minimum value of 22% at ca. pH 7. When the platinum electrode was precathodized at -4.0 V vs SCE [8b] in a sulfuric acid solution of low pH's, the As(III) oxidative current, at an applied potential of +1.2 V, was initially high and then decayed as a function of electrolysis time. However, if the platinum electrode was preanodized at +4.0 V, the initial oxidative current was only one-tenth of that at the precathodized one and remained constant during the electrolysis. Macnevin claimed therefore that the surface oxides formed at positive potentials retarded the As(III) oxidation.

Zahkarov and Songina [9] studied As(III) oxidation in 1 M sulfuric acid using a rotating Pt wire electrode. They found that iodide ion prevented the formation of platinum oxide and that As(III) oxidation was not observed at potentials more negative than ca. +1.4 V, the potential necessary to oxidize adsorbed iodide. If the adsorbed iodide ion was removed by mercury ion, the electrode was reactivated. The conclusion was that surface oxygen promoted As(III) oxidation as follow:
Catherino [12] studied As(III) oxidation in 1 M perchloric acid by analyzing the Tafel slope of the oxidative i-E profile. He observed two Tafel slopes, and proposed, assuming a consecutive one-electron transfer model, that an As(IV) intermediate was involved:

\[ \text{As}(\text{III}) \rightarrow \text{As}(\text{IV}) + e^- \]  
\[ \text{As}(\text{IV}) \rightarrow \text{As}(\text{V}) + e^- \]

It is interesting to note that none of the above studies has reported the existence of arsenic ad-atoms on the platinum electrode. Loucka [14], and Motoo [15] have reported that arsenic ad-atoms are formed in the potential region of +0.6 to +0.2 V vs SCE when As(V), the product of the As(III) oxidation, is in the solution. The ad-atoms are also reported to change the i-E profile of surface oxide formation on a platinum electrode.

The objective of the present work is to clarify the role of surface oxides and arsenic ad-atoms and the relationship of these two factors to the mechanism of As(III) oxidation. The oxidation of As(III) was studied at Pt as a function of applied potential, time and arsenic concentration by cyclic voltammetry and chronocoulometry. The presence of arsenic ad-atoms on Pt and the relationship of these ad-atoms to platinum oxide formation were established by X-ray photoelectron spectroscopy.
EXPERIMENTAL

A Pt electrode from BAS (Bioanalytical Systems, Inc., West Lafayette, IN) with a geometric area of 0.02 cm$^2$ was polished with 0.25 um diamond compound (METADI, Buehler Co., Chicago, IL), washed in hot 60% perchloric acid, rinsed thoroughly with double distilled water and stored in 1 M sulfuric acid. Before transferring to a test solution, the electrode was pretreated in 1 M $\text{H}_2\text{SO}_4$ by cycling the potential repetitively between -0.2 and +1.5 V vs. a reference Ag/AgCl (sat'd KCl) electrode at a scan rate of 500 mV/s until a reproducible current-potential (i-E) profile (trace A, Fig. 3) was obtained. The cycling was terminated in the double layer region at ca. +0.40 V. An electrode prepared by such a treatment with a reproducible profile will, henceforth, be referred to as a "clean" electrode. A Pt foil electrode with a geometric area of 0.22 cm$^2$ was "cleaned" following the same procedure and was used in the XPS studies. This electrode was rinsed thoroughly with double distilled water and air dried prior to XPS analysis.

A PARC (Princeton Applied Research Corp., Princeton, NJ) Model 174 Polarographic Analyzer and a PARC 175 Universal Programmer or a BAS CV-1A potentiostat were employed for the electrochemical studies. An Omnigraphic 2000 X-Y (Houston Instrument Co., Austin, TX) or a Linear strip chart recorder (Linear Instrument Co., Irvine, CA) were used for data acquisition. A PHI (Physical Electronics Industries, Eden Prairie, MN) Model 548 XPS instrument with a sample introduction and a computer support system for surface analysis have been previously described [47]. Electrode potentials are reported with respect to a reference Ag/AgCl.
(sat'd KCl) electrode.

Ultrapure $\text{As}_2\text{O}_3$ (National Bureau of Standards or Alfa Co., Danvers, MA) and $\text{As}_2\text{O}_5$ (Alfa Co.) were used without further purification. A stock solution of arsenious acid was prepared by dissolving $\text{As}_2\text{O}_3$ in 0.5 M NaOH and acidifying to a final 1 M sulfuric acid solution. $\text{As(V)}$ stock solutions were prepared by dissolving $\text{As}_2\text{O}_5$ in 1 M $\text{H}_2\text{SO}_4$. The arsenic solutions in their respective oxidation states were stable during the experimental work without deaeration in accord with the literature [48]. Fresh doubly distilled water was used for the preparation of solutions and the cleaning of electrodes.

RESULTS AND DISCUSSION

A cyclic voltammogram of a clean Pt electrode in 1 M $\text{H}_2\text{SO}_4$ (dashed curve, Fig. 1) is comprised of three regions: I) the oxygen region in which Pt oxides are formed and reduced; II) the double layer region (between ca. 0.20 V and 0.60 V for the anodic scan and between 0.40 V and 0.20 V for the cathodic scan) in which no faradaic current is observed; and III) the hydrogen region in which the hydrogen adsorption-desorption occurs. This profile will be referred to as the "Pt background" wave henceforth.

Electrochemistry of $\text{As(III)}$ at Pt

The electrochemical oxidation of arsenious acid to arsenic acid has
been proposed to be a two-electron process with the transfer of an oxygen atom \([8,9,11,12,14]\) from water as follows:

\[
\text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^-
\] (4)

If the potential at a clean Pt electrode was scanned from +0.60 V to +1.30 V in 1 M sulfuric acid containing \(1.0 \times 10^{-2} \) M As(III), the CV i-E wave (curve A, Fig. 1) of the first scan exhibited a well-defined, reproducible wave with an anodic peak potential, \(E_{pa}\), at +0.90 V. The peak current, \(i_{pa}\), increased linearly with the square-root of the scan rate (Fig. 2A) and was directly proportional to the As(III) concentration in the range of \(5 \times 10^{-4}\) to \(2 \times 10^{-2}\) M (Fig. 2B). It was also found that the shape and position of the CV i-E wave recorded on the second scan in these solutions was dependent on the cathodic switching potential. When the switching potential of the cathodic scan (curve A', Fig. 1) was made less positive (B', C', D', E', Fig. 1), the \(E_{pa}\) of the second CV i-E wave shifted to more positive potentials and the \(i_{pa}\)'s increased correspondingly (B, C, D, E, Fig. 1). Repetitive cycling between +0.60 and +1.50 V in a stirred solution gave a reproducible CV i-E wave with current reaching a maximum at +1.00 V and then decreasing at higher potentials.

In Fig. 1 the peak potential of curve A represents an apparent overpotential of +0.54 V with respect to the thermodynamic redox potential of +0.36 V (\(E^0 = +0.56\) V vs. NHE) for the As(V)/As(III) couple [49]. If the cathodic portion of this cyclic voltammogram for As(III) oxidation (curve A', Fig. 1) was compared to the Pt background waves, it was found that the reduction wave of the Pt oxide layer was suppressed.
Figure 1.

Cyclic voltammograms of 0.01 M As(III) oxidation in 1.0 M sulfuric acid. Trace A is the first anodic scan from +0.60 to +1.30 V. Traces B - E are the anodic scans after the cathodic scans are reversed at potentials of +0.50, +0.40, +0.30 and +0.20 V. Dashed profile is the background. Scan rate: 0.050 V/s. Electrode area: 0.02 cm².
and a broad wave appeared in the double layer region. The addition of 1 M As(V) to these solutions did not affect the cyclic voltammograms for As(III) oxidation under any of the above conditions, and the reduction of As(V) to As(III) was not observed.

It is interesting to note that, if the diffusion coefficient of As(III) is calculated from the slopes of $i_p$ vs $u^{1/2}$ and $i_p$ vs $C_{As}$ curves (Fig. 2A and 2B), assuming the applicability of the Randles-Sevcik equation [50] and $n = 2$, values of $1.00 \pm 0.03 \times 10^{-5}$ cm$^2$/s and $0.92 \pm 0.03 \times 10^{-5}$ cm$^2$/s are found respectively. These values are in surprisingly good agreement with the literature value of $0.97 \times 10^{-5}$ cm$^2$/s [51] which is calculated from a titration curve of rotating ring disk voltammetry.

Electrochemistry of As(V) at Pt

Cyclic voltammograms at Pt in 1 M H$_2$SO$_4$ containing varying concentrations of As(V) (traces B, C, D, Fig. 3) were compared to the Pt background (trace A, Fig. 3). As the As(V) concentration was increased, the current in the double layer region increased, the shape of the oxide formation profile changed and the hydrogen adsorption-desorption fine structure [52-55] diminished while the oxide reduction wave in the oxygen region was least affected. For As(V) concentrations greater than ca. $5 \times 10^{-3}$ M the $i$-$E$ profile remained unchanged. The current in the double layer region has been attributed to the formation and dissolution of arsenic ad-atoms [14,15]. This also explains the waves in the double layer region obtained in As(III) solutions (Fig. 1).
Figure 2.
Linear plots of the peak current for As(III) oxidation versus (A) the square root of scan rate, (B) bulk concentration of As(III).
Figure 3.
Cyclic voltammograms for Pt surface oxidation and reduction in 1.0 M sulfuric acid containing A. 0, B. 0.05 mM, C. 0.10 mM, D. 5.00 mM arsenic acid at a sweep rate of 0.050 V/s. Electrode area: 0.02 cm$^2$. 

The effect of the anodic switching potential on the cyclic voltammogram of $1 \times 10^{-2}$ M As(V) in 1 M $\text{H}_2\text{SO}_4$ at a clean Pt electrode is shown in Fig. 4. The ratio of the charge of the cathodic to the anodic waves in the double layer region was approximately unity, indicating that the dissolution of arsenic ad-atoms involved the direct oxidation of As(0) to As(V) and was complete at a potential of ca. +0.90 V. If the CV scan was stopped at ca. +0.90 V and the electrode was removed from the As(V) solution, washed with a stream of distilled water and then transferred to a 1 M $\text{H}_2\text{SO}_4$ solution, the CV i-E profile of the clean Pt background was observed. The absence of the broad i-E waves in the double layer region substantiated the premise that arsenic ad-atom dissolution was completed at ca. +0.90 V.

The oxide reduction wave at ca. +0.55 V did not appear until the anodic potential was scanned to a value more positive than +0.80 V. Apparently, the anodic peak at +0.90 V was due to the formation of surface oxides which occurred after dissolution of the ad-atoms. It should be noted that this peak potential for oxide formation coincided closely with the peak potential for As(III) oxidation (trace A, Fig. 1).

Since the anodic waves (Fig. 3) from ca. -0.15 V to +1.20 V are comprised of three regions, the anodic charge under the waves integrated from -0.15 V, $Q_T$, should be the sum of the charges due to, in sequence, hydrogen desorption in the hydrogen region ($Q_{\text{H}}$), arsenic ad-atom dissolution in the double layer region ($Q_{\text{As}}$) and formation of platinum oxides in the oxygen region ($Q_{\text{ox}}$). On a clean smooth Pt electrode, the charge which corresponds to a monolayer coverage of adsorbed hydrogen, $Q_{\text{H}}$, is constant and has been reported to be 210 $\mu\text{C/cm}^2$ [54]. This constant also represents the total number of active sites on Pt. If $Q_T$
Figure 4.
Cyclic voltammograms for the Pt background in 1.0 M sulfuric acid containing 0.01 M As(V). Anodic scan is reversed at various potentials. Scan rate: 0.050 V/s.
is normalized to $Q_H$ and plotted as a function of the potential at which the integration is terminated, the traces in Fig. 5 result.

Without As(V) in solution, hydrogen adsorption-desorption fine structure on Pt is well-defined (trace A, Fig. 3) and $Q_T/Q_H = Q'_H/Q_H = 1$ at potential of +0.20 V (boundary of hydrogen region) since $Q'_H$ is the only component of $Q_T$ (curve A, Fig. 5). This $Q_T/Q_H$ ratio is constant throughout the double layer region and becomes greater than 1 at potentials more positive than ca. +0.60 V due to the formation of oxides ($Q_T = Q'_H + Q_{ox}$, $Q_{As} = 0$). As the bulk As(V) concentration increases, this fine structure diminishes (trace B, C, D, Fig. 3) and $Q_T/Q_H$ at +0.20 V becomes smaller than 1 (curve B, C, D, Fig. 5). At the higher As(V) concentrations, $Q_T/Q_H = 0$ (curve D) indicating that the active sites for hydrogen adsorption are totally replaced by arsenic ad-atoms. This result agrees with a literature report [56] that arsenic blocks hydrogen adsorption. The dissolution of arsenic ad-atoms, $Q_{As}$, causes the $Q_T/Q_H$ ratio to increase in the double layer region (see Fig. 5).

If it is assumed that a) the total number of active sites is constant and not affected by the presence of arsenic; b) surface oxides are not formed in the double layer region (see Fig. 4); c) each arsenic ad-atom is in its elemental state and occupies 2.5 active sites of Pt; and, d) the formation-dissolution of ad-atoms is a five electron process [14,15], i.e.

$$\text{As}^0_{ads} \leftrightarrow \text{As(V)} + 5e^- \quad (5)$$

then the charge for dissolution of a monolayer of ad-atoms will be $Q_{As} = (5/2.5) \times (Q_H - Q'_H)$ or $Q_T = Q_{As} + Q'_H = 2Q_H - Q'_H$. Thus, the potential
Figure 5.
Plots of electrochemical charge where the i-E profiles in Fig. 3 have been integrated from -0.15 V to the potentials of the X-axis.
at which \((Q_T + Q_H^+)/Q_H = 2\) corresponds to the complete dissolution of ad-atoms. From Fig. 5, it is noted that this potential shifts to more positive values as the As(V) concentration increases. At high As(V) concentration \((Q_H = 0)\), this potential is equal to +0.86 V. The potential of +0.86 V falls on the rising portion of the background wave for oxide formation (trace D, Fig. 3). However, the current for oxide formation at this potential is small, implying that dissolution of ad-atoms is essentially completed at a more positive potential and that oxide formation proceeds after the dissolution of the ad-atoms. This is in accord with the above discussions.

Mechanistic Considerations

Considering the \(Q_T/Q_H\) charge ratio, the cyclic voltammograms of Pt in As(V) solutions, and the As(V) concentration dependence of ad-atom formation, it appears that formation of ad-atoms is limited to a monolayer coverage and that platinum oxide does not form until the dissolution of ad-atoms is completed. As has been described, the onset potential for surface oxide formation shifts anodically from ca. +0.60 to +0.86 V (curve A, D, Fig. 5) as the As(V) concentration increases. This indicates that arsenic ad-atoms inhibit the oxide formation. Also, since the cyclic voltammogram for As(III) oxidation maximizes at +0.90 V on clean Pt, the oxidation is not catalyzed by arsenic ad-atoms although the electrocatalysis by arsenic ad-atoms has been reported in some other systems [15].

In the oxygen region (trace D, Fig. 3), \(Q_{ox}/Q_H = 2\) or \(Q_T/Q_H = 4\) at
+1.20 V (Fig. 5) which indicates the formation of a PtO monolayer. At potentials more positive than +1.20 V, $Q_{T}/Q_{H}$ becomes greater than 4 which could indicate a possible phase transition from PtO to the higher oxides, e.g. $PtO_{x,x>1}$. However, the actual potentials for the onset of such oxide formation and phase transition have not been identified.

For As(III) oxidation at glassy carbon (GC) and lead dioxide ($PbO_2$), catalytic oxidation of As(III) was not observed before the onset of oxygen evolution at ca. +1.40 V. It has been reported that active oxides are not formed on GC [17-19] or on $PbO_2$ [57] at potentials less positive than +1.40 V. Thus, it appears that the formation of active oxides such as the lower valent, PtOH and PtO [54,55] initiates and catalyzes As(III) oxidation by transferring oxygen to arsenious acid according to the following ec mechanism:

\[
\begin{align*}
Pt + H_2O & \rightarrow PtOH + H^+ + e^- \quad (6) \\
PtOH & \rightarrow PtO + H^+ + e^- \quad (7) \\
PtOH + H_3AsO_3 & \rightarrow Pt + H_3AsO_4 + H^+ + e^- \quad (8) \\
PtO + H_3AsO_3 & \rightarrow Pt + H_3AsO_4 \quad (9)
\end{align*}
\]

If the potential was stepped from +0.60 V to +1.20 V at a clean Pt electrode in 1 M $H_2SO_4$ containing As(III) concentrations of $5 \times 10^{-3}$ to $2 \times 10^{-2}$ M, the charge for As(III) oxidation increased linearly with the square root of time (Fig. 6), and the slopes were proportional to the As(III) concentration. The extrapolation of the linear plots to $t = 0$ gave a common intercept value of ca. 250 $\mu$C/cm$^2$ (corrected for double layer charging). This value was close to the charge required for the formation of PtOH/PtO [55]. The anodic charge of the Pt background at
+1.20 V has a value greater than 600 \( \mu \text{C/cm}^2 \). These results support the assumption that the Pt oxide as PtO\(_2\) or PtO catalyzed the oxidation of As(III), i.e. competitive reactions of the surface oxide formation and the removal of oxide by As(III). Also, the slope of a logarithmic plot of the anodic peak current versus the As(III) concentration is 0.97, indicating that the oxidation is first order in As(III).

The agreement of the As(III) diffusion coefficient calculated from Fig. 2 using the Randles-Sevcik (R-S) equation and the coefficient reported in the literature has been noted above. It has also been mentioned that oxidation of As(III) occurred on clean Pt with an overpotential of 0.54 V which indicates this process is highly irreversible. This apparent contradiction can be resolved if all the steps in the above mechanism are fast. The R-S equation is derived for a single reversible, diffusion controlled electron transfer process. However, if the e steps are reversible (eqn. 6, 7) and the c steps are diffusion controlled (eqn. 8, 9), the overall reaction will essentially conform to the restrictions of the R-S equation. The formation of the higher oxides leading to an electrode deactivation therefore takes place at potentials more positive than \( E_{pa} \).

When a Pt electrode was preanodized at +2.00 V in 1 M \( \text{H}_2\text{SO}_4 \) for at least 60 seconds to form a thick PtO\(_2\) film [52-55] and transferred to a test solution of As(III), the CV scan initiated at +0.60 V gave a broad As(III) oxidation wave with a decreased current level as compared to that at a clean Pt. When such an oxide covered electrode is open-circuited for varying periods of time, \( t_d \), in the As(III) solution prior to the anodic scan, the cyclic voltammograms in Figure 7 resulted. As \( t_d \) increased, the \( E_{pa} \) shifted to slightly more positive potentials, \( i_{pa} \).
Figure 6.
Linear $Q$ vs $t^{1/2}$ plot for single potential step coulometry of As(III) oxidation in 1.0 M sulfuric acid containing A. 0.02 M, B. 0.01 M, C. 0.005 M As(III). $E_{\text{app}} = 1.20$ V, electrode area: 0.22 cm$^2$. 
increased and the process appeared more reversible (sharper peak). When \( t_d \) was greater than ca. 35 minutes, the position and the shape of the CV waves (trace D, Fig. 7) were similar to those obtained at a clean Pt electrode (trace E, Fig. 7). These results are in agreement with the report that As(III) slowly reduces the surface Pt "oxides" [58]. The reaction for this Pt oxide removal is:

\[
\text{PtO}_x + \text{H}_3\text{AsO}_3 \xrightarrow{\text{slow}} \text{PtO}_{x-1} + \text{H}_3\text{AsO}_4, \quad x > 1 \quad (10)
\]

The removal of oxides by As(III) (reaction 8, 9, 10) also explains the absence of the oxide reduction peak at +0.55 V (Fig. 1).

It was stated earlier that the oxidation of As(III) under stirred conditions exhibited a current decay at potentials greater than ca. +1.00 V. This deactivation can be attributed to the formation of the higher oxides of Pt at these potentials. In the presence of these higher oxides, the mechanism must include reaction (10) which would result in a decrease in the rate of As(III) oxidation, and thus, a decrease in the observed current. The dependence of the peak current in the cyclic voltammograms for As(III) oxidation (Fig. 1) on the cathodic switching potential, discussed above, are also the result of this deactivation mechanism. At potentials less positive than +0.60 V the higher oxides are electrochemically reduced, thus, reactivating the electrode.
Figure 7.

Linear sweep voltammograms of 0.020 M As(III) oxidation on a pre-anodized Pt electrode at a sweep rate of 0.050 V/s. Before each scan, the electrode was open-circuited and immersed in the As(III) solution for A. 1.5 min., B. 10 min., C. 20 min., D. 35 min. after the anodization of Pt electrode in 1.0 M sulfuric acid. Trace E is the voltammogram for As(III) oxidation on an oxide free Pt electrode.
Surface Analysis

The results of the XPS analysis of a Pt electrode after a variety of pretreatments are summarized in Table 1. An electrode removed from a solution of $1 \times 10^{-2}$ M As(V) in 1 M H$_2$SO$_4$ while potentiostated at +0.70 V exhibited Pt 4f electron binding energies (BE) characteristic of Pt(0) which indicated that no surface oxides were present (sample a). An electrode removed from a solution of $1 \times 10^{-2}$ M As(III) in 1 M H$_2$SO$_4$ also exhibited Pt 4f BE of Pt(0) (sample b). If the potential was scanned from +0.60 V to +1.10 V to deactivate a Pt electrode in a solution of 0.01 M As(III) in 1 M H$_2$SO$_4$, the Pt 4f BE peak shifted toward higher BE (sample c), indicating the presence of Pt oxides. The shifts were less than the value reported for oxide formation under similar anodization conditions, in the absence of As(III) [59]. This may be due to the competitive reduction of surface oxides by As(III) (reaction 9 and 10). An electrode removed from an As(V) solution at a potential where arsenic ad-atoms were supposedly formed gave an As signal (BE of 43 eV) [60]. This peak appeared as satellite of the Pt 5p peak (BE of ca. 50 eV). No conclusions were drawn concerning the oxidation states of the arsenic ad-atoms or the coverage. The XPS data confirmed the previous electrochemical results which indicated that it is the formation of Pt oxides on the surface, at potentials greater than +1.0 V, which deactivates the electrode. The activity can be restored by reducing the oxides either chemically with As(III) or electrochemically.
Table 1. Binding Energies of 4f electrons of Pt Electrode under Different As(III) Oxidation Conditions.

<table>
<thead>
<tr>
<th>sample</th>
<th>Pt 4f7/2 (eV)</th>
<th>Pt 4f5/2 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>70.9</td>
<td>74.1</td>
</tr>
<tr>
<td>b</td>
<td>70.7</td>
<td>73.9</td>
</tr>
<tr>
<td>c</td>
<td>72.6</td>
<td>75.8</td>
</tr>
<tr>
<td>Pt***</td>
<td>70.7</td>
<td>74.0</td>
</tr>
<tr>
<td>PtO***</td>
<td>73.3</td>
<td>76.6</td>
</tr>
</tbody>
</table>

* See text for reaction conditions.
** Data are reported with respect to C1s as 284.0 eV.
*** Data taken from reference 59.
The Effect of Reactivation Pulse on the Oxidative Charge

Several experiments have been designed to monitor the effect of varying As(III) concentration, oxidation potential, and pulse length at a reactivation potential on the oxidative charge of As(III). Under the diffusion controlled conditions, reactivation of the anode does not increase the oxidative charge since the charge is limited by the mass flow. However, if the potential applied is in the current rising region or if the solution is stirred, such that the rate of oxidation is controlled by the heterogeneous process, the effect of reactivation is significant. The results are summarized in Table 2. The reactivation potential, +0.20 V, is chosen to avoid the disturbance of side reactions like hydrogen evolution or possible reduction of arsenious(-ic) acid at lower potentials.

The potential was initially stepped from +0.60 V to +1.20 V for 10 seconds and the oxidative charge was recorded. Then, the potential was stepped to +0.20 V for a period of time, noted as the reactivation time in Table 2, followed by an anodic step to the applied potential, the $E_{\text{app}}$ in Table 2, for 10 seconds and the oxidative charge was recorded again. The difference between the two measured charges are listed in Table 2 as the net oxidative charge.

As seen in Table 2, the net oxidative charge reached a maximum value when the reactivation pulse length was greater than 0.1 second. For a reactivation pulse shorter than 0.1 second, the net oxidative charge increases linearly with increasing reactivation pulse length and appears to be a first order dependency on time. This can be explained if the rate of electrochemical reduction of surface oxide is first order.
Table 2. Effect of Pulse Length on Net Oxidative Charge

<table>
<thead>
<tr>
<th>C_A$ = 0.01$ M</th>
<th>( E_{\text{app}} = 0.9 ) V for 10 sec.</th>
<th>( E_{\text{act}} = 0.2 ) V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution: static</td>
<td></td>
<td>charge passed, ( Q^* ) (mcoul/cm²)</td>
</tr>
<tr>
<td>activation time (msec.)</td>
<td></td>
<td>(mcoul/cm²)</td>
</tr>
<tr>
<td>0</td>
<td>2.424</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3.030</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>4.242</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>5.758</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>6.136</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C_A$ = 0.004$ M</th>
<th>( E_{\text{app}} = 1.2 ) V for 10 sec.</th>
<th>( E_{\text{act}} = 0.2 ) V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution: stirred</td>
<td></td>
<td>net oxidative charge, ( Q^* ) (mcoul/cm²)</td>
</tr>
<tr>
<td>activation time (msec.)</td>
<td></td>
<td>(mcoul/cm²)</td>
</tr>
<tr>
<td>0</td>
<td>4.074</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5.135</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>9.428</td>
<td></td>
</tr>
</tbody>
</table>

* See text for the definition of \( Q \).
in time, the available active surface area due to oxide reduction is thus first order in time and so is the net oxidative charge. For reactivation pulses longer than 0.1 second, for which all the oxides are probably reduced, the rate of generation of active surface area diminishes and thus the net oxidotive charge reaches the maximum and becomes independent of reactivation time.

These results can be practical in an industrial process of As(III) oxidation since one can avoid the deactivation of the platinum anode by simply applying a reactivation potential, e.g. +0.20 V, as a short pulse, e.g. 0.1 second, compare to the anodic oxidative period, e.g. 10 seconds. The kinetic measurements to determine the rate constants for this oxidation and to test further the proposed mechanism using rotating disk voltammetry are described in Chapter III.

CONCLUSIONS

The results indicate that the lower Pt oxides, presumably PtOH and PtO, initiate and catalyze the oxidation of arsenious acid. The rates of reactions (6) - (9) at a clean Pt electrode are sufficiently fast that the cyclic voltammetric peak exhibits properties similar to a reversible, diffusion controlled process. This accounts for the agreement between the calculated diffusion coefficient from the experimental CV data and the value reported in the literature.

Deactivation of the Pt electrode toward As(III) oxidation occurs at potentials more positive than ca. +1.00 V. The deactivation is attributed to the formation of the higher oxides of Pt, i.e. PtO$_x$, $x>1$,
which is supported by the XPS data. This deactivation is the result of the slow reaction of As(III) with the higher oxides of Pt via reaction (10). Activity is restored by the removal of this oxide, via either an electrochemical or a chemical reduction. There is no evidence that the arsenic ad-atoms catalyze the oxidation of As(III). The ad-atoms do inhibit the formation of Pt surface oxides.

It appears that by applying a reactivation pulse at a low potential, at which surface oxides are reduced, after a period of anodic electrolysis, one can avoid the deactivation of the anode and increase the rate of As(III) oxidation.
CHAPTER III

KINETIC STUDIES OF THE ELECTROCATALYTIC OXIDATION
OF ARSENIOUS ACID AT A PLATINUM
ROTATING DISK ELECTRODE

In the previous chapter, an ec mechanism, which included a low valent platinum oxide formation and a chemical reaction between the oxide and As (III), was proposed for the electrocatalytic oxidation of arsenious acid at a platinum electrode in 1 M $\text{H}_2\text{SO}_4$. It was also proposed that higher valent forms of platinum oxides were responsible for the deactivation of As (III) oxidation when the potential was scanned to higher anodic values. As indicated by the previous results, the e and c steps were proposed to be fast at potentials less positive than 1.00 V (vs Ag/AgCl). It was difficult to measure the reaction rates of these steps by application of conventional voltammetry using stationary planar electrodes. However, one could attempt to resolve the potential dependent rate of oxide formation (e step) and to further test the proposed mechanism by applying rotating disk voltammetry.

Since the development of the theory by Levich in 1942 [61], rotating disk voltammetry has developed into a powerful technique for kinetic studies of electrochemical processes. By rotating a disk electrode in a solution, the pattern of hydrodynamic flow to the disk is
defined and the steady state of the solution transport is calculable. According to the theoretical calculations by Levich, a diffusion layer is developed with a constant thickness over the entire rotating disk surface, i.e.

\[ \delta_c = 1.62D^{2/3} \nu^{1/6} \omega^{-1/2} \]  

(11)

Where \( \omega \) is the angular velocity of the rotating disk, \( \nu \) the kinematic viscosity of the solution and \( D \) the diffusion coefficient of the redox substrates. For a simple redox process, the current contributed by the diffusing substrates is therefore

\[ i = nFAD(C_0 - C_s)/\delta_c \]

or

\[ i = 0.62nFAD^{1/3} \nu^{-1/6} \omega^{1/2}(C_0 - C_s) \]  

(12)

where \( C_0 \) and \( C_s \) represent the bulk and surface concentration respectively. When \( C_s \) equals zero, the current reaches a limiting value.

If the charge transfer process is coupled with a homogeneous or heterogeneous chemical reaction, the current function of equation (12) will be affected by the kinetics of the chemical reaction. There are several reports regarding the evaluations of current functions for various ec or ce mechanisms, with or without adsorption of reactants/products, published in the literature [62-74]. However, a satisfactory evaluation concerning the unique system involving both surface activation and deactivation, and a chemical reaction at the
electrode/solution interface, such as As(III) oxidation at Pt, has not been found.

The proposed mechanism for As(III) oxidation at Pt is

\[ \text{Pt} + \text{H}_2\text{O} \xrightarrow{k_{13}} \text{PtOH} + \text{H}^+ + e^- \quad E_{13}^{\circ} \]  

(13)

\[ \text{PtOH} + \text{As(III)} \xrightarrow{k_{14}} \text{Pt} + \text{As(V)} + \text{H}^+ + e^- \]  

(14)

\[ \text{PtOH} \xrightarrow{k_{15}} \text{PtO} + \text{H}^+ + e^- \quad E_{15}^{\circ} \]  

(15)

\[ \text{PtO} + \text{As(III)} \xrightarrow{k_{16}} \text{Pt} + \text{As(V)} \]  

(16)

\[ \text{PtO} + \text{H}_2\text{O} \xrightarrow{k_{17}} \text{PtO}_x + 2(x-1)\text{H}^+ + 2(x-1)e^- \quad E_{17}^{\circ} \]  

(17)

\[ \text{PtO}_x + \text{As(III)} \xrightarrow{k_{18}} \text{PtO}_{x-1} + \text{As(V)} \]  

(18)

The redox potentials \( E_{13}^{\circ}, E_{15}^{\circ}, \) and \( E_{17}^{\circ} \) for reactions 13, 15, and 17 have been reported to be ca. 0.74, 0.90, and 1.00 V vs Ag/AgCl respectively [54,75,76]. Reactions 14, 16, and 18 are proposed to be potential independent. The PtOH formation step has been proposed to be a reversible process when the surface coverage of the oxide, \( \theta_{\text{OH}} \), is small (e.g. < 0.2) [54,75,77] and As(III) is absent. In the presence of As(III), however, in the potential region where the rate of PtO formation is small (ca. 0.70 to 0.85 V) [54,76] the overall reaction can be considered an ee type with consecutive one-electron catalytic reactions (reaction 13 and 14) where the catalyst (PtOH) is adsorbed on the electrode surface. With a sufficiently fast mass transport, the overall reaction rate should be controlled by the charge transfer process (reaction 13) and the surface coverage of PtOH will thus be small. At small PtOH coverage, the changes of surface energy due to PtOH formation can be neglected and a Langmuir type isotherm can be applied. The reaction parameters can thus be determined from the Tafel
relationship \((E = a + b \ln i)\). The theoretical \(b\) value for a simple reversible process is \(59.1/a_n\) mV where \(a\) is the transfer coefficient and \(n\) the number of electron involved in the charge transfer process. However, this value will vary with potential if the rate-determining-step (rds) in the mechanism depends on the applied potential. The variation of the Tafel slope with the various type of rds of a mechanism has been discussed by Bockris [78].

In the potential region where the rate of PtO formation is sufficiently fast (e.g. 0.85 to 1.00 V), the oxidation can be considered as an overall two-electron ec catalytic reaction with catalyst adsorption. The current density observed will be the combination of both the e and the c steps [69]:

\[
j = Qv(d\theta_0/dE) + 2F(d[As(V)]/dt) \quad (19)
\]

where \(Q\) is the charge required for a monolayer coverage of PtO and \(v\) the scan rate. The second term of the equation (19) has a diffusion limited value predicted by equation (12) with \(C_6 = 0\).

Equation (19) is valid when a pseudo-equilibrium of surface oxide coverage is established. Under this assumption, the rds will be the c step, reaction (16). At low rotation rates, the second term of equation (19) should have the form of equation (12) for a diffusion-controlled process. At high rotation rates, on the other hand, the overall reaction rate of this system will be governed by the kinetics of the rds. When the c step is the rds, equation (19) can be rewritten as:

\[
j = Qv(d\theta_0/dE) + 2Fk_1\theta_0C_{As} \quad (20)
\]
where $C_{\text{As}}$ represents the bulk concentration of As(III) and $\theta_0$ the equilibrium coverage of PtO which is a function of potential. At slow scan rates, the first term of equation (19) and (20) are negligible. In this case, the current (the second term) will be a linear function of the square-root of the rotation rate in the low rotation rate region. The rate constant $k_{16}$ can be determined from the Koutecky-Levich equation:

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_t} \quad (21)
\]

where $i_k$ has the form of the second term of the equation (20) and $i_t$ is given by equation (12) with $C_a = 0$. When $\omega$ becomes very large, $1/i_t$ approaches zero and the kinetic current can be observed.

In the present work, the above proposed mechanism for As(III) oxidation is tested by comparing the theoretical with the experimental results. The effects of various factors including the scan rate, the rotation rate of the electrode, and the bulk concentration of As(III) to the current function is discussed. The rate constants for some elementary steps are estimated. No attempt is made to evaluate the rate of deactivation of the electrode via reaction (17) and (18) due to the insufficient knowledge of the electrochemistry of higher oxide formation on platinum and the subsequent chemical reactions with As(III) at potentials greater than 1.00 V.
EXPERIMENTAL

A platinum rotating disk electrode (RDE) (Pine Instrument Company, Grove City, PA) with a geometric area of 0.48 cm$^2$ was used. This electrode was polished and cleaned according to the procedure described in chapter II. A Pine RDE 3 dual potentiostat (Pine Instrument Company) or an in-house built potentiostat were used for potential control. An Omnipraphic 2000 X-Y/Y-t recorder (Houston Instrument Co., Irvine, CA) was used for data acquisition. The chemicals used and the procedures for preparation of stock solutions were the same as those described in chapter II. Potentials are referred to a Ag/AgCl(sat'd KCl) reference electrode.

RESULTS AND DISCUSSION

Cyclic voltammetry (CV) and chronoamperometry were applied to monitor As(III) oxidation at the platinum RDE. Figure 8 shows typical reproducible voltammograms of As(III) oxidation at a clean Pt RDE in 1 M H$_2$SO$_4$. Trace A is the CV of As(III) oxidation at a static Pt disk electrode. When the electrode is rotated at various rates (Traces B - M), the oxidative current begins to rise at ca. 0.70 V in an anodic scan initiated at 0.20 V. The anodic current reaches a maximum value in the potential region of 0.85 to 0.98 V. Then, instead of remaining constant at the limiting value as predicted by equation (12), the current decays as the potential is scanned to more positive values. The position of the "peak" in the voltammograms is dependent on the rotation rate. This
Cyclic voltammograms of As(III) oxidation at a Pt RDE. Solution contains $5 \times 10^{-3}$ M As(III)/1 M $\text{H}_2\text{SO}_4$, scan rate: 10 mV/s.
indicates that the process is not solely limited by mass transport of As(III) in the bulk solution to the RDE. An apparent explanation for this current decay is that it is due to the result of electrode deactivation.

When the potential is switched and scanned cathodically from 1.40 V (traces B' - M', Figure 8), the current potential profile, instead of retracing the anodic profile, decreases rapidly in the potential region of ca. 1.40 to 1.20 V. The profile becomes, more or less, an oxidative plateau in the potential region of 1.20 to 1.00 V. The cathodic profile then crosses the anodic profile at ca. 0.80 V before merging the cathodic reduction wave at ca. 0.50 V (Figure 8) which is due to the reduction of surface oxides and the formation of arsenic ad-atoms [14,15,75]. The magnitude of the current in the potential region of 0.90 to 1.40 V (traces B - M) in the anodic direction of scan is linearly dependent on bulk As(III) concentration, scan rate and the square-root of the rotation rate indicating a first order reaction with respect to As(III) and the involvement of a surface reaction. A similar reaction order with respect to As(III) has been reported in the literature [11,75]. For a cathodic scan in the same potential region, no linear relationship between the current and $C_{\text{As}}$ or $\nu^{1/2}$ is observed which is probably the result of a change in the reaction mechanism. In the anodic region of ca. 0.70 to 0.85 V, the current is nearly independent of $\nu$ and $C_{\text{As}}$ when bulk As(III) concentration is greater than ca. 5 x $10^{-3}$ M. This indicates that in this potential region the oxidation is probably the zero order in As(III) when the concentration is high. The current in the cathodic region of < 0.50 V is independent of $C_{\text{As}}$ and $\omega$ but is linearly dependent on $\nu$ revealing a surface
Lown and Johnson [10] observed similar "peak" shaped voltammograms for As(III) oxidation at a Pt RDE in 0.5 N HClO₄. They argued that the "peak" shaped anodic wave along with a plateau (see traces B' - M' in Figure 8 for example) for As(III) oxidation at a Pt RDE was diagnostic evidence for partial kinetic control of the electrode reaction by a step not involving electron transfer. The slow kinetic process was then proposed to be either diffusion (tunneling) of As(III) through the oxide film to reach a position near the platinum surface for electron transfer or cylindrical diffusion of As(III), within the hydrodynamic layer, to a small number of widely dispersed active sites which were caused by a non-uniform coverage of impermeable oxide film. Their argument, however, neglected the reactivity of the oxide toward As(III) which was reported in the literature [58,75] and was discussed in chapter II. Furthermore, the rapid current decrease at the initial cathodic reversal (Figure 8) essentially excluded the possibility of in-film diffusion and cylindrical diffusion of As(III) to active Pt sites since those diffusional processes were not affected under rotating disk conditions by the potential reversal when the growth of the oxide film was essentially terminated [76]. An alternative explanation was that formation of higher oxide and the slower reaction rate between As(III) and the high oxide caused the current decrease during the anodic scan. After the potential reversal at ca. 1.40 V, the growth of the oxide layer was probably terminated but the chemical reaction between As(III) and the oxide was still taking place. The turnover of the higher oxide continued and a new steady state was established. Since the rate of electrochemical reduction of oxide in this potential region was small,
the oxidative current observed, therefore, was the static current required to sustain the equilibrium coverage of the oxide. This accounted for the plateau current in the potential region of ca. 1.20 to 1.00 V (traces B' - M', Figure 8). In the potential region of 0.80 to 0.60 V (traces B' - M', Figure 8), the rate of electrochemical reduction of oxide was increased and the turnover rate of oxide by As(III) was correspondingly decreased. This caused the rising of cathodic current and the hysteresis. This model could also fulfill the diagnostic criteria applied by Lown and Johnson [10].

It has been mentioned that the current in the potential region of 0.70 to 0.85 V is zero order with respect to As(III) at high As(III) concentration. The logarithm of the anodic current at the "foot" of an anodic voltammogram is plotted as a function of potential (Tafel plot). The result is shown in Figure 9. The slopes of the Tafel plots at various concentration levels of As(III) are approximately the same. The b value, evaluated from the Tafel slopes is 75.9 ± 3.1 mV. This b value corresponds to an \( a_n \) value of 0.78 ± 0.04 which is in agreement with a literature value of 0.75 ± 0.04 for As(III) oxidation at Pt in sulfuric acid [13]. The b value is greater than that predicted for a simple one-electron transfer process. However, it is close to 1.5(2.3RT/F) which is characteristic of a two consecutive one-electron charge transfer process [68,78] with the first step, the rate determining step, involving surface adsorption. Thus, the Tafel slopes appear consistent with the proposed reaction (13) and (14) for As(III) oxidation in this potential region.

Catherino [12] observed two discrete slopes of about two-to-one ratio in a Tafel plot for As(III) oxidation at Pt in perchloric acid.
Figure 9.
Tafel plot for As(III) oxidation at a Pt RDE. $C_{\text{As}}$: A. $1 \times 10^{-2}$, B. $5 \times 10^{-3}$, C. $1 \times 10^{-3}$ M.
He attributed the different slopes to a consecutive one-electron oxidation involving an intermediate As(IV). However, Bockris [78] claimed, based on a theoretical calculation, that two discrete linear Tafel slopes could be due to a change of the rds with potential in a consecutive one-electron transfer mechanism. Since only one Tafel slope was observed in this experiment, it was reasonable to assume that the rde did not change from these reactions described by (13) to (14) with changes of potential in the region of 0.70 to 0.85 V.

If reaction (13) is the rds, it is reasonable to assume that \( \theta_{\text{OH}} \) is small in this potential region and a Langmuir type isotherm for PtOH formation can be applied. In other words, assuming \( k_{13} \) to be independent of \( \theta_{\text{OH}} \), one can attempt to evaluate \( k_{13} \) from the intercept of a Tafel plot at \( E_{13}^{\circ} \). However, it is noted that the intercepts from Figure 9 are a function of \( C_{\text{As}} \). This can be explained that when \( C_{\text{As}} \) is small, rate 14 is small since it is first order in As(III). Under such circumstance, \( \theta_{\text{OH}} \) may increase and reduce rate 13 since rate 13 is proportional to \( (1 - \theta_{\text{OH}}) \). By extrapolating a plot of intercept versus \( C_{\text{As}} \) or \( 1/C_{\text{As}} \) to \( C_{\text{As}} \to \infty \) or \( 1/C_{\text{As}} \to 0 \), the limiting intercept is obtained which is related to \( k_{13} \) according to the following equation:

\[
\text{intercept}(C_{\text{As}} \to \infty) = \log(2Q_{\text{OH}}A\theta_{\text{OH}}k_{13}) \tag{22}
\]

where \( Q_{\text{OH}} \) is the charge required for a monolayer coverage of PtOH, i.e. 210 \( \mu \text{C/cm}^2 \). The limiting intercept is estimated to be \( 1.15 \times 10^{-4} \) \( \text{A} \) which corresponds to a \( k_{13} \) value of ca. 0.57 \( \text{s}^{-1} \). The evaluation of \( k_{14} \) is difficult since rate 15 may become competitive and change the rds in the mechanism when rate 14 is small. For the same reason, there is no
attempt to analyze the current in the potential region of 0.80 to 0.90 V where rate 13 is fast and the rds of the oxidation may vary with the potential.

The oxidative current at potentials more positive than 0.90 V is found to be scan rate dependent. If the current at a given potential is plotted versus the scan rate, a linear relationship is obtained. Typical i/v plots are shown in Figure 10. It is interesting that when the intercepts of these i/v plots at the current axis are plotted versus the square-root of rotation rate, a linear relationship with a Levich slope in the low rotation rate region (e.g. f < 1500 rpm) is observed (Figure 11, 12). In these two figures, the dashed lines are the theoretical Levich slopes calculated using equation (12) assuming \( D_0 = 0.97 \times 10^{-5} \text{ cm}^2/\text{s} \) and \( \nu = 0.01 \text{ cm}^2/\text{s} \). The plot, however, gradually deviates toward a limiting value at high rotation rates. This is due to the change of the rds from a diffusion process to a kinetic process. This deviation is more pronounced at lower potentials (e.g. 0.90 V, see Figure 11). Such a case, when the current is nearly independent of \( \omega^{1/2} \), is indicative of the zero order process and a possibility that reaction (15) becomes the rds. The rotation rate at which the i vs \( \omega^{1/2} \) plot begins to deviate from the theoretical Levich slope is dependent on the potential (Figure 11) and the bulk As(III) concentration (Figure 12). This observation appears to be consistent with the diagnostic criteria for an ec surface catalytic mechanism [69] with a current density predicted by equation (19) and (20). At low rotation rates and low As(III) concentrations, the reaction is diffusion controlled and the Levich equation applies. At high rotation rates or high As(III) concentrations, when the mass transfer is not the limiting step, the system
Figure 10.
Linear plot of the current at 0.92 V, taken from the cyclic voltammograms, versus scan rate. $C_A$: $5 \times 10^{-3}$ M. The rotation rates applied are denoted in the same way as those indicated in Figure 8.
Figure 11.
Levich plot for As(III) oxidation. $C_{As} = 1 \times 10^{-2}$ M. The current at various potentials are recorded.
Figure 12.

Levich plot for As(III) oxidation at 0.98 V for various \( C_{As} \): A. \( 1 \times 10^{-2} \), B. \( 5 \times 10^{-3} \), C. \( 1 \times 10^{-3} \) M.
becomes kinetic controlled by either reaction (16) for which equation (20) applies or by reaction (15) at potentials close to 0.90 V.

Under the kinetic control conditions, the rds should be reaction (16) at potentials between ca. 0.92 V and 1.00 V. The current contributed by this step (the current passed is presumably necessary to maintain the equilibrium coverage of PtO which is reduced by As(III)) is thus qualified for the kinetic current in equation (11). Koutecky-Levich Plots for As(III) oxidation are shown in Figure 13 and the kinetic current, $i_k$'s are determined. The $i_k$ plotted as a function of potential (Figure 14) exhibits a maximum in the potential region of 0.98 to 1.05 V. The peak potential is dependent on As(III) concentration (traces A, B). The results are consistent with the proposed mechanism. When the high valent oxides form, the rds of the ec mechanism gradually shifts from reaction (16) to the slower reaction (18) which causes the decrease of the $i_k$. For low As(III) concentration, $i_k$ is nearly independent of potential in the region of 0.90 to 1.20 V (trace C, Figure 14). This indicates that the growth of the oxide layer is probably due to the slow rate of the oxide reduction by As(III). A similar plateau observed in the anodic CV with low As(III) concentration supports the above argument. The maximum $i_k$ at a potential more positive than 1.00 V is observed when the bulk As(III) concentration is high (e.g. 10 mM). This is probably due to the faster reaction rate between As(III) and the higher oxide when $C_{As}$ is high for which rate of reaction (17) might be comparable to rate of reaction (18). Not until higher overpotential is applied, should the reaction (18) become the rds.

If it is assumed that (a) the rds of As(III) oxidation is reaction
Figure 13.

Koutecky-Levich plot for As(III) oxidation. $C_{As} = 1 \times 10^{-2}$ M.
Figure 14.

Kinetic current evaluated from the Koutecky-Levich plots as a function of potential. $C_{As}: A. 1 \times 10^{-2}$, B. $5 \times 10^{-3}$, C. $1 \times 10^{-3}$ M.
(16) in the potential region of 0.90 to 1.00 V, (b) pseudo-equilibrium of the Langmuir type surface oxide coverage is established, and (c) there is no adsorption or no effect due to the adsorption of As(III) in this potential region, $k_{16}$ normalized to As(III) concentration can be estimated by applying equation (11) when the coverage of oxide, $\theta_0$ in this potential region is evaluated assuming $\sigma = 0.5$. The results are summarized in Table 3. The average of $k_{16}$ is estimated to be $(5.23 \pm 1.59) \times 10^{-5} \text{ M}^{-1} \text{s}^{-1}$.

It appears that the rds of the As(III) oxidation at Pt changes from reaction (13) stepwise to each of the subsequent reaction when the potential is increased from 0.70 V to more positive values. However, the results as shown in Figure 14 and the linear relationship between the current and the square-root of the rotation rate suggests that the largest turnover rate can be achieved in the potential region of 0.92 to 1.05 V, depending on the bulk As(III) concentration. It may also be possible to find a potential at which the oxidation of As(III) would proceed without electrode deactivation. Potential step experiments were thus conducted in which the potential was stepped from an initial value of 0.2 V to various final values. The rotation rate of the RDE was also varied. Typical data are summarized in Figure 15. It was found that the current reached a steady-state value when the final potential was less than ca. 0.80 V. The current level is of course, larger as the potential is increased. However, the deactivation becomes apparent at potentials greater than 1.00 V as indicated by the larger rate of current decay. Slow deactivation is also evident even though the applied potential is less positive than $E^{0\prime}_{17}$ to avoid the possible formation of higher oxides. So, it becomes a trade-off between a larger
Table 3. List of estimated $\theta_0$ and $k_{16}$ at various potentials.

<table>
<thead>
<tr>
<th>$E(V)$</th>
<th>$\theta_0$</th>
<th>$C_{As} = 1$ mM</th>
<th>5 mM</th>
<th>10 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.50</td>
<td>5.76</td>
<td>4.95</td>
<td>2.74</td>
</tr>
<tr>
<td>0.92</td>
<td>0.69</td>
<td>5.25</td>
<td>5.25</td>
<td>3.68</td>
</tr>
<tr>
<td>0.98</td>
<td>0.96</td>
<td>4.51</td>
<td>10.00*</td>
<td>7.60</td>
</tr>
<tr>
<td>1.00</td>
<td>0.98</td>
<td>4.55</td>
<td>10.05*</td>
<td>7.97</td>
</tr>
</tbody>
</table>

Average of $k_{16}$ is $(5.23 \pm 1.59) \times 10^{-5}$ M$^{-1}s^{-1}$ when the two values marked with *'s are not counted.
Current-time profile of constant potential oxidation of As(III) at various applied potentials.
$C_{As} = 5 \times 10^{-5}$ M, rotation rate: 400 rpm.
turnover rate versus deactivation as a function of the applied potential.

Lown and Johnson have suggested application of 1.00 V [10] for the quantitative electrochemical analysis of As(III) species in acidic aqueous solutions using a platinum electrode. This potential appears consistent with the result described above for the maximum turnover rate. However, when the deactivation trade-off is considered, the optimal potential for preparative oxidation of As(III) in sulfuric acid appears to be between 0.85 and 0.92 V. This optimum may vary depending on solution conditions such as As(III)/(V) concentration and acidity. The slow deactivation process seems to be unavoidable irrespective of the applied potential. Although speculative, this deactivation may be associated with a surface phase transition of "active" platinum oxide transforming to a more stable crystalline form [54]. A short reduction pulse at a potential of ca. 0.20 V restores the electrode activity [75].

CONCLUSION

The RDE results are consistent with the earlier postulated mechanism that suggested the involvement of platinum oxides in the catalytic oxidation of As(III) as well as in the deactivation. The maximum turnover rate for As(III) is attained in the potential region of 0.92 to 1.00 V vs. a reference Ag/AgCl electrode. As a trade-off between catalysis and deactivation, the optimal potential for As(III) oxidation at a Pt electrode appears to be in the potential range of 0.85
to 0.92 V. Slow deactivation seems to be unavoidable irrespective of the applied potential for controlled-potential oxidation of As(III). A short reduction pulse at a potential of ca. 0.20 V applied periodically during a constant potential electrolysis seems sufficient to maintain the electrode activity. $k_{13}$ and $k_{16}$ estimated from the experimental results are $0.57 \text{ s}^{-1}$ and $(5.23 \pm 1.59) \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$, respectively.
OXYGEN REDUCTION CATALYZED BY ADSORBED
AND POLYMER BOUND PORPHYRINS

Reduction of molecular oxygen has been a great concern in the advanced technology of energy conversion/storage systems like fuel cells [55,79-82]. The major problem encountered is the slow reductive rate and the overpotential for \( O_2 \) reduction to water at most electrode materials. The large overpotential often facilitates the production, via an alternate mechanism, of the unwanted product, \( H_2O_2 \) [55,79-82], which, by degrading the activity of the system or the catalysts, reduces the output power of the cell. The reduction is due to a change from a four electron to a two electron reduction process.

Thermodynamically, molecular oxygen undergoes a four electron reduction to water at a potential of 1.03 V (vs Ag/AgCl) and a two electron reduction to \( H_2O_2 \) at 0.48 V [83]. However, with the best available oxygen electrode, Pt, oxygen reduction to water occurs at a potential of ca. 0.70 V in strongly acidic solutions, which represents an apparent overpotential of 0.33 V with respect to the thermodynamic redox potential. The overpotential is caused by the slow reduction of the stable platinum oxides [69]. Other remarkable catalysts for oxygen reduction are the metal macro-cyclic compounds such as metallophthalato-
cyanine and metalloporphyrins which resemble the active sites of the oxygen carriers in biological systems [84].

Jasinski [85] was among the first to apply metallomacrocyclic compounds for electrochemical reduction of oxygen. He adsorbed cobalt phthalocyanine on carbon and nickel structures which reduce oxygen to \( \text{H}_2\text{O}_2 \) at 80 °C with an output voltage of 0.6 V and current density of 100 mA/cm². Iron phthalocyanine adsorbed on a pyrolytic graphite electrode was reported to catalyze reduction of oxygen to water [86,87] while the adsorbed cobalt(II) tetrasulphonatephthalocyanine catalyzed the reduction to \( \text{H}_2\text{O} \) [21]. However, the iron cyclic compound coated electrode lost activity after only one cyclic voltammetric scan in acidic solutions. Van Veen [88] reported that the stability of the metal phthalocyanine electrodes could be improved by heat treating the coated electrodes at a temperature above 300 °C under an inert atmosphere due to, as proposed, a bond formation between the macrocycles and the carbon electrodes.

The electrocatalytic reduction of oxygen by iron porphyrins was first introduced in 1930's by Brdicka and co-workers [89]. In their subsequent works [90] and that by Brezina [91], reduction of \( \text{O}_2 \) and \( \text{H}_2\text{O}_2 \) was promoted by iron hemes which were adsorbed at the electrode surfaces. Similar results were obtained by Swafford and Kolpin [92] who claimed that oxygen underwent a four electron reduction process at a rate of \( 6 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \) with a polarographic half wave potential of -0.12 V vs SCE at an iron heme adsorbed hanging mercury drop electrode (HMDE). Swafford also reported that \( \text{H}_2\text{O}_2 \) was catalytically reduced at a rate of \( 1 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \) with a reduction potential of -0.37 V vs SCE. The rate determining step was proposed to be the formation of a ferrous heme-
hydrogen peroxide complex.

Other porphyrins which have been reported as adsorbed catalysts for oxygen reduction include iron(II) tetraphenyl porphyrin [20], cobalt tetraphenyl porphyrin [22], and the "face-to-face" dicobalt porphyrins [23]. Generally, iron complexes catalyze oxygen reduction to water and cobalt analogs except the "face-to-face"porphyrins catalyze oxygen reduction to the $\text{H}_2\text{O}_2$ intermediate. However, all of the adsorbed catalysts lose their activity after a few turnovers. The loss of activity may be caused by desorption, demetallization and/or oxidation of the porphyrin ring. It was found that a critical step in the oxidation of the metalloporphyrin ring was the formation of a u-peroxo dimer [93]. By introducing sterically bulky groups into the porphyrin molecules, such as the picket-fence cobalt porphyrins [94], one could prevent the oxidation of the porphyrin ring. Another approach to possibly improve the electrode stability was to incorporate porphyrins into polymeric matrices. The application of the porphyrin incorporated polymer for oxygen reduction has been reviewed in chapter I. The kinetics is similar to that of adsorbed porphyrins.

Kuwana and co-workers explored the use of water soluble porphyrins such as tetrakis(4-N-methylpyridyl) porphine iron or cobalt [95,96] for homogeneous catalytic reduction of oxygen in aqueous solutions. The solubility of the porphyrins facilitated the mechanistic studies for oxygen reduction, which would be difficult for adsorbed catalysts due to the irreproducible surfaces of modified electrodes and the unknown states of the catalyst on the surfaces. The catalytic capabilities of these dissolved catalysts were similar to the adsorbed analogs. From the experimental data, it was proposed that the catalysis followed an ec
mechanism:

\[
M^{III/II}\text{Py} + e^- \rightarrow M^{II/II}\text{Py} \quad (23)
\]

\[
nM^{II/II}\text{Py} + O_2 + nH^+ \rightarrow nM^{III/II}\text{Py} + H_2O_2(H_2O) \quad n=2(4) \quad (24)
\]

in which the oxygen reduction potential was determined by the reduction potential of the catalysts, e.g. -0.05 V for FeTMPyP and +0.22 V for CoTMPyP in strongly acidic solutions.

It is noted that the overpotential for an EC catalytic reduction of oxygen is governed by the catalyst. A desirable catalyst would have a redox potential close to the thermodynamic redox potential of the O_2/H_2O couple. A possible trade-off to low overpotential is the slow reaction rate between the reduced catalyst and oxygen since the driving force of such a reaction is determined by the difference in chemical potentials of the reactants. A macrocyclic with a redox potential close to that of the O_2/H_2O couple may be relatively ineffective as a catalyst. In addition, the question of how to maintain the activity for long periods of time is of concern.

In this chapter, a study of the electrocatalytic capabilities and stability of two polymer bonded porphyrins and of an adsorbed side-chained porphyrin (compound I, see next page) for oxygen reduction is presented. By applying polymers and the side-chain, one can expect improvement in the stability because of the possibility that desorption and oxidation of the catalysts can be reduced.
EXPERIMENTAL

α,α,β,β-Tetra(o-N-methyl-4-carbonyl pyridinium phenyl) porphyrioto cobalt(II) tetrapерchlorate, to be denoted as compound I (see below for the structure), was received as a gift from Dr. C. M. Elliott. Test solutions were prepared by dissolving compound I directly into triply distilled water. The supporting electrolyte was 1 M KCl. The working electrode from Bioanalytical System, Inc. (BAS) was a Kel-F sheathed glassy carbon electrode with a geometric area of 0.062 cm². Glassy carbon (GC) electrodes, as GC-10, GC-20 or GC-30 from Tokai Carbon Co. (Tokyo, Japan), or as V-19, V-25 from Atomergic Chemetals Corp. (New York, N. Y.) were also used for the electrochemistry and the surface analysis. A platinum wire was used as the auxiliary electrode. Potentials were referenced to a Ag/AgCl (sat'd KCl) reference electrode. The facilities used for electrochemistry and surface analysis are described in Chapter II. All chemicals were used as received.
Pretreatment of GC Electrodes

The GC electrodes were first pretreated by polishing with 1.0, 0.3 and 0.05 μm alumina (Buehler Co., Chicago, Ill.) on an optical flat (Harrick Scientific Corp., Ossining, NY) to a mirror-like finish followed by ultrasonic cleaning with triply distilled water for at least 15 minutes to remove any residual alumina on the surface [3,97]. The electrodes were then washed with a stream of triply distilled water and dried.

Polymer Coating

The polyvinyl acetic acid (PVAA) coating was formed on GC surfaces by refluxing in neat vinyl acetic acid (3-butenoic acid) (Aldrich Chemical Co., Milwaukee, WI) monomer at 165 °C under nitrogen for at least 16 hours [98]. The electrodes were then subjected to a Soxhlet extraction with acetone for ca. 24 hours.

Binding of Porphyrins on Polymeric Electrodes

Cobalt(II) tetra(o-amino)phenyl porphyrin perchlorate, CoT(o-A)PP(ClO₄)₂, or iron(III) tetra(o-amino)phenyl porphyrin chloride, FeT(o-A)PP·Cl₃, were bound to the polymer matrices via a covalent bonding of the amino functional groups on porphyrins and the acetic acid functional groups on the polymer. The reaction is:
The chlorination of the acidic polymer was performed by refluxing the polymer coated GC in neat oxalitic chloride at ca. 60 °C under nitrogen for two hours. The electrodes were then dried in the hood and immersed in porphyrin/THF solutions at the ambient temperature for 24 hours for amidization. The porphyrin coated electrodes were then washed with dry THF, air dried and stored in a dessicator until use.

RESULTS AND DISCUSSION

Characterization of Compound I

Compound I is water soluble. Figure 16 shows the visible spectrum of compound I in a l M KCl aqueous solution. A Soret band peak at 432 nm is observed. The extinction coefficient, $\epsilon$, calculated from the absorbance is $1.45 \times 10^5$ assuming 100% purity of the compound. Changes of the solution pH and the concentration of the supporting electrolyte have little effect on the absorbance.

Two GC electrode samples were prepared for XPS analysis. One was polished, cleaned, and then soaked in 10 $\mu$M compound I solution for 24 hours. Before transferring into the vacuum chamber, this electrode (sample a) was rinsed with triply distilled water. The other sample
Figure 16.

Visible spectrum of compound I/1 M KCl solution. 1 liter of the solution contains 7.3 mg of compound I.
(sample b) was prepared by simply spreading two drops of the above solution on the GC surface and drying in air. The elements identified on these surfaces and the atomic ratio of these elements are listed in Table 4. Both samples gave the signals for cobalt metal and chlorine which is a good indication of the adsorption of compound I. It was surprising that a sodium metal signal was detected for sample b. Such a sodium signal was absent on sample a. The chlorine signal for sample b also was larger than a. This could be an indication that sodium perchlorate was present in compound I since NaClO₄ was used to precipitate compound I in the final step of the synthesis [99]. If this was the case, the extinction coefficient given above would be smaller than the real value.

Oxygen Reduction Catalyzed by Compound I

Figure 17 shows the cyclic voltammograms of 10 μM compound I in a sulfuric acid solution of pH 2.65 at a GC electrode under (a) nitrogen, (b) air, and (c) oxygen. The reductive current for oxygen exhibited a peak potential (b and c) close to that for the reduction peak of compound I at ca. +0.10 V (a). This is consistent with the diagnostic criterium of an EC regeneration mechanism for oxygen reduction. If the electrode was removed from the solution, rinsed with triply distilled water, then put into a solution containing only the supporting electrolyte, the cyclic voltammograms obtained under the similar conditions are shown in Figure 18. The reductive peak potential was about the same as for the bulk solution while the peak current was decreased by about 10%. Continuous potential cycling at this electrode
Table 4. Elements identified and atomic ratio of compound I/GC

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak* position (eV)</th>
<th>Atomic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sample a</td>
<td>sample b</td>
</tr>
<tr>
<td>C1s</td>
<td>284.5</td>
<td>1.00</td>
</tr>
<tr>
<td>C2p3/2</td>
<td>780</td>
<td>2.40E-4</td>
</tr>
<tr>
<td>Cl2p</td>
<td>200</td>
<td>9.23E-4</td>
</tr>
<tr>
<td>N1s</td>
<td>400</td>
<td>6.62E-3</td>
</tr>
<tr>
<td>Na1s</td>
<td>1071</td>
<td>—</td>
</tr>
</tbody>
</table>

* uncertainty ± 0.5 eV
** calculated from the formula of compound I
Figure 17.

Cyclic voltammograms of 10 μM compound I solution under (A) nitrogen, (B) air and (C) oxygen. pH 2.65, scan rate: 90 mV/s.
Figure 18.

Cyclic voltammograms of compound I adsorbed GCE in 1 M KCl under (A) nitrogen, (B) air and (C) oxygen. pH 1.23, scan rate: 90 mV/s.
(GC with adsorbed compound I) caused slow deactivation for oxygen catalysis which was evidenced not only by a current decrease but also by a shift of the potential in a negative direction. The deactivation was probably due to the desorption of compound I. Reinjection of 10 μM compound I solution into the cell restored the electrode activity for oxygen.

Figure 19 shows the cyclic voltammograms for the O₂ saturated solution containing 10 μM compound I. If the reductive peak current is plotted versus the square-root of the scan rate, a linear relationship is obtained which indicates that the reduction is diffusion controlled. The slope of this plot is \(1.25 \times 10^{-4} \text{ As}^{1/2}/\sqrt{\text{V}}\). This value corresponds to a \(n^{3/2}D^{1/2}\) value of \(6.29 \times 10^{-3} \text{ cm/s}^{1/2}\) when calculated using the Randles-Sevcik equation [50], assuming a geometric electrode area and a concentration of 1.3 mM for oxygen.

If the peak current is normalized to the theoretical peak current [100], calculated using Randle-Sevcik equation, and then plotted versus the bulk concentration of compound I, Figure 20 results. The normalized current increases initially and approaches a limiting value as the concentration becomes greater than ca. 10 μM. If \(n=1\) is used in the theoretical calculation assuming a one-electron process reduction, the limiting value from the plot is 2 suggesting that oxygen is being reduced to hydrogen peroxide. When \(n=2\) is used in the calculation, the limiting value is much less than 1 indicating that oxygen is probably not reduced via a two-electron process. Similar normalization is performed for the oxygen reductive peak current at GC electrode with adsorbed compound I. The normalized current is listed in Table 5. It should be noted that the limiting value in this case is less than that
Figure 19.

Cyclic voltammograms of 10 µM compound I solution under oxygen. Inset shows a linear relationship between the peak current and the square-root of scan rate. Scan rate in mV/s: A. 10, B. 22.5, C. 40, D. 62.5, E. 90, F. 160.
Figure 20.

Plot of normalized peak current versus concentration of compound I. The n values used in calculation for curve A and B are 1 and 2, respectively.

•, ▲ measured under air
○, △ measured under oxygen
Table 5. Normalized Peak Current for Oxygen Reduction at Compound I Adsorbed GCE

<table>
<thead>
<tr>
<th>pH (pH)</th>
<th>Conc. **</th>
<th>n = 1 ( i_{\text{exp}}/i_{\text{calc}} )</th>
<th>n = 2 ( i_{\text{exp}}/i_{\text{calc}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>air oxygen</td>
<td>air oxygen</td>
</tr>
<tr>
<td>1.23</td>
<td>80</td>
<td>1.46 1.19</td>
<td>0.51 0.42</td>
</tr>
<tr>
<td>9.30</td>
<td>10</td>
<td>1.43 1.23</td>
<td>0.50 0.43</td>
</tr>
<tr>
<td>1.30</td>
<td>10</td>
<td>1.29 0.82</td>
<td>0.46 0.31</td>
</tr>
</tbody>
</table>

* \( n \) is the number applied in Randles-Sevcik equation for theoretical calculations
** The concentration of the compound I solution in which the adsorption occurs.
with compound I in the solution by about 10% which is probably due to the absence of catalysis by the compound I in the solution.

It has been reported [100a] that when the concentration ratio of catalyst/reactant is very small, a very large value of homogeneous rate constant (e.g. $5 \times 10^5 \text{M}^{-1}\text{s}^{-1}$) is required for high turnover of the reactant. As the homogeneous rate constant gets large, the current contributed by the reactant approaches the limit of 1.35 times of that contributed by the catalyst assuming unit stoichiometry of each reaction. For a two-electron process, the limit of the corrected normalized current will thus be 2.70 since the catalytic current is linearly dependent on the stoichiometry of the homogeneous chemical reaction. The normalized current observed in this experiment (Figure 20) is much smaller than the limit which is probably due to a small homogeneous reaction constant or due to the catalysis by the adsorbed catalyst.

The oxygen reductive current for the electrode with compound I adsorbed from an 80 µM solution is essentially the same as that with compound I adsorbed from a 10 µM solution. This may indicate that the adsorption is in equilibrium and reaches a maximum coverage with a solution at the concentration level as low as 10 µM. The gradual deactivation of the electrode in the absence of compound I in the solution is also explained by the equilibrium model.

The oxygen reductive peak potential is found to be linearly dependent on the solution pH. The peak potential shifts about 30 mV cathodically per pH unit in the pH range of 2 to 13. This dependency is not affected by the bulk concentration of compound I. The potential shift of 30 mV per pH unit may suggest that the rate determining step
Table 6. XPS Peak Positions and Atomic Ratio

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak Position (eV)</th>
<th>Atomic Ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CoT(o-A)PP-PVAA/GC</th>
<th>FeT(o-A)PP-PVAA/GC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Theo.&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Theo.&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fresh</td>
<td>Fresh</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Used</td>
<td>Used</td>
</tr>
<tr>
<td>C&lt;sub&gt;1s&lt;/sub&gt;</td>
<td>284</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>N&lt;sub&gt;1s&lt;/sub&gt;</td>
<td>400</td>
<td>1.92E-1</td>
<td>4.31E-2</td>
<td>5.19E-2</td>
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<tr>
<td>Cl&lt;sub&gt;2p&lt;/sub&gt;</td>
<td>200</td>
<td>3.85E-2</td>
<td>5.86E-3</td>
<td>3.62E-2</td>
</tr>
<tr>
<td>Co&lt;sub&gt;2p3/2&lt;/sub&gt;</td>
<td>780</td>
<td>1.92E-2</td>
<td>2.12E-3</td>
<td>1.83E-3</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2p3/2&lt;/sub&gt;</td>
<td>710.6</td>
<td>---</td>
<td>---</td>
<td>1.92E-2</td>
</tr>
<tr>
<td>Co/N</td>
<td>0.10</td>
<td>0.049</td>
<td>0.035</td>
<td>---</td>
</tr>
<tr>
<td>Fe/N</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.10</td>
</tr>
</tbody>
</table>

<sup>a</sup> uncertainty ± 0.5 eV
<sup>b</sup> normalized to carbon unless specified
<sup>c</sup> The theoretical ratio is calculated based on the assumption that a porphyrin molecule is bounded to two units of VAA.
involves two protons. This behavior is different from that of other adsorbed cobalt porphyrins [22,96] in which the proton equilibrium of the axially coordinated water is involved in the pH dependence. The reason for this unusual pH dependence is presently unknown and requires further study.

Oxygen Reduction Catalyzed by Polymer Bound Porphyrins

Freshly prepared polyvinyl acetic acid bonded cobalt and iron porphyrins, CoT(o-A)PP-PVAA/GC and FeT(o-A)PP-PVAA/GC were examined by XPS. The elements identified and the atomic ratios based on the carbon signal are listed in Table 6. Also listed are the XPS data for used electrodes which will be described later. On freshly prepared electrodes, the presence of the porphyrins is supported by the signals of the central metals. It is reasonable to assume that the presence of porphyrins is due to the bond formation with the polymer substrate. However, strong adsorption by the porphyrin, even after thorough rinsing of the electrode, is also possible.

Figure 21 and 22 show cyclic voltammograms of CoT(o-A)PP-PVAA/GC and FeT(o-A)PP-PVAA/GC in H_2SO_4 under nitrogen, air, and oxygen respectively. With nitrogen, the redox current-potential profiles buried in the broad background of PVAA/GC are not well defined. Determination of E_0' and the coverage of the porphyrins from the cyclic voltammograms is thus difficult. However, when oxygen concentration in the solution is increased, the reductive peak current for oxygen is increased at potentials, determined at slow scan rates, ca. -0.04 V for FeT(o-A)PP-PVAA/GC and +0.06 V for CoT(o-T)PP-PVAA/GC. The difference
Figure 21.

Cyclic voltammograms for CoT(o-A)PF-PVAA/GC in 1 M H₂SO₄ under (A) nitrogen, (B) air and (C) oxygen. Scan rate: 10 mV/s, S = 2, 10 and 50 µA for A, B and C, respectively.
Figure 22.
Cyclic voltammograms for FeT(o-A)PP-PVAA/GC in 0.1 M H$_2$SO$_4$ under (A) nitrogen, and (B) oxygen. 1 and 2 represent the first and the second cycle, C. under nitrogen after scan B. Scan rate: 10 mV/s for A, 20 mV/s for B and C. S = 2 μA for A, C; 100 μA for B.
between $E_p$ and $E_{0.85p}$ was ca. 50-60 mV for both electrodes. The reduction potential for FeT(o-A)PP-PVAA is slightly more negative than the previously reported potential for polymethyl acryl chloride bound FeT(o-A)PP [36].

FeT(o-A)PP-PVAA/GC is very unstable. In the presence of oxygen, the electrode loses its oxygen activity after one complete CV cycle. The oxygen reduction peak observed in the second cycle (Figure 22, B) is essentially the same as that at a bare GCE. Without oxygen in the solution, the reduction wave of the porphyrin is obvious for a few cycles. Then, the reduction wave becomes indistinguishable from the background and the electrode loses the capability of catalyzing reduction of oxygen when oxygen is injected into the solution. Due to this instability, no further electrochemical study on this system was attempted. In contrast to FeT(o-A)PP-PVAA/GC, CoT(o-A)PP-PVAA/GC remained active towards oxygen reduction even after twelve hours of consecutive electrolysis. The electrode activity also survived twenty day soaking in 1 M $\text{H}_2\text{SO}_4$. Thus, it appeared that hydrolysis of the amide bond between porphyrin and polymer was ineffective at this polymeric porphyrin electrode in that time period. However, the electrode slowly deactivated when the soaking was longer than twenty-six days.

Number of electron involved in the catalytic reduction of oxygen by CoT(o-A)PP-PVAA/GC was evaluated using the same method described previously. A $n^{3/2}d^{1/2}$ value was determined to be $6.45 \times 10^{-3}$ cm/s$^{1/2}$ which was very close to that reported for compound I. Normalization of peak current also revealed that the reduction of oxygen to hydrogen peroxide was catalyzed by an one-electron reduction process. However,
thin-layer coulometry is the method required to support the conclusion.

Both deactivated FeT(o-A)PP-PVAA/GC and CoT(o-A)PP-PVAA/GC were examined using XPS. The results, as compared with the freshly prepared electrodes, are listed in Table 6. For deactivated FeT(o-A)PP-PVAA/GC, no iron was detected while nitrogen and chlorine signals were slightly attenuated. Thus, loss of the central metal may be responsible for the deactivation of FeT(o-A)PP-PVAA/GC. Since the hydrolysis of amide bond is less likely, loss of the central metal is probably caused by demetalization or oxidation of porphyrin ring. For the deactivated CoT(o-A)PP-PVAA/GC, the metal signal indicated that the deactivation was probably not caused by loss of the central metal. Further studies are required to understand the deactivation mechanisms.

Conclusions

At the compound I adsorbed or CoT(o-A)PP-PVAA coated glassy carbon electrodes, oxygen is reduced at +0.04 V (peak potential) to hydrogen peroxide in acidic media. This represents a potential shift of ca. +0.50 V for oxygen reduction at glassy carbon. The catalytic activity coupled with the high stability makes them attractive as oxygen catalysts.

FeT(o-A)PP-PVAA/GC is active in catalytic reduction of oxygen. However, similar to previously reported adsorbed iron phthalocyanine [86,87], the stability is poor. The polymer seems ineffective in stabilizing FeT(o-A)PP.
CHAPTER V
ELECTROCATALYSIS USING ELECTROGENERATED PLATINUM
MICRO-S PHERICAL PARTICLES DISPERSED
POLYMERIC ELECTRODES

Many transition metals are known catalysts. Technically, these metal catalysts are in a high state of dispersion so as to maximize the surface area for a given mass of metal. Such catalysts may be widely separated as particles in catalyst supports, or may be close together, but more or less, separated by small amount of refractory oxide stabilizer like the Raney catalysts [101]. By distributing the metal particles in a support, the catalysts can attain a stability towards agglomeration and still remain accessible to reactants. The support also provides convenient mechanical properties for incorporation as an element in a process system.

The conventional support materials for metal particles include alumina, silica, glass, clay, zeolite and active carbon. The dispersion of metal catalysts is usually prepared by impregnating the support with a solution of the metal salt followed by drying and chemical reduction. In a few cases, polymers such as nylon, polyterephthalate ester, polyacrylonitrile and polyvinylalcohol have been used as supports for easily reducible metals such as platinum and palladium [102,103]. Ion exchange resins have also been used as supports for platinum group metals [39].
The metal is usually reduced directly by the polymer support and such supported metal catalysts have found applications in fuel cells.

On the other hand, since the introduction by Miller [104] in 1975, polymeric electrodes have been extensively used as an anchor for catalysts or redox mediators [1,3b,105-109], and as supports for thin metal films [110,111] or colloids [103,112]. It is well recognized that a polymeric electrode has an advantage of permanently modifying the electrode surface which possesses a surface with unique and widely varying properties. By incorporating metals into the modifying polymer, one can change dramatically the electrochemical properties of the electrode. However, the presence of reaction sites, redox sites or ion exchange sites has played a critical role for dispersing metals into the polymeric matrices.

It would be significant if one could disperse metal in a polymer by electrochemical reduction regardless of the presence of redox or ion exchange sites. From a practical point of view, this technology is important for processes like metal plating on plastics and for electrocatalysis. Thus, the idea of electrochemically dispersing metal particles in polymeric electrodes for electrocatalysis has never been tested, to the author's knowledge, prior to this work. Although Murray [40] published an article regarding electrodeposition of metal particles and films by a reducing redox polymer during the preparation of this dissertation, a reducing redox polymer was emphasized as a necessary reactant to disperse the metal particles. As such, these particle-films are in contrast to the work described in this chapter.

Wrighton [113] used an ion exchange type polymer to impregnate a platinum complex in the polymeric matrices. Dispersed platinum
particles were then formed by photoreduction or electrochemical reduction which improved the efficiency of hydrogen evolution at p-type silicon semiconductor photocathodes. However, data regarding the shape, size, dispersion and location of the reduced platinum particles were not reported. Doblhofer and Durr [114] studied the charge transfer mechanism for small particle dispersed polymeric electrodes. One proposed mechanism considered charge transfer to occur only at particles in contact with the electrode surface. The other was an electron hopping mechanism. These factors, including particle shape, size, distribution and charge transfer mechanism, are important for the application of such electrodes in electrocatalysis.

In this chapter, an approach to electrochemical dispersion of metal micro-particles into a polymer matrix without any ion exchange or redox sites is described and experimentally demonstrated. The initial preparation of such an electrode was quite circumstantial. When the CV background of PVAA/GC in 1 M sulfuric acid was examined with a stream of nitrogen passing through the cell, the current increased at a potential of ca. -0.25 V and bubble formation was observed after two hours of consecutive potential cycles. The low potential coupled with gasing pointed toward catalytic hydrogen generation. This unusual PVAA/GC electrode was then carefully examined using SEM. Small spherical particles were observed and X-ray fluorescence analysis (EDX) indicated the presence of platinum. An attempt was made to remove these Pt particles by sonication which was usually applied to clean the electrode surface [3a,97]. However, the electrode remained active for hydrogen generation and the particles were still observed after 15 minutes of sonication. By comparison, platinum metal was electrochemically
deposited on a bare GC electrode and then the electrode was subjected to sonication. The electrode without polymer lost its hydrogen activity after 2 minutes of sonication due to the loss of the Pt metal. It was interesting that the polymer would protect the metal particles from mechanical ablation such as sonication. This protection might provide meaningful stabilization for the particle catalyst used in fuel cells.

Comparing this electrochemically produced particle dispersed electrode with that formed by chemical reduction, it appears that the former possessed several advantages including: (a) the metal loading could be controlled; (b) size and distribution of particles could be controlled; (c) different combination of mixed metal or metal alloys may be deposited for specific purposes. However, prerequisites to a successful utilization of these advantages are: (a) an understanding of nucleation/growth mechanism of metal particles to be deposited in the polymer and (b) well-controlled conditions of deposition. A detailed study of such metal particle dispersed polymeric electrodes for electrocatalysis is described herein.

EXPERIMENTAL

Pretreatment of GC Electrodes and Polymer Coating

The procedure for GCE pretreatment and PVAA coating has been described in the previous chapter. Polyvinyl sulfonate (PVS) is coated on a GCE by refluxing in neat sodium vinyl sulfonate (Air Products and Chemicals, Calvert City, KY) monomer at its boiling temperature under
nitrogen for at least 5 hours. Polyacrylic acid (PAA), polymethyl methacrylate (PMMA), polystyrene (PS) and Gulf PA-18 are formed on GC surfaces by a spin coating method. The thickness of the spin coated polymer films was at the order of 1 μm or less. All the chemicals are used as received.

Dispersion of Pt Particles

Three electrochemical methods, cyclic voltammetry (CV), single-, and double-potential-step electrolysis (SPSE and DPSE), were applied to disperse Pt particles into the polymeric film from an acidic bath containing sodium or potassium hexachloroplatinate(IV) and 1 M H₂SO₄ or 1 M HClO₄. The typical potential limits for CV were +0.80 and -0.40 V. For SPSE the potential was stepped from +0.80 to 0.00 V. A square wave (+0.80 to -0.40 V) at a frequency of 0.05 Hz was applied for DPSE. The amount of Pt deposited was quantitated from the electrochemical charge consumed during electrolysis for SPSE, assuming a 100% current efficiency and a four-electron process for the reduction of Pt(IV) to Pt⁰. For CV and DPSE the quantity of Pt dispersed was controlled by the exhaustive electrolysis of a known amount of hexachloroplatinate contained in a stirred 1 mL cell. The quantitation of Pt from the electrochemical charge consumed was not applicable for CV or DPSE because of the difficulty in correcting for the charge due to platinum oxide formation and possible dissolution of Pt. The loading levels of Pt on the electrodes were between 0.2 and 50 μg/cm² (geometric area of GC). The electrodes employed for hydrogen generation and oxygen reduction studies and those examined by the scanning Auger microprobe
Surface Analysis of Modified Electrodes

Electrode surfaces were examined by using either an ISI Model SX-30 scanning electron microscope (SEM) (International Scientific Instruments, Inc., Santa Clara, CA) or a Cambridge Stereoscan Model S4-10 SEM (Cambridge Instruments, Cambridge, England) equipped with an Ortec Model 6200 Multichannel Energy Dispersive X-ray Analyzer (EDX) (EG and G, Oakridge, TN). The elemental identity of the particles was determined with EDX and with a PHI (Physical Electronics Instruments, Inc., Eden Prairie, MN) Model 595 Scanning Auger Microprobe (SAM). Prior to surface analysis, Pt-PVAA/GC electrodes were washed with a stream of doubly distilled water and air dried.

Particle Size Imaging

Particle size distribution was determined by a computer imaging system (Videoplan by Carl Zeiss, Inc., West Germany) using enlarged SEM photographs. The distribution function of the particle diameters was determined as well as the average and the standard deviation of the diameters, the apparent surface areas and the particle volumes. The smallest particle diameter that could be imaged was 50 Å.
RESULTS AND DISCUSSION

Characterization of the Polymeric GCE's

Examination of the PVAA/GC surface by SEM revealed a smooth, uniform film of PVAA on the GC. Films that were formed by refluxing more than 16 hr were also found to be pinhole free. The film thickness was estimated to be on the order of 400-1000 Å from SEM photomicrographs of boundaries of the film on GC. These boundaries were edges of ruptures in the film which was formed after extensive hydrogen generation.

Bulk PVAA (16-24 hr) is soluble in acetone. Since a film remained on the electrode after a 24 hr Soxhlet extraction with acetone, the film must be "bound" to the surface in some way. Grafting of acrylate polymers to carbon fibers has been postulated to involve interaction of carboxyl groups on the polymer and the carbon [115] (Grafted polymer was defined as polymer that remained on the carbon after a 24 hr Soxhlet extraction with acetone.)

Examination of the PVS/GC by SEM also revealed a smooth, uniform, and pin-hole free film. The PVS film also remained on carbon after the Soxhlet extraction with acetone. For those polymeric GCE's prepared by the spin coating method, the SEM photographs showed smooth and "transparent" films mixed with, in a few cases, aggregates of the polymer precipitates.
Characterization of Pt

Examination of the Pt-PVAA/GC surfaces by SEM indicated that the Pt particles were spherical and randomly distributed throughout the polymeric film (Figure 23). The distribution function, the average diameter at various loading levels and the density of particles on electrodes prepared by the three different methods are listed in Table 7. A histogram for the particle diameter distribution obtained from the SEM in Fig. 23A is shown in Fig. 24. All the particles studied had diameters in the range of 50-3000 Å, but the size distribution for a given electrode depended on the preparation method. The distribution for the particles produced by CV and DPSE matched a normal Gaussian distribution function with a confidence level greater than 95%. SPSE produced particles with a distribution curve skewed toward the smaller diameters. CV and DPSE produced distributions with a smaller average diameter, a smaller standard deviation and a higher particle population density than SPSE. Slower CV scan rates, e.g. 10 mV/sec, produced smaller diameter particles with a higher density than higher scan rates, e.g. 40 mV/sec. An increase in the concentration of hexachloroplatinate for a given SPSE deposition time resulted only in an increase in particle size, whereas, for CV and DPSE the particle size and density both increased (e.g. Fig. 23). The weight of the dispersed Pt metal calculated from the average diameter and particle density, assuming solid spheres and bulk Pt properties, and the amount of Pt electrodeposited agreed within ±20%.

A variation in the brightness of the SEM particle images was observed within a given micrograph. This brightness variation was
Scanning electron micrographs of micro Pt particle dispersed PVAA/GC electrodes. The electrodes were prepared by CV method using a 16 hour polymer film with Pt weight of A.) 9.3 μg/cm² B.) 50 μg/cm².

Figure 23.
Histogram of particle diameter distribution measured from Figure 23A.
Table 7. The size distribution, average diameter and population density of particles at various loading levels prepared by the three electrochemical methods.

<table>
<thead>
<tr>
<th>method of preparation</th>
<th>loading (µg/cm²)</th>
<th>diameter (Å)</th>
<th>density (counts/µm²)</th>
<th>distribution function</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV, 40 mV/s</td>
<td>9.3</td>
<td>647 ± 233</td>
<td>14.7</td>
<td>Gaussian</td>
</tr>
<tr>
<td>CV, 40 mV/s</td>
<td>50.0</td>
<td>1755 ± 474</td>
<td>12.2</td>
<td>Gaussian</td>
</tr>
<tr>
<td>CV, 10 mV/s</td>
<td>5.5</td>
<td>452 ± 177</td>
<td>35.2</td>
<td>Gaussian</td>
</tr>
<tr>
<td>CV, 10 mV/s</td>
<td>11.9</td>
<td>378 ± 230</td>
<td>57.9</td>
<td>Gaussian</td>
</tr>
<tr>
<td>SPSE</td>
<td>7.9</td>
<td>2931 ± 800</td>
<td>0.80</td>
<td>neg. skewness</td>
</tr>
<tr>
<td>SPSE</td>
<td>19.2</td>
<td>3221 ± 674</td>
<td>1.40</td>
<td>neg. skewness</td>
</tr>
<tr>
<td>DPSE</td>
<td>14.6</td>
<td>532 ± 91</td>
<td>74.7</td>
<td>Gaussian</td>
</tr>
</tbody>
</table>
independent of particle size. The brighter images are believed to be particles nearer the surface where poor electrical contact with the GC substrate may promote charging and the signal is not attenuated by the film. Thus, this difference in intensity is an indication that the particles are dispersed three-dimensionally throughout the polymer film rather than only two-dimensionally at the electrode/polymer interface. At low loading levels, occasionally, a few large particles were observed (e.g. Figure 23A). Since these particles were always brighter than the others, they were speculated to be due to the preferential growth of the nuclei near or at the polymer surface.

Preliminary results of point analysis by SAM (resolution ca. 5-10 Å) confirmed the elemental identity of the particles. However, when the point analysis was performed on the "clean" areas where Pt particles were not observed by SEM, a finite Pt signal was detected. It is uncertain whether the platinum SAM signal from the clean areas arose from small amounts of trapped hexachloroplatinate in the polymeric film or from Pt particles that were not visible by SEM.

The Pt particles formed at the polymeric GCE's other than PVAA/GCE appeared, as examined by SEM, similar to that of Pt-PVAA/GC. However, on thick spin-coated polymeric GCE's, the particles had preferential growth at the polymer surface. These particles were observed as the brighter spots in SEM and were easily removed by sonication.

Mechanistic Nucleation/Growth Consideration for Pt Particles in PVAA/GC

Well-established current-time (i-t) relations have been documented [116,117] as diagnostic criteria for various nucleation/growth
mechanisms. There are two models for nucleation processes. One is the instantaneous nucleation and the other is the progressive nucleation. In general, these two nucleation mechanisms can be expressed by the following equation assuming a first-order nucleation law:

\[ N = N_0 \{1 - \exp(A't)\} \] (25)

where \( N \) is the number of nuclei formed, \( N_0 \) the total number of sites, and \( A' \) the nucleation rate constant in units of \( s^{-1} \). The additional assumptions are that: (a) the thin polymer layer is sufficiently porous and has essentially no resistance to the transport of the platinum complex, and (b) the nucleation sites on the polymer, if any, are considered the extent of a rough surface of the substrate with no overlap of the substrate sites. When \( A't \gg 1 \), \( N = N_0 \) and the instantaneous nucleation mechanism applies. At \( A't \ll 1 \), \( N = N_0(A't) \), the progressive nucleation is linearly dependent on time.

The \( i-t \) relationship for three-dimensional growth, assuming no overlap of nuclei and no diffusion, which is valid only in the initial short period of time, are given \[116,117\] by:

\[ i_{\text{prog}} = (2nF\pi M^2 AK^3/3\rho^2)t^3 \] (26)

and

\[ i_{\text{inst}} = (2nF\pi M^2 N_0 K^3/\rho^2)t^2 \] (27)

where \( M \) is the molar mass and \( \rho \) the density of the coating, \( K \) the electrochemical rate constant, and \( A \) is defined as \( A'N_0 \), which is dependent \[118\] on overpotential :
\[ A = K \exp(-k\sigma^3/\eta^2) \]  \hspace{1cm} (28)

where \( K \) and \( k \) are constants and \( \sigma \) is the surface energy. So, the nucleation mechanism can be changed by varying the overpotential. The methods usually used for studies of nucleation/growth mechanisms are single- and double- potential-step chronoamperometry for which deposition conditions are controlled.

Figure 25 and 26 show the i-t profiles for Pt deposition in PVAA/GC when various overpotentials are applied. The profiles are composed of three sections. The "peak" close to \( t=0 \) is due to the double layer charging. Next to the "peak" is a constant current region which is due to the progressive nucleation. The induction time, \( t_o \), for the progressive nucleation is a function of the potential applied. As shown in Figure 27, \( \log(t_o) \) is a linear function of the potential indicating that the nucleation rate is governed by the heterogeneous charge transfer rate. The rising current beyond the induction period is due to the growth of the nuclei. The growth current shows a linear relationship with respect to the cube of growing time \((t - t_o)^3\), as shown in the insets of Figure 25 and 26, indicating a three-dimensional growth mechanism according to the diagnostic criterion [117] of the following relationship:

\[ i = \frac{(2nF\pi\eta^2AK^3/3\rho^2)(t-t_o)^3}{(t-t_o)^3} \]  \hspace{1cm} (29)

The spherical shaped particles revealed by SEM also support the three-dimensional growth rather than a cylindrical two-dimensional growth.
Figure 25.
Current-time response curve for single-potential-step deposition of Pt on PVAA/GC. Solution contains 20 mM hexachloroplatinate and 1 N HClO₄. The potential is stepped from 0.80 V to 0.20 V vs Ag/AgCl. The inser shows that the growing current is a function of cube of growing time.
Figure 26.

Current-time response curve for single-potential-step deposition of Pt on PVAA/GC. Solution contains 20 mM hexachloroplatinate and 1 N HClO₄. The potential is stepped from 0.80 V to 0.18 V vs Ag/AgCl. The inset shows that the growing current is a function of cube of growing time.
Figure 27.

Plot of the logarithm of the induction time, $t_o$, as a function of applied potential for single-potential-step deposition of Pt on PVAA/GC.
mechanism.

When a pre-pulse with high overpotential, e.g. $-0.40\,\text{V}$, for ca. 100 ms is applied prior to the deposition, the nucleation mechanism changes from the progressive type to the instantaneous type as indicated by Figure 28 in which the induction period is too short to be real. The growing current, in this case, is governed by equation (27) for a three-dimensional growth mechanism. As predicted, the growth current is a linear function of $t^2$ (see the inset of Figure 28). The SEM photograph of such a Pt-PVAA/GC shows spherical and roughly equal-sized Pt particles, supporting the above conclusions. The nucleation/growth mechanisms of Pt deposition on other polymeric GCE's were not studied.

Electrochemical Generation of hydrogen and Reduction of Oxygen

Figure 29 shows cyclic voltammograms illustrating the catalytic generation of hydrogen (trace A) and oxygen reduction (trace B) at a Pt-PVAA/GC electrode with a Pt loading of 25 $\mu$g/cm$^2$, compared to $\text{H}_2$ (trace C) and $\text{O}_2$ (trace D) at an unmodified GC electrode in 1 M $\text{H}_2\text{SO}_4$. The overpotential for $\text{H}_2$ generation was decreased by ca. 600 mV (compare trace A to C) and the electrogenerated $\text{H}_2$ could be reoxidized during the reverse scan. The overpotential for $\text{O}_2$ was decreased by ca. 800 mV. The overpotentials for $\text{H}_2$ and $\text{O}_2$ observed on Pt-PVAA/GC were the same as those observed on a smooth Pt electrode.

The typical adsorption-desorption fine structure [54,55] of hydrogen at a smooth Pt surface was evident, although ill-defined, on Pt-PVAA/GC at higher scan rates, e.g. 500 mV/s, but it was indistinguishable from the background at lower scan rates; e.g. 40 mV/s.
Figure 28.

Current-time curve for the double-potential-step deposition of Pt on PVAA/GC; pre-pulse with -0.40 V vs Ag/AgCl for 100 ms. Final potential 0.15 V. Solution is the same as that in Fig. 25.
Figure 29.

Cyclic voltammograms for hydrogen evolution and oxygen reduction at Pt-PVAA/GC electrode (A, B) and bare GC (C, D) in 1 M sulfuric acid: S: 200 µA for A, C; 50 µA for B, D; 16 hour refluxed film; geometric electrode area 0.55 cm²; Pt loading 25 µg/cm²; scan rate 10 mV/sec.
Determination of the "real" active Pt surface area from the electrochemical charge for the hydrogen adsorption was therefore not possible. The reason for this loss of fine structure is not known, but it does indicate that the film may have an effect on hydrogen adsorption.

The logarithm of the cathodic current for H₂ evolution was plotted versus the potential (Tafel plot) [50] up to an overpotential, \( \eta \), of ca. 150 mV. The current in this potential region was the same in both static and stirred solutions, indicating an absence of mass transfer effects. The linear portion of each Tafel plot was extrapolated to the current axis (\( \eta = 0 \)) to determine the exchange current. Since the particle size distribution and population are known, the total surface area of Pt could be computed, assuming that all of the particles imaged were smooth spheres and active. When the exchange currents were normalized to their respective surface areas and plotted as a function of the Pt loading, the curve shown in Figure 30 resulted. The exchange current density, \( I_0 \), increased dramatically with loading up to a level of approximately 12 \( \mu \text{g/cm}^2 \). Above this level, \( I_0 \) appeared to plateau and become independent of loading. The \( I_0 \) values obtained for H₂ of ca. 1 \( \times 10^{-3} \) to 5 \( \times 10^{-2} \) A/cm² for Pt loadings of 0.25 to 25 \( \mu \text{g/cm}^2 \) are of the same order of magnitude or larger than the literature values of 1 \( \times 10^{-4} \) and 1 \( \times 10^{-3} \) A/cm² for smooth Pt in sulfuric acid solutions [79,119]. This implies, within experimental uncertainty, that all the particles are active.

When Pt particles were examined by SEM at the higher magnifications of 50 to 100 KX, the outer edge of the spheres appeared to have angular structures. These structures suggested that the particles might be formed as polycrystalline particles or as coalesced particle clusters.
Figure 30.

Plot of exchange current density Gaussianized to apparent Pt surface area, vs Pt loading. The Pt-PVAA/GC electrodes with mean particle diameter between 300 and 600 Å were used.
Since the $I_0$ values were normalized to an area that assumed a smooth surface, the $I_0$ values calculated could be high. It is reasonable to assume that such surface roughness will increase as the particle diameter increases up to some critical value, after which the roughness factor will remain essentially constant. Thus, the variation of $I_0$ with Pt loading can be explained.

The cathodic $i$-$E$ curves for $H_2$ generation at a Pt-PVAA/GC (10.5 μg/cm²) as a function of pH are reproduced in Figure 31. The cathodic current at each pH was observed to increase linearly with the applied potential beyond the Tafel region. If the linear region of each curve was extrapolated to the potential axis, this "intercept" potential plotted as a function of pH was linear with a slope of $-56$ mV/pH. Similar behavior was observed at a smooth Pt electrode.

For $O_2$ the CV peak current, $i_p$, increased linearly with the square root of scan rate indicating a mass transfer limited reaction in aqueous acidic solutions ($H_2SO_4$ or $HClO_4$). The $i_p$ was also linearly dependent on the oxygen concentration at a given scan rate. The exchange current for $O_2$ reduction was determined from the Tafel plots using the "foot" of the CV $i$-$E$ curves. Both the pH dependence of the peak potential and the calculated exchange current density for $O_2$ reduction at Pt-PVAA/GC were similar to those determined at smooth Pt [80,119]. The loading effect on $I_0$ for $O_2$ reduction was not studied.

The electrocatalytic hydrogen generation and oxygen reduction at other Pt-polymeric GCE's behave similarly to that at Pt-PVAA/GCE. However, irreversibility is evident by the potential shift at Pt-PS/GC and other spin-coated polymeric GCE's. This is speculated to be primarily caused by the flooding of the products, gaseous $H_2$ and water,
Figure 31.
Cathodic i-E profile for $H_2$ generation at a Pt-PVAA/GC electrode in A: 1 N HClO$_4$, B: 0.1 N HClO$_4$, and 0.1 M phosphate buffer of pH C: 2, D: 3, E: 4, F: 5, G: 6, H: 7, I: 9. Pt loading 10.5 $\mu$g/cm$^2$; geometric electrode area 0.55 cm$^2$; scan rate 10 mV/sec.
which are entrapped in the thick polymer film and retard the diffusion of the reactants.

Stability

The platinum particles on Pt-PVAA/GC were not removed by ultrasonic cleaning for periods up to 15 minutes. Longer periods were not employed since it had been reported that 15 minutes was sufficient for removal of particles dispersed on bare GC [3a,97]. Pt particles deposited on a bare GC electrode were rapidly lost from the surface in the ultrasonic bath (less than 2 minutes). The enhanced mechanical stability of the Pt against ultrasonic ablation was probably due to the physical entrapment of the particles in the polymeric film which adheres strongly to the GC surface, although the adsorption or adherence of the carboxylate groups of PVAA on the Pt particles may also have an effect [120].

The stability of the Pt-PVAA/GC for H₂ generation was tested by controlled potential electrolysis in an aqueous H₂SO₄ solution at ambient temperatures. The current averaged 20 mA/cm² for more than 400 hours. The Iₒ was constant within experimental error over this time period. The mean geometric diameter of the Pt particles, as determined by SEM, before and after 400 hours also did not change. Thus, there was no particle degradation due to sintering and recrystallization as had been observed at Pt fuel cell cathodes operating at higher temperatures [81,121]. At these ambient temperatures, the entrainment of the particles in the polymer apparently prevents particle aggregation. The other Pt-polymeric GCE's possess similar stability against the sonication. However, their electrochemical stabilities have not been
The cyclic voltammetry of $1 \times 10^{-3}$ M ferricyanide in 0.1 M KCl was determined at a Pt-PVAA/GC electrode. The peak separation in a CV of ferricyanide was less for Pt-PVAA/GC than for PVAA/GC, but both were greater than that at Pt or bare GC. This indicated that ferricyanide behavior at Pt-PVAA/GC was different from that of $H_2$ and $O_2$. In contrast to this behavior, positively charged metal complex such as hexammineruthenium showed high reversibility at both PVAA/GC and Pt-PVAA/GC. The reversibility was speculated to be due to the low film resistance and the different charge transfer mechanism through the film. A detailed study of the charge and mass transfer mechanism through the film was thus conducted. The results are discussed in the next chapter.

CONCLUSIONS

The reasonably large surface area achieved with low loading levels, the high catalytic efficiency, and the excellent stability possible with dispersed micro-particles in polymer film coated electrodes make them attractive for a variety of redox applications including photocatalysis [108,113,122]. By imbedding the metal particles in polymeric films, the loss of catalytic activity or efficiency due to physical or chemical loss of the catalyst and the poisoning by adsorption of large molecules can be suppressed. Since other metals such as Pd and Ni, can be similarly deposited into PVAA/GC [6], the method described herein should
be applicable to dispersion of other metals, multilayer metals or alloys as particles. Thus, fabrication of catalytic electrode based on a combination of substrates, polymers and electrochemically dispersed metals, mixed metals, or metal oxides appears possible.
Electrocatalysis of electrochemical reactions by chemically modified electrodes has been of great interest recently. Applications of polymeric coatings on electrode surfaces for catalytic electrochemical reactions [5,36,123-128] or photoelectrochemical reactions [113,129-131] can be found in the literature. For electrocatalysis, attachment or incorporation of active catalytic or mediating species in the polymer is usually required. This is often accomplished by covalent bonding of catalysts on the polymer, by dispersion of metal micro-particles or colloids [5,113], or by incorporation of mediators such as small transition-metal complexes (e.g. ferricyanide, iridium hexachloride, and hexaaaminoruthenate) [125,126,128]. There are several possible current-limiting processes in the overall catalytic reaction. These include (a) mass transport of solution substrates to the electrode, (b) mass transport of substrates within a film to the electrode surface or active sites, (c) transport of charge, either electronic or ionic, within a film, and (d) the rate of electron transfer between the catalyst/mediator and the substrates. The kinetics of these processes have been widely investigated and some theoretical
models have been proposed [114,125,132-136]. Generally, process (a) is primarily controlled by the diffusion or convection of solution substrates. Process (b) involves the partitioning or "dissolving" of solution substrates into the solid polymer or solvent swelled slurry film structure (membrane diffusion), and/or diffusion of substrates through pinholes or channels in the film. The rate of process (c) is determined by the conductivity of the film, penetration of counter ions, electron hopping between active sites, and/or electrostatic barrier or the so-called $\phi_2$ effect [137]. The $\phi_2$ effect is primarily the result of a charged film. The charge on a film may change the interfacial potential distribution and thus alter the potential experienced by reactants at their closest approach to the electrode. The rate of electronic charge transfer is therefore related to the $\phi_2$ effect.

It was described in the previous chapters that a polyvinyl acetic acid (PVAA) film could be formed at a glassy carbon (GC) surface. With dispersion of platinum microparticles [5], this electrode exhibited electrocatalysis for oxygen reduction and hydrogen generation. In contrast, the redox of ferri/ferrocyanide at this electrode with or without Pt particles showed considerable irreversibility when 0.1 M KCl was used as the supporting electrolyte (Figure 32). Several factors could account for this irreversibility: (a) exclusion of ferri/ferrocyanide anions by the film; (b) electrostatic barrier for charge transfer or $\phi_2$ effect due to the anionic characteristics of the film in neutral solutions [138]; and (c) resistance of ionic charge transport within the film due to low concentration of the supporting electrolyte. Factor (c) was partially supported by the fact that when 1.0 M KCl was used as the supporting electrolyte, the reversibility for
Cyclic voltammograms for redox of 1 mM ferricyanide at (I) PVAA/GC, (II) Pt-PVAA/GC of loading 10 µg/cm² in solutions of (A, A') 0.1 M, (B, B') 0.2 M, (C, C') 0.5 M and (D, D') 1.0 M KCl. Scan rate: 10 mV/s.
Illerri/ferrocyanide couple was improved. Nevertheless, the other two factors may also play an important role in the overall process.

In order to understand the charge and mass transport mechanism through the PVAA film and to clarify the above speculations, the redox behavior of several transition-metal complexes with various molecular sizes and charges at PVAA/GC and Pt-PVAA/GC in various electrolyte media was monitored. The same experiments were performed at polyvinyl sulfonate (PVS) coated GC for comparison. Cyclic voltammetry (CV), chronoamperometry and impedance measurements were the techniques applied in the study.

EXPERIMENTAL

GC electrodes as GC10, 20, 30 (Tokai Carbon Co., Tokyo, Japan) or V19, 25 (Atomergic Chemetals Corp., NY) were cleaned and coated with PVAA according to the previously described procedures [5]. PVS coating was prepared following the procedure described in chapter V. Platinum microparticles with a loading level of ca. 10 to 20 μg/cm² were dispersed using the CV method described in Chapter V. All the transition-metal complexes except molybdenum octacyanide and iron tetra(2-pyridyl)porphyrin, FeT(2-Py)P, were reagent grade commercial chemicals. Molybdenum octacyanide was synthesized from molybdenum trioxide and potassium cyanide following the published procedure [139]. The Mo(CN)₈⁶⁺ was obtained as a golden-yellow crystal after recrystallization from methanol in accord with the literature [139]. FeT(2-Py)P was synthesized by my colleague Oliver Su. The synthetic
procedure will be reported in his thesis. 0.05 M sulfuric acid was the
supporting electrolyte for FeT(2-Py)P. Solutions of KCl at concentra-
trations of 0.1, 0.2, 0.5, 0.8 and 1.0 M were the supporting electrolyte
for the rest of complexes. The supporting electrolytes for ferricyanide:
system were 1 N HClO₄, 0.1 N HClO₄ + 0.9 M KCl, and 0.1 M phosphate
buffer solutions of pH 2, 3, 4, 5, 6, 7, 8 and 9 with ionic strength
adjusted by KCl to 1 M. Doubly distilled water was used in preparation
of solutions.

The CV and chronoamperometry instrumentation have been described in
the previous chapters. Impedance measurements were performed by using a
Solartron 1172 Frequency Response Analyzer (The Solartron Electronic
Group Ltd, Farnborough Hampshire, England) which was connected to an
Apple II+ microcomputer for function controls and data acquisition. A
two-compartment all glass electrochemical cell with a platinum gauze
counter electrode with surface area greater than 50 cm² was used for the
impedance measurements. A large surface area was necessary to reduce
the contribution to the impedance from the counter electrode. The
potentials reported were referred to a Ag/AgCl(sat'd KCl) reference
electrode.

RESULTS AND DISCUSSION

The redox potential, E₀'s, for the complexes are listed in Table 8.
These potentials were determined by averaging the peak potentials of
CV's obtained at a bare GCE in 0.1 M or 1 M KCl. These complexes were
chosen so that their redox potentials were located within the potential
Table 8. $E_0^{+*}$ for redox of metal complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>charge</th>
<th>media</th>
<th>$E_0^{+*}$(vs Ag/AgCl)(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(2-TPyP)</td>
<td>+3/+2</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>0.028</td>
</tr>
<tr>
<td>Fe(CN)$_6$</td>
<td>-3/-4</td>
<td>1 M KCl</td>
<td>0.270</td>
</tr>
<tr>
<td>(NH$_3$)$_6$Ru</td>
<td>+3/+2</td>
<td>1 M KCl</td>
<td>-0.160</td>
</tr>
<tr>
<td>Ru(bpy)$_3$</td>
<td>+2/+3</td>
<td>1 M KCl</td>
<td>1.055</td>
</tr>
<tr>
<td>IrCl$_6$</td>
<td>-2/-3</td>
<td>0.1 M KCl</td>
<td>0.720</td>
</tr>
<tr>
<td>Fe(bpy)$_3$</td>
<td>+2/+3</td>
<td>1 M KCl</td>
<td>0.843</td>
</tr>
<tr>
<td>Mo(CN)$_8$</td>
<td>-4/-3</td>
<td>1 M KCl</td>
<td>0.630</td>
</tr>
</tbody>
</table>

*$E_0^{+*}$s are measured from a CV at a scan rate of 10 mV/s.*
window accessible to PVAA/GC and PVS/GC; i.e. +1.20 V to -0.40 V. All the redox reactions reported herein involved a one-electron transfer process. Typical cyclic voltammograms for these complexes at a PVAA/GC electrode are shown in Figure 33. The reversibility criterion will be the peak-peak separation of a cyclic voltammogram obtained at a scan rate of 10 mV/s.

Effect of Supporting Electrolyte Concentration

At a bare GC electrode, FeT(2-Py)P in 0.05 M sulfuric acid and other complexes in 0.1 M KCl solution exhibited reversible one-electron redox reaction (peak-peak separation of 60 mV). The peak current of the CV's was linearly dependent on the square-root of the scan rate, which is characteristic of diffusion controlled reactions. In the presence of the PVAA coating, irreversible redox behavior for ferricyanide (Figure 32) and molybdenum octacyanide was observed while the cationic complexes and the anionic complexes with an \( E^0 \) more positive than ca. +0.7 V remained reversible (Figure 33). If the concentration of KCl was increased, the reversibility for ferricyanide and molybdenum octacyanide was improved as evidenced by the smaller peak-peak separation. Similar results were obtained at PVS/GC. Typical CV peak-peak separations for each redox complex in various media are listed in Table 9. Although the absolute values of the peak-peak separation for those irreversible processes in various media changed from one polymeric electrode to another, the trends were unchanged. The changes were probably due to different thicknesses of polymer coating.

It is noted that for all redox complexes but the \((NH_3)_6Ru^{2+}\), the
Cyclic voltammograms for redox of transition-metal complexes at PVAA/GC in 0.1 M KCl. Concentration: A, E, F, G: 0.5 mM; B, C, D: 1 mM. Electrode area: A, C, E, F: 0.55 cm²; B, D, G: 0.35 cm². S in uA: C: 10; A, B, D, E, F, G: 20. Scan rate in mV/s: C: 10; B, D, E, F: 40; A: 62.5; G: 90.
<table>
<thead>
<tr>
<th>case</th>
<th>complex</th>
<th>electrode</th>
<th>media</th>
<th>(E_{pc}+E_{pa})/2 (V)</th>
<th>ΔE_p (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(2-TPyP)\textsuperscript{3+}</td>
<td>PVAA/GC</td>
<td>0.05 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.028</td>
<td>0.060</td>
</tr>
<tr>
<td>2</td>
<td>Fe(CN)\textsubscript{6}\textsuperscript{3-}</td>
<td>PVAA/GC**</td>
<td>0.1 M KCl</td>
<td>0.210</td>
<td>0.560</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 M KCl</td>
<td>0.240</td>
<td>0.380</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 M KCl</td>
<td>0.270</td>
<td>0.200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.8 M KCl</td>
<td>0.280</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0 M KCl</td>
<td>0.280</td>
<td>0.110</td>
</tr>
<tr>
<td>3</td>
<td>Fe(CN)\textsubscript{6}\textsuperscript{3-}</td>
<td>Pt-PVAA/GC**</td>
<td>0.1 M KCl</td>
<td>0.220</td>
<td>0.180</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 M KCl</td>
<td>0.230</td>
<td>0.120</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 M KCl</td>
<td>0.250</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.8 M KCl</td>
<td>0.268</td>
<td>0.070</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0 M KCl</td>
<td>0.270</td>
<td>0.070</td>
</tr>
<tr>
<td>4</td>
<td>Fe(CN)\textsubscript{6}\textsuperscript{3-}</td>
<td>PVS/GC</td>
<td>0.1 M KCl</td>
<td>0.230</td>
<td>0.200</td>
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<td></td>
<td></td>
<td></td>
<td>0.2 M KCl</td>
<td>0.235</td>
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<tr>
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<td></td>
<td>0.5 M KCl</td>
<td>0.258</td>
<td>0.118</td>
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<tr>
<td></td>
<td></td>
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<td>0.8 M KCl</td>
<td>0.270</td>
<td>0.086</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0 M KCl</td>
<td>0.275</td>
<td>0.086</td>
</tr>
<tr>
<td>5</td>
<td>(NH\textsubscript{3})\textsubscript{6}Ru\textsuperscript{3+}</td>
<td>PVAA/GC</td>
<td>0.1 M KCl</td>
<td>-0.130</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 M KCl</td>
<td>-0.145</td>
<td>0.062</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.5 M KCl</td>
<td>-0.150</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.8 M KCl</td>
<td>-0.155</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0 M KCl</td>
<td>-0.160</td>
<td>0.060</td>
</tr>
<tr>
<td>6</td>
<td>Ru(bpy)\textsubscript{3}\textsuperscript{2+}</td>
<td>PVAA/GC</td>
<td>0.1 M KCl</td>
<td>1.090</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 M KCl</td>
<td>1.080</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 M KCl</td>
<td>1.070</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.8 M KCl</td>
<td>1.060</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0 M KCl</td>
<td>1.055</td>
<td>0.060</td>
</tr>
<tr>
<td>7</td>
<td>IrCl\textsubscript{6}\textsuperscript{2-}</td>
<td>PVS/GC</td>
<td>0.1 M KCl</td>
<td>0.720</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 M KCl</td>
<td>0.732</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 M KCl</td>
<td>0.760</td>
<td>0.060</td>
</tr>
<tr>
<td>8</td>
<td>Fe(bpy)\textsubscript{3}\textsuperscript{2+}</td>
<td>PVS/GC</td>
<td>0.1 M KCl</td>
<td>0.880</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 M KCl</td>
<td>0.870</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 M KCl</td>
<td>0.860</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.8 M KCl</td>
<td>0.850</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0 M KCl</td>
<td>0.840</td>
<td>0.060</td>
</tr>
<tr>
<td>9</td>
<td>Mo(CN)\textsubscript{8}\textsuperscript{4-}</td>
<td>PVAA/GC</td>
<td>0.1 M KCl</td>
<td>0.600</td>
<td>0.130</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 M KCl</td>
<td>0.600</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 M KCl</td>
<td>0.615</td>
<td>0.070</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.8 M KCl</td>
<td>0.620</td>
<td>0.070</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0 M KCl</td>
<td>0.628</td>
<td>0.070</td>
</tr>
</tbody>
</table>

** same PVAA/GC electrode
average peak potentials shifted toward lower overpotentials when the concentration of the supporting electrolyte was increased. The biggest potential shift observed was ca. 70 mV for ferricyanide when the concentration of KCl was increased from 0.1 M to 1.0 M. This potential shift is probably due to the results of a combination of the $\phi_2$ effect and a decrease of ionic charge resistance within the film.

The CV for the redox of ferricyanide at Pt-PVAA/GC was also examined. To evaluate the enhancement of the charge transfer rate by dispersion of Pt particles without complications introduced by a varying film thickness, Pt particles were dispersed (case 3, Table 9) after the experiments of case 2 (Table 9) were done. As noted, the reversibility for redox of ferricyanide was significantly improved in the presence of Pt particles but retained irreversible characteristics in solutions with low concentrations of supporting electrolyte. It was assumed that there was no potential drop across a metal particle. Thus, the redox species at their closest approach to a metal particle might experience a smaller iR drop than that experienced at the same depth of approach in the absence of metal particles. An alternative viewpoint is that Pt particles within the film may essentially reduce the in-film diffusion layer for the reactants. This effect is similar to the incorporation of active sites three-dimensionally within the film. However, the irreversibility of ferricyanide at Pt-PVAA/GC at a low loading level (ca. 10 $\mu$g/cm$^2$) in 0.1 M KCl medium could be due to other factors such as a slow rate of ionic transport within the film or slow membrane diffusion of ferricyanide. If the heterogeneous charge transfer rate constant was evaluated by applying Nicholson's criteria [140], the charge transfer rate in the presence of Pt particles (ca. 10 $\mu$g/cm$^2$) was greater than
that without platinum by about two orders of magnitude. Increase of Pt loading level also improved the rate of charge transfer.

**pH Effect**

The redox of ferricyanide at PVAA/GC and PVS/GC in phosphate buffer solutions was also examined. At pH 0 and 1, a blue coating on the electrode surface was observed after a few potential cycles. This coating was believed due to the formation of Prussian Blue (PB). In the pH range of 2 to 5, this ferri/ferrocyanide reaction was reversible. In neutral and basic solutions, however, irreversible characteristics were evident. It was interesting that the average of the cathodic and the anodic peak potentials shifted as a function of the solution pH. The results are summarized in Figure 34. The pH effect is similar to that described above. In the neutral or basic pH range, the polymer film is negatively charged and the electrostatic resistance between the film and anionic redox species and the $\phi_2$ effect are probably significant. Thus, the potential shift and increase of peak-peak separation (Figure 34) for ferricyanide occur in solutions of pH greater than 5.

**Memory Effect**

If PVAA/GC or PVS/GC electrodes were soaked in Ru(bpy)$_3^{2+}$, Fe(bpy)$_3^{2+}$, or (NH$_3$)$_6$Ru$^{3+}$ solutions or if the Prussian Blue was deposited on the polymeric electrode, the cyclic voltammograms for the redox of these complexes were observed even though the polymeric electrode was pre-washed with a stream of water. When these cationic
Figure 34.

Typical plots of $E_{pK} (\bigcirc, \bullet)$, $E_p (\bigtriangleup, \blacktriangle)$, and $E_p (\bigcirc, \blacklozenge)$ for redox of ferricyanide at PVAA/GC (close) and PVS/GC (open) as a function of solution pH.
complexes or Prussian Blue were imbedded in the polymeric film, the redox of ferricyanide exhibited reversibility ($\Delta E_p = 60$ mV) even though the concentration of the supporting electrolyte was as low as 0.1 M. One possible explanation for this memory effect was that the reduction of ferricyanide was mediated by the incorporated cation via a fast outer-sphere charge transfer [126b,126c,141]. However, since (a) the redox of ferricyanide was not taking place at the redox potential of the mediating cations, and (b) some cationic complexes such as Ru(bpy)$_3^{2+}$ and Fe(bpy)$_3^{2+}$ were thermodynamically unfavored as a mediator for ferricyanide reduction, the mediation was an unlike possibility. Other possible explanations include: (a) the incorporation of cations within the polymer matrices that facilitates electron hopping through the film thereby increases the charge transfer rate for ferricyanide reduction; (b) the cations in the polymer essentially neutralize the negative charge of the film and thereby reduce the resistance for diffusion of the ferricyanide anion within the film; and (c) the electric conduction through the Prussian Blue thin film.

Hexaaminoruthenate was reported as a mediator for reduction of cobalt porphyrin incorporated in a Nafion film which was coated on an electrode [126c,142]. Without bulk ($\text{NH}_3$)Ru$^{2+}$ species to sustain the equilibrium of partitioning, the mediating electrode gradually deactivated due to the leaching of the cationic mediator out of the film. The loss of the cations out of a PVAA or PVS film was not significant in this study as evidenced by the fact that the peak current was decreased by less than 10% after soaking in water for twenty-four hours. Longer periods of soaking are probably necessary to remove the cations from the polymer film.
Molecular size of reactants is crucial to the redox reversibility at a polymeric electrode [136]. Among the complexes examined in this work, ferricyanide and molybdenum octacyanide are small molecules compared to FeT(2-Py)P. The redox of FeT(2-Py)P is reversible at both PVAA/GC and PVS/GC. Thus, the irreversibility of ferricyanide and molybdenum octacyanide at these polymeric electrodes appears not to be caused by size exclusion with the film. Furthermore, it is noted that the anionic complexes with redox potentials more positive than 0.7 V exhibit reversible behavior.

A possible explanation of the irreversibility of ferricyanide and molybdenum octacyanide is due to the electrostatic repulsion between the anions and the negatively charged polymer film. This repulsion not only slows down the diffusion of the redox anions within the film but also the ionic charge transfer rate within the film. The resistance of the ionic charge transfer can be reduced by increasing the concentration of charge carriers within the film.

In solutions of low pH's, the PVAA film remains protonated as an undissociated carboxylic acid [138] and is therefore neutral. The redox of ferricyanide at such a "neutral" polymer surface appears reversible. At higher pH values, the PVAA film is deprotonated and negatively charged, and the CV waves of Fe(CN)$_6^{3-/4}$ are less reversible. By incorporating cations such as Ru(bpy)$_3^{2+}$ and Fe(bpy)$_3^{2+}$ into the film, the negative charge on the polymer is decreased and the charge transfer rate (and therefore the reversibility) of ferricyanide increases. At potentials more positive than 0.7 V, on the other hand, one can probably "neutralize" the film. The effect of such "neutralization", of course, depends on the potential of zero charge of the polymeric surface. Since
the redox of iridium hexachloride is reversible at ca. 0.72 V while molybdenum octacyanide is irreversibly oxidized at ca. 0.63 V, the potential of zero charge for these polymeric electrodes may be at a potential near 0.7 V.

Impedance measurements were performed to monitor the changes of charge transfer resistance through the polymer thin film as a function of the concentration of KCl. Bare GC electrode and PVAA/GC, with and without dispersed platinum particles, were examined for comparison. Also, the uncompensated solution resistance and the double layer capacitance at the solution/electrode interface were measured. By varying the frequency of a sine wave potential perturbation, the measured imaginary and real portion of impedance forms a semicircle which starts at high frequencies on a plot in the complex plane, the so-called Nyquist plot. The low frequency data forms a negative linear slope when the perturbation results from a diffusion controlled redox process. This system can be described by the Randles equivalent circuit [143]:

\[
\begin{align*}
\text{R}_\text{g} & \quad \text{R}_\text{ct} & \quad \text{C}_\text{dl} & \quad \text{Z} \\
\text{Ref} & \quad \text{W} & & \\
\end{align*}
\]

where \( R_g \) represents the solution resistance; \( R_{ct} \), the charge transfer resistance which includes the resistance caused by the \( \phi_2 \) effect; \( C_{dl} \), the double layer capacitance; and \( Z \), the so-called Waburg impedance which is primarily related to the mass diffusion of the redox species.

Figure 35 shows the typical Nyquist plot for the redox of ferricyanide at bare GC, PVAA/GC and Pt-PVAA/GC electrodes. The applied potential was set at the \( E^0' \) of ferri/ferrocyanide. The supporting
Figure 35.
Nyquist plot for ferricyanide at (A) bare GC, (B) PVAA/GC and (C) Pt-PVAA/GC of 10 μg/cm² loading.
electrolyte was 0.1 M KCl. The Nyquist plot suggests that the redox of ferricyanide is similar to the equivalent circuit described above in the frequency region of ca. 10 kHz to 1 Hz. However, the impedance response at lower frequencies of ca. 0.1 Hz, is random and irreproducible. The Waburg impedance is more pronounced in the low frequency region. However, the perturbation at low frequencies such as 0.1 Hz is probably not applicable to an equilibrium state when diffusion or convection processes become effective. Thus, the equivalent circuit may no longer be applicable. No attempt was made to evaluate the charge and mass transfer rates from the Waburg impedance due to this difficulty. $R_s$ can be measured from the high frequency intercept at the real axis and $R_{ct}$, from the diameter of the semicircle. An estimated value of $C_{dl}$ is calculated from the equation, $C_{dl} = 1/|Z|\omega$, where $\omega$ is the frequency and $|Z|$ is the total impedance [143]. The results are summarized in Table 10.

It is noted that the uncompensated solution resistances of KCl solutions are small (Table 10). The possibility that the irreversibility of ferricyanide is caused by the iR drop due to the solution resistance, is thus excluded. The double layer capacitances of PVAA/GC and Pt-PVAA/GC are nearly identical in value and are independent of bulk KCl concentration. These capacitances are greater than those at bare GC's by a factor of ca. 2.5. Such a difference could be due to an uncertainty in the evaluation of the double layer capacitance. Thus, no conclusion is attempted from these results.

In contrast, the charge transfer resistance, which is evaluated from the diameter of the semicircle in the Nyquist plot, is highly dependent on the concentration of KCl and the dispersion of the Pt
Table 10. Impedance data* for Fe(CN)$_6^{3-/4-}$ redox at polymeric electrodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$C_{KCl}$ (M)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.5</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>uncompensated resistance (ohm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>38.1(0.5)</td>
<td>21.2(0.4)</td>
<td>9.4(0.2)</td>
<td>7.5(0.8)</td>
<td>5.8(0.1)</td>
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<tr>
<td>B</td>
<td></td>
<td>35.8(0.9)</td>
<td>21.0(0.1)</td>
<td>8.9(0.3)</td>
<td>5.9(0.1)</td>
<td>5.0(0.1)</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>39.7(0.9)</td>
<td>20.2(0.1)</td>
<td>8.6(0.9)</td>
<td>5.9(0.4)</td>
<td>4.8(0.4)</td>
</tr>
<tr>
<td></td>
<td>charge transfer resistance (Kohm)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>2.70(2.00)</td>
<td>1.66(0.43)</td>
<td>0.57(0.06)</td>
<td>0.38(0.02)</td>
<td>0.30(0.08)</td>
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<tr>
<td>B</td>
<td></td>
<td>8.94(1.65)</td>
<td>5.81(1.75)</td>
<td>2.72(0.52)</td>
<td>1.64(0.34)</td>
<td>0.88(0.07)</td>
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<tr>
<td>C</td>
<td></td>
<td>1.91(0.02)</td>
<td>1.29(0.11)</td>
<td>0.44(0.02)</td>
<td>0.34(0.05)</td>
<td>0.35(0.02)</td>
</tr>
<tr>
<td></td>
<td>double layer capacitance ($10^{-5}$ F)</td>
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<td></td>
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</tr>
<tr>
<td>A</td>
<td></td>
<td>3.02(0.91)</td>
<td>1.20(0.16)</td>
<td>0.84(0.10)</td>
<td>0.84(0.03)</td>
<td>0.85(0.03)</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>3.80(1.86)</td>
<td>2.99(1.15)</td>
<td>2.47(0.55)</td>
<td>2.05(0.20)</td>
<td>2.39(0.57)</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>2.97(0.02)</td>
<td>3.09(0.07)</td>
<td>2.83(0.10)</td>
<td>3.22(0.53)</td>
<td>2.39(0.06)</td>
</tr>
</tbody>
</table>

* The experimental data without normalization to an electrode area are reported.
A: bare GC
B: PVAA/GC, 20 hr film
C: Pt-PVAA/GC, 10 µg/cm$^2$ loading
Numbers in the parentheses are the standard deviation.
particles. With the polymer on GC surfaces (electrode B, Table 10), the charge transfer resistance is increased by an average of ca. 4.7. By dispersing Pt particles in the film, the charge transfer resistance is reduced to about the same order of magnitude as that of a bare GC. The reduction in the charge transfer resistance is probably due to the conductivity of Pt particles in the film. The possibility that the Pt particles protrude through the film is not excluded. These results, however, support the arguments described above.

The charge transfer resistance observed for electrode B (Table 10) is the same order of magnitude, within the experimental error, as the ohmic resistance calculated from CV assuming that the peak potential shifts primarily due to an ohmic potential drop. It appears that the charge transfer resistance is one of the primary factors limiting the redox rate of ferricyanide at PVAA/GC. By increasing the KCl concentration or by dispersing Pt particles in the polymer film, one can improve the reversibility of ferricyanide by reducing the charge transfer resistance. The charge transfer resistance is probably the result of a combination of the electronic and the ionic charge transfer resistance. When Pt is dispersed, the electronic charge transfer resistance is reduced significantly. The ionic charge transfer resistance, however, remains to affect the reversibility of ferricyanide at Pt-PVAA/GC.

The relationship of the chronoamperometric current vs \( t^{-1/2} \) has been reported to be affected by the film resistance of either charge or mass transfer [144]. For ferricyanide at PVAA/GC and PVS, linear \( i/t^{-1/2} \) relationships with a Cottrell slope have been observed in 1.0 M KCl with an applied overpotential of at least 400 mV. In 0.1 M KCl
solutions, however, a non-linear \( i/t^{1/2} \) relationship is observed. The applied overpotential of 400 mV should be more than sufficient to overcome any ohmic potential loss. This non-Cottrell behavior for ferricyanide in 0.1 M KCl is reported to be caused by the charge or mass transfer resistance within the polymer film, according to the literature [144]. The chronoamperometric results are consistent with the argument that the charge transfer resistance within the film is responsible for the observed irreversibility of ferricyanide at PVAA/GC.

CONCLUSIONS

It appears that the charge transfer resistance, due to either electronic or ionic charge transfer, is responsible for the irreversibility of ferricyanide and molybdenum octacyanide at PVAA/GC and PVS/GC. Such irreversibility can be improved by the entrapment of positively charged complexes within the polymer films, by the dispersion of Pt micro particles in the films or by the increase of the supporting electrolyte concentration. The results of impedance and chronoamperometric measurements are supportive of the conclusions regarding the charge-transfer resistance. It appears that the redox of an anionic complex with an \( \text{E}^0 \) more positive than 0.7 V is not affected by the presence of the polymer.
CHAPTER VII

SUMMARY

Activation of a platinum or a glassy carbon (GC) electrode for various redox systems can be achieved by a variety of methods. In this dissertation, several activation methods for electrocatalytic purposes are demonstrated. These include cleaning, chemical modification by adsorption, attachment of polymers, covalent bonding of the catalyst to polymeric thin films and dispersion of metal particles into polymeric matrices on the electrode surfaces. The scope for application of these activation methods and the kinetic features of several redox systems at such modified electrodes are presented and discussed.

For As(III) oxidation at a platinum electrode, a clean electrode surface is crucial to the electrode activity. The potential for the formation of lower valent forms of surface oxides depends on the cleanliness of a Pt electrode surface. It is found that lower valent forms of the oxide, presumably PtOH and PtO, initiate and catalyze As(III) oxidation via an ec type reaction mechanism. At a clean Pt electrode, the rates for the formation of these oxides and the subsequent chemical reaction between the oxides and As(III) are sufficiently fast that the cyclic voltammetric peak exhibits properties similar to a reversible, diffusion controlled process. Deactivation of
the Pt electrode occurs, however, at potentials more positive than ca. 1.00 V vs Ag/AgCl. The deactivation is attributed to the formation of the higher oxides of Pt. This argument is supported by XPS data. This deactivation is the result of the slow reaction of As(III) with the higher oxides of Pt. Activity is restored by the removal of the oxide, either by an electrochemical or a chemical reduction. Under-potential deposition of arsenic ad-atoms inhibit the formation of Pt surface oxides. The dissolution of these ad-atoms, however, is complete at ca. 0.85 V.

The postulated mechanism for the As(III) oxidation at a platinum electrode is also supported by RDE results. The data of RDE experiments suggest that the maximum turnover rate for As(III) is attained in the potential region of 0.92 to 1.00 V when the mass transfer of As(III) to a platinum electrode is sufficiently fast. However, as a trade-off between catalysis and deactivation, the optimal potential for As(III) oxidation at a Pt electrode appears to be in the potential range of 0.85 V to 0.92 V. Slow deactivation seems to be unavoidable irrespective of the applied potential for controlled-potential oxidation of As(III). This deactivation is speculated to be due to a surface phase transition of "active" platinum oxide transforming to a more stable crystalline form. A short reduction pulse at a potential of ca. 0.20 V applied periodically during a constant potential electrolysis seems sufficient to maintain the electrode activity. Under fast mass transfer conditions, the rate constants for PtOH formation, which is normalized to surface coverage, and the chemical reaction between PtO and As(III) are estimated to be $0.57 \text{ s}^{-1}$ and $(5.23 \pm 1.59) \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$, respectively.

The other activation methods were mainly applied to a glassy carbon
electrode. Cleanness of a glassy carbon surface might be crucial to the activity of the electrode toward some reactions such as oxidation of ascorbate or hydroquinone [145]. The modifications described herein were applied after glassy carbons were cleaned following a "standard cleaning procedure". The "standard cleaning procedure" has been defined as polishing a GC surface with 1, 0.3, 0.05 μm alumina followed by 15-20 minutes of sonication.

Electrocatalytic reduction of oxygen was studied at a GC electrode adsorbed with \( \alpha,\alpha,\beta,\beta \)-tetra(o-N-methyl-4-carbonyl pyridinium phenyl) porphyrinato cobalt(II) tetraperchlorate (compound I). The reduction of oxygen was also attempted at GC surfaces made by a coating of polyvinyl acetic acid thin films which were covalently bonded with cobalt or iron tetra(o-ami no)pyridyl porphyrin. All three modified electrodes showed electrocatalysis toward oxygen reduction. The overpotential was decreased by ca. 0.50 V. For compound I adsorbed onto GC, the electrode remained catalytic for a long period of time when the solution electrolyte contained ca. 10 μm of compound I to sustain the adsorption equilibrium. For the modified polymeric electrodes, cobalt porphyrin remained active after some 20 days of consecutive electrolysis. Iron porphyrin, on the other hand, became inactive after even one potential scan. The polymer did not stabilize the iron porphyrin.

It was found that spherical metal micro-particles could be electro-chemically dispersed into a PVAA film on a glassy carbon electrode. A PVAA/GC electrode with Pt loading in the range of 5 to 50 μg/cm\(^2\) was capable of electrocatalytically reducing oxygen and generating hydrogen. Pt micro-particles could be dispersed in PVAA/GC by using cyclic voltammetry (CV), single-potential-step and double-potential-step
electrolysis (SPSE and DPSE). The size, distribution and population of the particles were highly dependent on the methods of preparation. Generally, CV and DPSE produced smaller spherical particles and a higher density than SPSE. However, the particle-size distribution produced by the DPSE method was much narrower than that by the CV method. SPSE gave larger and fewer particles with a skewed size distribution.

The particle features are controlled by a nucleation/growth mechanism. At low overpotentials, progressive nucleation is the favored mechanism for Pt deposition which generates particles with size widely distributed size. When a pre-nucleation pulse is applied, the particle size is nearly constant since the instantaneous nucleation mechanism is followed and the rate of the three-dimensional growth on each nucleus is probably the same. Platinum micro-particles can also be dispersed electrochemically in the matrices of a polyvinyl sulfonate coated glassy carbon (PVS/GC) electrode. The dispersed Pt particles in both PVS/GC and PVAA/GC are stable toward ablation by sonication.

Reasonably large surface areas can be achieved by dispersing small particles at a low loading level. The high catalytic efficiency and the excellent stability possible with dispersed micro-particles in the polymer coated electrodes make them attractive for a variety of redox applications. Other metals such as Pd, Ni, Ag, and Cd, and metal composites can also be deposited into PVAA/GC [6]. Thus, fabrication of catalytic electrodes based on a combination of substrates, polymers and electrochemically dispersed metals, mixed metals or metal oxides appears possible.

Both PVAA/GC and PVS/GC electrodes exhibit various electrochemical properties toward the redox of a variety of cationic or anionic
transition metal complexes. The redox of cationic complexes such as iron tetra (2-pyridyl) porphyrin, \((\text{NH}_3)_6\text{Ru}^{3+}\), \(\text{Ru(bpy)}_3^{2+}\), and \(\text{Fe(bpy)}_3^{2+}\) or an anionic complex whose redox potential is more positive than 0.70 V such as \(\text{IrCl}_6^{2-}\), at both polymeric electrodes are reversible. For anionic complexes such as ferricyanide and molybdenum octacyanide, whose redox potentials are in the region of 0.20 and 0.70 V, the polymeric electrodes exhibit irreversible characteristics when 0.1 M KCl is used as the supporting electrolyte. This phenomenon is attributed to the effect of a combination of electrostatic repulsion between the anionic polymer and the complexes, the resistance of ionic charge transfer within the film and the so-called \(\Phi_2\) effect. By increasing the concentration of the supporting electrolyte or by dispersing platinum micro-particles in the polymeric matrices, the reversibility is improved. The results of impedance measurements show that the total charge transfer resistance in the polymeric electrode is significantly decreased when the concentration of the supporting electrolyte is increased or the platinum micro-particles are dispersed.

In 0.1 M phosphates buffered solutions, irreversibility is evidenced at pH values higher than ca. 6. This is speculated to be due to the same effect described above since the carboxylic acid functional groups on PVAA are totally deprotonated at high pH values. The polymeric electrodes show a significant memory effect for redox of the metal complexes. If the electrodes are soaked in a solution containing any of the above cationic complex, the redox of ferricyanide is reversible even though 0.1 M KCl or a solution of high pH value is used as the supporting electrolyte. This reversibility is probably not due to the mediation of the entrapped cations. More likely, it results from the
reduction of the charge transfer resistance through the film and the reduction of electrostatic repulsion due to the imbeddment of the cationic complexes. The results of chronoamperometric experiments also indicate that the rate for the redox of ferricyanide at PVAA/GC is controlled by the rate of in-film charge transfer and mass diffusion.

Exploration for new catalytic electrodes and investigation for thermodynamic and kinetic properties of electrodes toward redox systems have been of great interest to electrochemists. In addition to the known modification methods such as adsorption, covalent linkage and polymeric modification, cleaning activation and dispersion of a second material in a primary electrode substrate, as demonstrated in this work, are found to be significantly effective for electrocatalysis.
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138. The pk of PVAA was measured to be 4.19.


APPENDIX

IR spectrum of compound I
Figure 36.

IR spectrum of compound I.