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PHOTOELECTROCHEMISTRY AND ELECTROCHEMISTRY
OF ELECTROACTIVE LAYERED MOLECULES ON
PHTHALOCYANINE AND METAL ELECTRODE SURFACES

by
Alaganandan Nanthakumar

A Thesis Submitted to the Faculty of the
DEPARTMENT OF CHEMISTRY
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

1986
STATEMENT BY AUTHOR

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______________
NEAL R. ARMSTRONG
Professor of Chemistry
ACKNOWLEDGEMENTS

I would like to express my deep appreciation to Dr. Neal R. Armstrong for his guidance throughout the duration of this project.
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ABSTRACT

A new method of derivatizing Au / GaPc-Cl electrode surfaces by electroactive ferricyanide/ferrocyanide redox couple was developed. This method is unique to Pc electrodes and was based on the interaction between ferricinium and ferricyanide ions in an ethanol/water solvent, which ultimately led to the apparent decomposition of ferricinium ion to form a film similar to Prussian Blue. GaPc-Cl electrodes modified with Poly(vinylferrocene) were shown to mediate the oxidation of ascorbic acid. The deposition process induced p-type character on the Pc electrode and this rectifying behaviour was utilized to irreversibly oxidize ferrocene and hence trap charge in the form of ferricinium ion. The adsorption of electroactive and electroinactive ions in the Au MPOTE surface was also studied with the view of generating useful electrode properties.
CHAPTER 1

HISTORY AND THEORY

Introduction

Modification of electrode surfaces has generated tremendous interest in recent years with the recognition of the advantages and potential of polymer modified electrodes when compared with monolayer attachment of redox species. Recent discoveries have laid the foundation for studies leading towards tailoring the electrode surfaces to suit a particular objective such as electrocatalysis and energy conversion (1).

Our research group has been involved in the preparation and characterization of thin film trivalent and tetravalent metal phthalocyanine photoelectrodes (2,3,4). One of the most promising photoconductor systems is the electrode prepared by sublimation of chloro gallium phthalocyanine (GaPc-Cl) on a metallized plastic optically transparent substrate (MPOTE). The primary objective of my research project was to develop a method to derivatize or attach an electrochemically active layer on the surface of these electrodes. Such layered materials would act as a model system for xerographic photoconductors and solid state electrochemical photovoltaic cells with which charge
transport between the phthalocyanine layer and the redox layer could be studied.

The ferricyanide-ferrocyanide aqueous electrochemical couple is one of the most widely studied due to its rapid electron transfer kinetics and chemical stability. This study describes a method to anchor this redox couple on the Au-MPOTE and GaPc-Cl modified electrodes by making use of a unique interaction between ferricenium ion and ferricyanide ion. Electrochemical and IR spectroscopic data have been used to put forward a chemical model for this interaction. Various other thin film coatings based on similar ion-molecule interactions have been developed with the view of using them as catalytic surfaces.

Modification of Metal Electrodes by an Electroactive Overlayer: History

The interest in modified electrodes was generated in the early 1970's where the prime objective was the development of a catalyst for sluggish organic reactions and the search for an alternate source of energy by using photoelectrochemical reactions at these electrodes (5). The early attempts were focused in the covalent attachment of monolayers of electroactive molecules and the chemisorption of organic molecules on metal and semiconductor electrode surfaces. Lane and Hubbard studied the chemisorption of alkenes on Pt electrode surfaces (6,7). Chelates connected
to the electrode surface through an olefinic side chain allowed metals to be selectively chemisorbed. The covalent attachment of molecules was based on linking organic and organometalic redox molecules via hydroxyl and other functional groups on metal and metal oxide surfaces (Review articles by Murray (5), Albery and Hillman (8) summarize the various methods used to anchor a wide spectrum of molecules using this approach). Although rapid progress in this pursuit was achieved, it was soon evident that monolayer attachment severely limits the usage of these electrodes for any practical purposes. In the late 70's and early 80's polymer modified electrodes captured the interest of many scientists due to their potential advantages over monolayer attached electrodes (9-12). Since the redox ions are incorporated within the polymer matrix, rapid oxidation or reduction of several monolayers is possible. The propagation of charge was postulated to be via exchange of electrons between neighbouring sites and hence was termed as the "hopping mechanism" (1,5,13). The more popular redox ions used for this purpose include ferrocenes, ferricyanide/ferrocyanide, viologens (i.e., polymers containing N,N-alkylated bipyridines) and bipyridine complexes of ruthenium.
Methods of Attaching Redox Polymers on Electrodes

The following approaches are generally used to immobilize redox ions on electrodes. 1. Electrostatically binding large ions such as ferricyanide and methyl viologen by generating a permanent +ve or -ve charge (fixed ionic groups) within the polymer matrix. An example for this method is the binding of ferricyanide ions to protonated polyvinyl pyridine (14,15). In this case the film becomes ionic when exposed to acids. This method, although simple, is limited by the leaching of the bound ions into the electrolytic solution by ion exchange processes.

2. Another approach was to attach a polymer in which the monomer itself shows reversible electrochemical behaviour. Since the redox center is a permanent part of the polymer backbone the electroactivity was expected to be maintained for a longer period of time. These polymers are generally overlayed on the electrode surface by dissolving the polymer in a suitable solvent and allowing the evaporation of the solvent from the electrode surface (drop evaporation). A more uniform coating is achieved by evaporating the drop from a spinning electrode (spin coating), however this method is limited to very thin films. Poly(vinylferrocene) and polymers of bipyridine complexes of ruthenium are examples of such polymers. Poly(vinylferrocene) has
been overlayed by spin coating (16) and drop evaporation (17,18) techniques.

3. The electrochemically initiated polymerization of monomer molecules has been used to generate both electroactive and conductive polymers on electrodes. Electrochemically generated polymers of heterocyclic compounds such as polythiophene (19,20) and polypyrrole (21,22) have been well studied due to their metal like properties (high electrical conductivity). These polymers are deposited under oxidative conditions (i.e., holding at positive potentials or continuous scanning through positive potentials). Electroactive polymers such as polyruthenium bipyridine (23,24) and polyviolegens (25) have been electro-generated under reductive conditions. Electrochemically deposited films are generally free of pin holes whereas other techniques of deposition generally require several layers of material to be completely nonporous. Poly(vinylferrocene) could also be electrochemically deposited by oxidation to the less soluble ferricinium state from nonaqueous solvents (10,26).

4. Exposing vapors of monomers to a radio-frequency plasma discharge is a well known method to modify electrodes with a polymeric overlayer. Poly(vinylferrocene) which is a subject of my project has also been deposited by plasma polymerization of the vinyl monomer (27,28).
The major part of my project involved developing ways to attach electroactive layers on Au MPOTE electrodes and apply the same methodology to generate electroactive layers on phthalocyanine modified electrodes, or to generate electroinactive (nonconductive) polymers to passivate the exposed Au substrate on porous Pc-modified electrodes. Such bilayer systems would act as models for photoconductors in electrophotographic devices. Initially my studies were directed towards attaching poly(vinylferrocene) on Au and phthalocyanine electrodes and to electrochemically characterize these modified electrodes. Later studies on the interaction of these electrodes with ferricyanide ions in solution led to the development of a new technique to electrochemically deposit the ferricyanide/ferrocyanide couple, which was based on the interaction of ferricinium with ferricyanide ions. Although the electrochemical activity of the ferrocene/ferricinium couple was apparently lost by this interaction, the incorporation or deposition of the ferricyanide/ferrocyanide ions could be controlled electrochemically to vary the electroactivity or the thickness of the film due to the slow reaction rate. This was found to be a unique technique for the deposition of electrochemically reversible and stable redox couples on phthalocyanine (Pc) electrodes. The methods described earlier are not suitable, due to the dissolution of Pc in
nonaqueous solvents or its instability when subjected to a continuous potential scan treatment. Fairly non-porous, films could be deposited until the growth of the film was slowed or terminated after a particular thickness due to the resistive nature of the film.

Another aspect of my research was to investigate the possible practical applications of this electroactive film overlayed by this new technique. The electrocatalytic oxidation of ascorbic acid mediated by the ferricinium-ferricyanide film was studied by rotating disk voltammetry. The charge trapping of ferricinium ion on p-type Pc electrodes was also investigated as a possible chemical sensor.

**Semiconductor Electrochemistry**

The electrochemistry of semiconductor electrodes is a relatively new field and requires an understanding of the principles behind solid state physics and electrochemistry. The earlier interest in semiconductor electrochemistry could be attributed to the experiment by Fujishima and Honda (29) by which they demonstrated the photolysis of water into hydrogen on n-type TiO₂ electrodes. This result captured the interest of many scientists due to the energy crisis which prevailed during that period and the possibility of using hydrogen as a source of energy. Since then such studies have been extended from well ordered single crystal
electrodes to polycrystalline organic and inorganic semiconductors. In a semiconductor the direct overlap of all the highest occupied molecular orbitals (HOMO) leads to the formation of a closely spaced band of energy levels called the valence band and the overlap of the lowest unoccupied molecular orbitals (LUMO) forms the conduction band. In contrast to metals, both bands are separated by an energy gap which is termed the band gap. The energy scale is calibrated with respect to a free electron in vacuum which is assumed to have zero energy. In an intrinsic semiconductor the band gap is free of allowed energy states. However, even in semiconductors which have a high degree of molecular and atomic order, the atoms on the surface would have several imperfections associated with them. These arise since the atoms on the surface are surrounded by fewer atoms than in the bulk and hence are coordinatively unsaturated. The electrons associated with these atoms would have different energy than the valence or conduction band and would introduce states within the band gap. A surface state formed by the removal of electron density in the HOMO causing the formation of holes or vacancies would have an allowed energy level close to the valence band. Such states could be formed by the adsorption of gases or ions containing electronegative atoms or by the introduction of impurity atoms. Similarly an increase in electron
density in the LUMO near the surface would introduce an energy level in the band gap closer to the conduction band. Such states are formed by the removal of electronegative atoms from the lattice (e.g., oxygen vacancy) or other lattice imperfections on the surface. Electrons or holes in these interband gap states could be excited into the conduction band or valence band by thermal energy or illumination with light. The Fermi level is the average electrochemical energy of an electron entering or leaving the solid and its position in the band gap is dependent on the nature of the dopants in the bulk. A dopant which is n-type moves the Fermi level close to the conduction band and p-type doping moves it towards more positive energy (closer to the valence band). The position of the Fermi level can also be moved by applying a potential to the semiconductor (versus some external reference). The Fermi level is a statistical energy term and is an energy level at which the probability of electron occupancy is equal to 0.5, and should not be viewed as an allowed state within the band gap.

The Semiconductor-Electrolyte Interface

When a semiconductor is in contact with an electrolyte an electron associated with a surface atom experiences a different potential energy when compared to a corresponding electron in a bulk atom, due to electrostatic interaction with ions in solution. Unlike a metal a
semiconductor is limited in the amount of charge carriers it normally possesses. This causes an unequal distribution of charges or a potential gradient in the surface region which is termed the space charge region. The thickness of the space charge region could vary from 500-1500 Angstroms and the potential gradient in this region could be high as $10^6$ V/cm. The application of extreme positive or negative potentials would move the Fermi level into the band regions. The appearance of Faradaic currents under dark conditions is an indication of such phenomena. For a p-type semiconductor, if the potential is moved negative of the conduction band inversion occurs. By inverting the surface, excess electrons are added to the conduction band. Accumulation occurs when the Fermi level is moved positive of the valence band of a p-type semiconductor. Both accumulation and inversion cause metal like behaviour in semiconductors since at equilibrium, the HOMO and LUMO of the redox ion overlaps with the valence and conduction bands respectively.

The Kinetics and Thermodynamics of Electrochemical Reactions at Semiconductor Electrodes

The kinetics of a photoelectrochemical or electrochemical reaction at semiconductor electrodes is dependent on the efficiency of charge injection from the electrode into the electrolyte solution or an electroactive
overlayer. Hence the magnitude of photocurrent generated by illumination is dependent on the potential gradient within the space charge region, the amount of charge carriers and the quantum efficiency (number of free carriers generated per incident photon). If the surface or defect states are deep within the band gap they could act as traps for the photogenerated carriers causing a reduction in the current. For solar energy conversion purposes a semiconductor with a low band gap (1.5 ev) is preferred since it absorbs most of the solar spectrum and hence produces a higher quantum efficiency for energy conversion.

The open-circuit photopotential (V_{oc}) of a photo-electrochemical reaction at a semiconductor electrode is dependent on the relative positions of the Fermi level and the E^0 of the contacting electrolytic medium. When in contact with an electrolyte solution or an electroactive overlayer both these levels approach an equipotential state at equilibrium which in turn manifests as a potential gradient in the space charge region (band bending). The potential required to bring the band edges back to the original flat band condition is equal to the maximum photopotential obtainable with that redox couple. The presence of deep surface or defect states will diminish the magnitude of the photopotential by making the potential gradient to be shallower.
Since the maximum output power of a photoelectrode is equal to the product of the short circuit photocurrent and the open circuit photovoltage, a balance between the two parameters has to be achieved for maximum energy conversion efficiency. In applications which do not require the generation of a photopotential, such as in a xerographic photoconductor, the photocurrent is maximized by the application of large potentials.

**Semiconductor Properties of Phthalocyanine Modified Electrodes**

Recent studies done indicate that trivalent metal phthalocyanines such as GaPc-Cl and InPc-Cl show predominantly p-type behaviour in their heavily oxygen doped states (30). The voltammograms are generally reversible under illumination for most redox couples at about millimolar concentrations in aqueous solutions, indicating the excellent photoconducting properties of these electrodes. The number of charge carriers created under illumination is large due to the favorable band gap (1.5 eV) and the excellent ordering of the phthalocyanine molecular stacks results in fewer defects (charge traps) than that expected for most organic thin films. The thermodynamic properties of the electrode system are extremely sensitive to the nature of the substrate and conditions of sublimation. The apparent $E^0$ values of redox couples at illuminated
electrodes move towards more positive potentials for electrodes kept exposed to atmospheric conditions for long enough periods (weeks or months). Among the phthalocyanine modified electrodes studied in our research group vanadyl phthalocyanine and titanyl phthalocyanine show the most p-type behaviour. The p-type behaviour is partially attributable to the uptake of oxygen during film growth.

**The GaPcCl Modified Electrode as a Model Electrophotographic System**

As mentioned earlier, for maximum power conversion efficiency both open circuit photo voltage and short circuit photo current in a Pc-solar cell have to be optimized. Since this imposes a serious problem a reasonable alternative would be to use these phthalocyanine thin films in applications which would require the optimization of only one of these properties. In photoconductor applications, as in electrophotographic systems, the optimization of the energetics at the interface is not as important as in solar cell applications.

As shown in Figure 1 the photoconductor in a photocopier consists of a charge generation layer (CGL) and a polymeric charge transport overlayer (CTL). Upon illumination charges (holes or electrons) are generated within the CGL which are subsequently injected into the CTL by the application of a large \((10^4-10^6 \text{ V/cm})\) potential
Figure 1. Multilayer photoconductor used in electro-photographic systems. Illumination generates an electron-hole pair in the CGL. The hole is then injected into the CTL and is propagated to the surface of the CTL by a solid state redox process where it is discharged.
gradient. The injected charge is propagated through the CTL and is discharged on the surface. The pattern of discharge duplicates the image of the letter to be copied and could be developed by depositing a toner of opposite charge on the surface. After this development is complete, paper contacts the toned image and the toner is electrostatically transferred to the paper (31). Pyrazoline and carbazole based polymers are some of the polymers used as the CTL in industrial applications (32-34). In order for a photoconductor to be successful in this application it should exhibit the following properties.

1. The CGL should show a high quantum efficiency for charge pair formation upon illumination with visible to near-IR light.

2. There should be high charge injection efficiency from the CGL to the CTL.

3. There should be fast charge propagation within the CTL.

4. The discharge pattern should be reproducible (i.e., no cross interaction between two neighbouring discharge sites).

Figure 1 could also be viewed as a possible electrochemical analog of this system. The CGL is a phthalocyanine thin film electrode and the CTL is an electroactive overlayer with a reversible redox couple. The
electric field gradient is provided by the space charge region which could be high as $10^6 \text{V/cm}$. Photoelectrochemical data could be used to evaluate the above mentioned properties for such a modified electrode system.

In order to study electrochemical models of a photoconductor in an electrophotographic device a semiconductor photoelectrode has to be modified with an overlayer of redox polymer. Wrighton et al. derivatized n-type GaAs photoelectrodes with (1,1'-ferrocenediyl)-dichlorosilane to produce surface attached ferrocene centers (35). More recently they attached a cobaltocenium polymer on a p-type Si photoelectrode (36). Apart from these examples few other attempts have been made to modify semiconductor photoelectrodes with an electroactive overlayer probably due to the nonavailability of low bandgap electrodes which exhibit a reversible photoelectrochemical response. GaPc-Cl was chosen as the best photoconductor (CGL) for this study since it showed reversible behaviour with most redox couples and showed negligible dark current.

The electrodes were made by methods already developed by the Armstrong research group (2-4). In order to complete the electrochemical analog of a xerographic model the following modifications had to be implemented.

1. Passivation of all the exposed Au sites through pores in the Pc film which contributed to dark currents.
2. The existing methods of overlaying electroactive polymeric layers were not suited for phthalocyanine electrodes due to the corrosive nature of the non aqueous solvents employed. Hence an alternate method had to be developed.

**Cyclic Voltammograms of Surface Attached Redox Ions**

Figure 2 illustrates the expected cyclic voltammogram of a monolayer of surface attached redox ion or molecule. The current \( i \) for a reversible monolayer redox surface film is given by Equation 1 (37,38).

\[
(1) \quad i = -4i_p \exp(x)/(1+\exp(x))^2
\]

where \( i_p \) is the peak current and \( x \) is given by Equation 2

\[
(2) \quad x = nF(\bar{E} - \bar{E}_{surf}^0)/RT
\]

Several parameters in the voltammetric peak are generally used to evaluate the kinetic properties of a surface attached redox film. The difference in the positions of \( \bar{E}^0 \) for both anodic and cathodic peak currents \( (E_{p,a} - E_{p,c}) \) can be used to estimate the rate of charge propagation. For monolayer films the peak-to-peak separation is zero since the currents are not due to a diffusion limited process. However, even in multilayered polymer modified electrodes a separation much less than that expected for Nernstian (diffusion limited) behaviour is
Figure 2. Cyclic voltammogram of a surface attached electrochemically active molecule.
observed (39). This implies an extremely rapid charge propagation mechanism. A mechanism which involves the hopping of electrons between two neighbouring redox sites has been put forth to account for this rapid propagation of charges (1,13). The peak-to-peak potential separation increases when the molecular and atomic order of the film is disturbed.

The dependence of peak current ($i_p$) on the scan rate ($v$) can also be used to understand the kinetic behaviour of electroactive films. For monolayer films the peak current is directly proportional to the scan rate ($i_p \propto v$). The relationship is given by Equation 3.

$$i_p = n^2 F^2 A c v/(4RT)$$

where $c$ is the total electroactive surface coverage and $A$ is the area of the electrode.

For films containing several layers of redox active molecules the relationship given by Equation 3 is observed only at low scan rates (39). The low scan rate overlooks the slight differences in the energetics between different redox sites causing this behaviour. At high scan rates however, this difference becomes apparent and the scan rate dependency approaches that of a diffusion limited process ($i_p \propto v^{1/2}$). Although the redox sites are immobilized within the film the laws of diffusion can be applied in
order to evaluate the kinetic properties of these films. The electron hopping is mathematically represented by diffusion laws and an effective diffusion coefficient \( D_{ct} \) can be calculated \((40,41)\).

The full width at half maximum (FWHM) of the current peaks is also a useful parameter in the evaluation of the charge transport properties. For a reversible surface electrochemical reaction the \( E_{FWHM} \) is given by

\[
E_{FWHM} = 90.6/n \text{ mV.}
\]

Experimental \( E_{FWHM} \) values could differ from this value due to several reasons including slight differences in surface structure, permeability of solvent, etc. which cause the formation of redox sites having a narrow spectrum of \( E^0 \) values \((42,43)\). Sharp peaks generally indicate attractive forces between the redox centers which makes the probability of collision between neighbouring sites to be high and equal causing a smaller range of \( E^0 \) values.

The area under the voltammetric peak is a measure of the amount of electroactive molecules present. The area is related to the amount \( (\text{moles/cm}^2) \) by Equation 4.

\[
(4) \quad c = \frac{Q}{nFA}
\]

where \( Q \) is the charge in coulombs calculated by integrating the voltammetric curve, \( A \) is the area of the electrode and \( F \) is 96,500 coulombs. This relationship could only be applied
to films which show a linear peak current vs scan rate dependency.

Several factors effect the shape of the cyclic voltammograms. They are: 1. The size of counter ions: The surface electrochemical reaction generally involves the movement of ions from the supporting electrolyte in order to maintain charge neutrality within the electroactive film. Hence the nature of these ions determines the shape of the voltammograms.

2. The solvent used for electrolysis: Polymers are permeable to certain solvents but are impermeable to others. The polymer film shows more swelling in the presence of permeable solvents causing rapid electron and ion transport behaviour in the voltammograms. Attractive forces between molecules caused by a poor solvating medium causes smaller \( E_{\text{FWHM}} \) (sharper peaks) in the voltammogram. Water is a poor solvating medium for poly(vinylferrocene) [PVF] due to the low polarity of the neutral ferrocene centers. However the oxidation of PVF generates fixed positive charges (ferricinium ions) within the polymer thus making water a more permeable solvent.
3. Method of coating: Several methods are generally used for coating the films. They include drop evaporation, spin coating, plasma polymerization and electrochemical coating. A slow controlled deposition is preferred since it causes a more ordered film with few pin holes. The presence of multiple voltammetric peaks is an indication of sites with different electron transfer energetics. The electrochemical technique is generally preferred since the growth of the film can be controlled, it is more strongly adherent to the metal and it is generally non-porous.

4. The thickness of the film: The ordered nature of the film can be maintained only for thin films. As we overlay thicker layers the electroactive sites on the surface tend to have slightly different $E_0$ values than the sites in the bulk. This causes tailing and broadening of the voltammograms since all electroactive sites in the film are not in equilibrium with the electrode potential (5). The peak currents also approach the square root dependency on scan rate, indicative of diffusion limited behaviour (slower rate of charge propagation).

**Electrochemical Reactions at a Metal/Electroactive Film/Electrolyte System**

Figure 3 illustrates the possible electrochemical reactions which could occur when an electroactive film is in
Figure 3. Possible electrochemical reactions occurring in a metal electrode/electroactive film (Fe$^{2+}$/Fe$^{3+}$)/electroactive electrolyte (R/O) system.
contact with a redox electrolyte. The electroactive film is loaded with Fe\textsuperscript{2+} / Fe\textsuperscript{3+} redox couple and is in contact with an electrolyte containing a redox ion R or O and a supporting electrolyte AX. For such a system the following steps could take place: 1) Diffusion of electrolytic ions (R/O) through the film to undergo reaction at the metal-film interface (membrane diffusion - Fig. 3a). 2) Migration of R or O through pin holes in film to react at the metal-film interface (Fig. 3b). 3) Electroactivity of the film itself and movement of counter ions in and out of the film to maintain charge neutrality (redox activity of Fe\textsuperscript{2+} / Fe\textsuperscript{3+} in film - Fig. 3c). 4) Reduction or oxidation of electroactive ions (R or O) at the film-solution interface mediated by charge transport through the film (Fig. 3d). In order for the Fe\textsuperscript{2+} / Fe\textsuperscript{3+} redox couple to mediate the oxidation of R the E\textsuperscript{0} of Fe\textsuperscript{2+} / Fe\textsuperscript{3+} couple should be more positive than the E\textsuperscript{0} of R/O.

Rotating disk voltammetry is an excellent technique to study the mechanism of charge transport and was first used to study mediated electrocatalytic reactions by Albery et al. (44) and Oyama and Anson (45). An increase in the rotation rate causes the Levich layer to be smaller, causing the limiting current due to oxidation of R or reduction of O to obey the following expected behaviour (Equation 5),

\[
(5) \quad i_{lev} = AnFD_s^{2/3} v^{-1/6} C_s w^{1/2}
\]
where A is the area of electrode, $D_s$ the diffusion coefficient of the ions in solution, $C_s$ is the bulk concentration of R and $w$ is the rotation rate. Deviation from Levich behaviour is observed for partial control of charge transport by diffusion through the film. The membrane diffusion theory assumes that the electroactive ion in solution dissolves into the polymer film at the film solution interface and subsequently diffuses within the film with a diffusion coefficient of $D_{s,\text{film}}$. The partition coefficient for this dissolution is given by $P = C_{s,\text{film}} / C_s$. The limiting current for such a mechanism would be given by Equation 6.

\begin{equation}
\frac{1}{i_L} = \left[ \frac{1}{(nFAD_{s,\text{film}}PC_s)} \right] + \left[ \frac{1}{(0.62nFAD_s^{2/3}w^{-1/6}C_s^{1/2})} \right]
\end{equation}

where $D_{s,\text{film}}$ and $P$ are the diffusion and partition coefficients for R in the film respectively and the right hand factor is the Levich term (46). The non linearity of the Levich plot ($i_L$ vs $w^{1/2}$) is consistent with partial control of current through the membrane. According to equation 6 for diffusion through the membrane a plot of $i_L^{-1}$ vs $w^{-1/2}$ is linear and the intercept of this plot ($1/w^{1/2}=0$) gives the flux through the film.
The diffusion of ions through pores and through membranes are generally hard to differentiate. Theories have been developed to study diffusion through pores \((47,48)\). Theories put forward to explain pore diffusion also show linear behaviour for \(i_L^{-1} \) vs \(w^{-1/2}\) plots and hence are similar to membrane diffusion theories.

A similar relationship holds for a catalytic reaction mediated by the oxidation of the electroactive ion in film and the expression for the limiting current is given by the Koutecky-Levich equation (Equation 7- \(45,46,49,50\)).

\[
\frac{1}{i_L} = \left[ \frac{1}{nFAk_{ch}c_s} \right] + \left[ \frac{1}{0.62nFAD_s^{2/3}v^{-1/6}w^{1/2}c_s} \right]
\]

where \(c_s\) is the concentration (coverage) of electroactive sites \((\text{in moles/cm}^2)\) bound to the surface and \(k_{ch}\) is the rate constant for the catalytic reaction between \(R\) or \(O\) and the catalytic sites in the film. This equation shows that a plot of \(1/i_L\) vs \(1/w^{1/2}\) is linear and the intercept \((1/w^{1/2}=0)\) gives an estimate of the electrocatalytic rate \((k_{ch}T_c \text{ cm sec}^{-1})\). If the catalytic reaction is the rate limiting step the \(i_L^{-1} \) vs \(w^{-1/2}\) relationship is observed (inverse Levich plot) and if the solution mass transport (Levich) flux is small the Levich behaviour holds. Generally at low rotation rates the Levich layer is thick hence this term becomes the rate limiting step, however at high rotation rates the Levich flux is large causing the
much slower catalytic reaction between the sites within the film and R to dictate the electrochemical behaviour (inverse Levich plot). The derivation of the Koutecky–Levich equation takes only the kinetic steps involved in the transport of R or O from the solution to the electrode (the Levich flux) and the catalytic reaction step into consideration (51). Therefore the above mentioned relationships are slightly altered by diffusion of ions through pinholes (pores) and through the membrane and the mass transport of R or O in the solution. Theoretical treatments including all these terms have been developed by Anson (52,45,49), Saveant (53,54) and Murray (55,56). The catalytic reaction is assumed to be first order and a reaction rate of about $3 \times 10^5 \text{M}^{-1} \text{s}^{-1}$ is considered to be fairly rapid (46). However for these films to act as a catalyst for practical purposes each site should be able to undergo a catalytic cycle repeatedly (high turnover rate). This is one of the frequently encountered problems in working with these systems, since the catalytic activity of the redox centers in the film is not maintained for long enough periods. Nevertheless, these modified electrodes provide a model system which could be utilised to study the mechanism of charge transport and catalysis.
CHAPTER 2

MATERIALS AND METHODS

Electrochemistry

Cyclic voltammetric measurements were made with a conventional 3 electrode potentiostat (Eco 551). A PAR model 174A Polarographic Analyser was also used for certain experiments. The potential scale was referenced to the saturated Ag/AgCl electrode (saturated with KCl). This electrode was separated from the analyte solution by a quartz frit. A coiled Pt wire was used as the auxiliary electrode. The water used to prepare the various electrolyte solutions was purified by double distilling deionized water from alkaline permanganate solution followed by storage in a Nalgene vessel. Solutions were purged of oxygen before use by vacuum degassing of the solutions. For the rotating disk experiments, 99.95% nitrogen was bubbled through the electrolyte for at least 20 minutes prior to analysis.

Electrode Preparation

The Au electrode was in the form of a thin film Au metallized plastic sheet (Au-MPOTE), obtained from the Sierracin Corporation. The electrodes were prepared by cutting 0.5 to 0.75 inch squares from the sheets, and
ultrasonically cleaning them in ethanol and water. The resistance of the films was measured before use by placing the electrical contacts at points 2 cm apart on the surface of the film and only films with a resistance less than 30 ohms were used for experiments.

The rotating disk electrode was made by Pine Instruments (geometric area= 0.196 cm$^2$). This electrode was cleaned by dipping for a few minutes in a chromic acid solution or polishing at a high rotation rate with alumina.

GaPc-Cl was deposited on Au MPOTE electrodes by suspending them about 2 inches above the bottom of a 3 inch diameter glass cylinder by an aluminium masking plate, held in place by indentations in the wall of the vessel. Several milligrams of GaPc-Cl was spread evenly across the bottom of the vessel. The vessel was placed on a heating mantle and glass wool was packed around the bottom. The vessel was then evacuated to 10$^{-6}$ torr and the temperature was increased until a steady temperature and sublimation was achieved.

**Photoelectrochemistry**

The light source used was a 450 watt Xenon arc lamp (Oriel) passed through a 470-nm long pass filter and a 4-inch water IR filter, creating a polychromatic (470-900 nm) radiation source of approximately 100-150 mW/cm$^2$. 
Synthesis of GaPc-Cl

The synthesis of GaPc-Cl was performed by slight alterations in the method described by Linkous (57). The experimental setup was similar except for the absence of the Vigreux column, (used to distill off benzene) which was not necessary since benzene was not used as a solvent. Nitrobenzene was distilled and stored in the presence of molecular sieves (type 4A). A 5 g ampule of GaCl₃ (99.95 % - Aldrich) was solvated in just enough nitrobenzene inside a glove bag which was purged with nitrogen several times before use. Phthalonitrile (1,2 dicyanobenzene) was also dissolved in nitrobenzene (phthalonitrile:GaCl₃ =4:1 - mol ratio). The GaCl₃ solution was placed in a round bottomed flask and heated until the nitrobenzene reached its boiling point (195 C). The phthalonitrile solution was then added slowly without allowing the temperature of the reaction mixture to drop below 180 C. The reaction mixture was then continuously refluxed for about 2 days until it turned from a purple to bluish green in color. The product was filtered, washed with benzene then with ethanol and was Soxhlet extracted for 2 days using ethanol as the solvent. The product was predominantly blue in color with slight traces of purple and was further purified by repeated sublimation.
Deposition of PVF on Au MPOTE and Au/GaPc-Cl electrodes

PVF was dissolved in toluene (1 mg/ml) and a few drops (from a micro pipet) were allowed to evaporate from the electrode surface. The electrode was placed in a beaker saturated with toluene vapor. This would ensure a slow growth of the film and hence a more uniform coating. The spin coating technique was not used since only extremely thin coatings could be overlayed.

Chemicals

All salts used in supporting electrolytes were ACS Reagent Grade and were used without further purification. Ferrocene was purified by sublimation of the Reagent Grade material by gentle heat and atmospheric pressure and hydroquinone was recrystallized from water.

Other methods

The scanning electron microscope (SEM) was an ISI DS-130, operated at an electron gun voltage of 20 kV. The samples were mounted on grounded, SEM studs with double stick tape and were sputter coated with a 300-Angstrom Au-Pd alloy film and a conductive connection to the stud was made with colloidal graphite.

Infra-red spectra were recorded using a Perkin-Elmer 983 instrument. The samples were pressed into a KBr disk for analysis.
CHAPTER 3

RESULTS AND DISCUSSION

**Ferrocene/Ferricinium Redox Couple**

The one electron oxidation of ferrocene leads to the formation of the ferricinium ion. The highest occupied molecular orbital of ferrocene contains metal localized d-electrons which give up the one electron to change the oxidation state of iron from Fe\(^{2+}\) to Fe\(^{3+}\), without changing the charge on the cyclopentadienyl rings. The electroactivity is reversible in most non-aqueous solvents with an \(E^0\) at + 0.4 volts vs SCE. Various methods have been developed to attach ferrocene on metal and metal oxide surfaces (5). Poly(vinylferrocene) [PVF] in which ferrocene units are linked by vinyl groups has been electrochemically well characterized due to the permanent electroactivity and ease of coating the polymer on electrode surfaces (17,18,27,28,40). The electrochemical characterization was performed on both Au MPOTE and GaPc-Cl modified with PVF.

\[
\text{Au/ PVF / KNO}_3
\]

Figure 4 shows the voltammogram of a poly(vinylferrocene) coated Au-MPOTE electrode. The polymer was deposited by the drop evaporation technique using toluene as
Figure 4. C-V of Au/PVF/0.2 M KNO₃. Scan rate = 50 mV/sec.
the solvent. The amount of electroactive ferrocene which could be overlayed by this technique is limited to about $5 \times 10^{-8}$ mol/cm$^2$. This limitation seems to be due to the physical limitations of producing a thick, non-porous PVF layer over the entire Au surface. The shape of the voltammogram is in agreement with previously reported data (28,58). As shown in Figure 5 the oxidation of ferrocene results in the migration of anions into the polymer film in order to maintain charge neutrality. The oxidation peak at $+0.53$ V vs Ag/AgCl is extremely narrow with an $E_{FWHM}$ of 38 mv and is an indication of the oxidation of isoenergetic ferrocene units at close proximity to each other. Due to the ionic nature of the oxidized film, the internal polymer network undergoes reorganization bringing the ferrocene molecules close to each other to facilitate the propagation of charges across the film. The neutral state of the reduced film causes expulsion of the counterions (Figure 5) and therefore less attractive forces are present. This results in a fairly wide spectrum of $E^0'$ values for reduction, which is apparent in the voltammogram as a broad reduction wave (Figure 5). This phase-like behaviour is observed only in aqueous medium due to the poor solvating ability of water within the polymer film, which causes the $\text{Fc}^+\text{X}^-$ to have different reduction energetics than the ferrocene (Fc) molecule. In addition to the broadened
Figure 5. Molecular interactions in oxidized and reduced PVF films. The electrode is in contact with an electrolyte AX.
reduction peak there is a separation of the peak positions for the oxidation and reduction waves.

The shape of the voltammogram is also dependent on the size of anion (counter ion) present in solution, which is not surprising due to the movement of counter anion in and out of the film during the redox process. In the presence of large ions such as the phthalate anion the peaks get broader and the electroactivity diminishes after several scans. KNO₃ appeared to be the best candidate to be used as a supporting electrolyte since the electroactivity of ferrocene is maintained for longer periods.

Au/GaPc-Cl/PVF/0.2M KNO₃

The same application method was applied to overlay the PVF film on Au/ GaPc-Cl surfaces. The voltammogram of such a modified electrode under dark and light condition is shown in fig 6. The initial scan under dark condition gives a large oxidation wave at + 0.9 V vs Ag/AgCl and shows negligible electroactivity for the reverse scan from + 0.9 V to 0.0 V indicating the absence of electrons for the reduction process consistent with a surface-modified p-type semiconductor photoelectrode. The magnitude of the oxidation current diminishes on repetitive scans between 0.0 and + 1.0 V. Figure 6 (A) is the voltammogram after 3 scans and Figure 6 (B) is the C-V under illumination from the back side of the cell. As shown in the voltammogram the
Figure 6. C-V of Au/GaPc-Cl/PVF/KNO₃. (a) In the dark, after 3 potential cycles. (b) Illumination (BS), after (a). (c) In the dark, first scan after treatment (b). Scan rate = 50 mV/sec in all cases.
reduction process is now enhanced under illumination. Figure 6 (C) is the voltammogram for the next scan which is performed under dark conditions and shows the reappearance of part of the electroactivity for the oxidation of ferrocene. In summary, electrons could be injected into the Pc film in the dark, but could not be reintroduced into the PVF film until illumination. After illumination, dark oxidation could once again be observed. Figure 7 shows the voltammogram of the Pc electrode before the modification treatment in contact with potassium ferricyanide (2 mM) solution. The almost complete absence of dark currents indicates that the p-type behaviour of the Pc film is introduced only during the PVF modification procedure and was not a property of the Pc film itself. The large contrast between light and dark currents demonstrates the excellent photoconducting properties of the GaPc-Cl electrode.

A model using energy band diagrams to explain the above observations is illustrated in Figure 8. The possibility of charge transfer from the metal substrate to the polymer film to cause the observed electroactivity of ferrocene could be rejected due to the absence of a reduction wave and the loss of electroactivity of ferrocene oxidation on repetitive potential scans. The PVF deposition process apparently introduces defect states on the surface
Figure 7. C-V of the GaPc-Cl electrode used in Figure (6) (before modification). The redox electrolyte was 2 mM potassium ferricyanide in 0.2 M KNO₃. D=dark, L=light from backside of the cell. Scan rate = 50 mV/sec.
Figure 8. Band model to explain charge trapping of ferricinium ions on p-type Pc electrodes. VB=valence band, CB=conduction band, h⁺=holes, e=electrons.
of the phthalocyanine whose energy levels are distributed just above the valence band edge. Since the energy level for ferrocene oxidation is positive of the valence band edge the oxidation would not occur in the absence of these mediating states even under accumulation conditions. A probable candidate for these states are displaced Pc molecules on the surface caused by the etching ability of the toluene solvent. These molecules could be held within the polymer matrix at the Pc-PVF interface.

Upon illumination the electrons are promoted into the conduction band to make the reduction process energetically more favourable (Figure 8b). Hence more ferrocene molecules are available for oxidation on the reverse scan under dark conditions which is seen as an enhanced oxidation wave (Figure 6c). The magnitude of the current due to oxidation is further increased if the potential is held at negative potentials under light or dark conditions, however the effect due to illumination is more pronounced. The ferricinium ions could be trapped for long periods in the dark and hence this modified electrode system provides a model to study charge trapping within the polymer film. Chapter 4 explains an electrocatalytic study by making use of this trapped charge. The observed results
under dark condition is in agreement with data reported by Murray et al. (59) on TiO₂ electrodes.

**Au/PVF/Ferricyanide, 0.2M KNO₃**

Unlike the ferrocene/ferricinium couple the ferricyanide/ferrocyanide electrochemical couple is kinetically fast and chemically reversible in aqueous media and therefore is the best candidate for the surface modification of phthalocyanine electrodes which are stable only in aqueous media. The interaction of ferricyanide and cyanides of copper, silver, molybdenum and gold with polyelectrolytes having permanent + ve charges has been well studied (50,60). The interaction is believed to be due to a strong ion pair formation (electrostatic), however other mechanisms such as the formation of a charge transfer complex via cyanide bridges (15) have been postulated in certain cases. Because of these results the interaction of ferricyanide ions and oxidized poly(vinylferrocene) was studied and the results are summarized below.

Figure 9 (a) shows the voltammogram of a PVF-coated Au-MPOTE electrode. The oxidation peak at about + .55 V versus Ag/AgCl is narrow and symmetric and the reduction peak at 0.4 V is broader as explained earlier. In the presence of 2 mM ferricyanide solution the electroactivity of ferrocene is lost under repetitive cyclic voltammetric scans, however the growth of a new peak is observed at
Figure 9. Voltammograms for the interaction of Au/PVF electrode with ferricyanide ions. 
(a) Au/PVF/0.2 M KNO₃. Scan rate = 50 mV/sec. 
(b) Au/PVF/potassium ferricyanide (2 mM) in 0.2 M KNO₃. The arrows indicate the direction of growth or decay of peak currents during continuous potential cycling. Scan rate = 50 mV/sec. (c) Au/PVF-ferricyanide/0.2 M KNO₃ (after the electrochemical treatment shown in b) Scan rate = 10 mV/sec.
+ 0.25 V (Figure 9 b). After about 25 scans between -0.1 V and + 0.8 V the new peak reached saturation intensity and the ferrocene electroactivity was not evident in the voltammogram at a scan rate of 50 mV/sec. The same electrode was then rinsed with triply distilled water and the voltammogram was performed in 0.2 M KNO₃ (Figure 9 c) at a sweep rate of 10 mV/sec. As shown in this Figure the peak due to the new redox species (E⁰ = + 0.25 V) was retained, indicating that the product is attached to the surface of the electrode. Figure 10 shows the voltammogram of this film at two different scan rates. At a lower scan rate (1 mV/sec) part of the ferrocene electrochemical activity is more apparent, which indicates a kinetic limitation imposed on the ferrocene electroactivity by the binding of ferricyanide ions with the oxidized PVF film. The apparent loss of ferrocene electroactivity is also observed in the presence of large anions such as phthalate and sulfonated phthalocyanines. The new voltammetric peak was stable to repetitive scans between - 0.1 V and + 0.6 V vs Ag/AgCl but was lost when held at negative potentials for long periods. The oxidized film was slightly blue in color, whereas the reduced form is colorless, however this electrochromic behaviour does not show the same contrast as in Prussian Blue films. since the apparent E⁰ of the new product is
Figure 10. Voltamogram of a Au/PVF electrode after the treatment with ferricyanide (Figure 9) at two different scan rates. Supporting electrolyte, 0.2 M KNO$_3$. 

(a) 50 mV/sec  
(b) 1 mV/sec
centered near the $E^0$ of the solution ferricyanide-/ferrocyanide couple it is reasonable to speculate that the HOMO of this product shows predominantly the characteristics of ferricyanide ions and the influence due to ferricinium ion is negligible. Figure 11 shows the voltammogram of a film two months after the treatment with ferricyanide (having been stored in laboratory atmosphere) and shows the presence of a new anodic peak at $+0.15$ V vs Ag/AgCl reference electrode (peak c). This peak is seen only at low scan rates or if held at negative potentials for long periods, which is indicative of a slow reduction process characteristic of poly(vinylferricinium) ions. The slow reduction kinetics allows the ferricinium ion to be trapped for long periods. Peaks a and b are not affected by changes in peak c which indicates that the ferrocene molecules associated with peak c are energetically isolated from those which are responsible for both a and b. It is still uncertain whether this large negative shift ($-350$ mV) of the oxidation peak is due to the interaction with ferricyanide ions or due to a different energetic site offered by the polymer network.

In order to further understand the mechanism of this interaction the oxidation of monomeric ferrocene was studied in the presence of ferricyanide.
Figure 11. C-V of a Au/PVF electrode (with incorporated ferricyanide) after storage in a dessicator for about 2 months. Scan rate = 50 mV/sec. Supporting electrolyte, 0.2 M KNO₃. The electrode was stored in the oxidized state and the C-V was performed after potentiostating at -0.5 V for one minute.
Au /Ferrocene.Ferricyanide

A major problem encountered in studying the interaction of ferrocene with ferricyanide is that the solubility of ferrocene is limited to non aqueous solvents whereas the solubility of ferricyanide is limited to only aqueous media. After trying various solvents it was found that an ethanol/water mixture was the most suitable for the purpose of obtaining reasonable concentrations of both molecules. This solvent was also less corrosive to phthalocyanine electrode surfaces and hence could be utilized for photoelectrochemical studies at these electrodes.

When ferrocene was oxidized in the presence of ferricyanide the growth of an electroactive film was observed on the electrode surface. This electroactive film could be deposited by several means which are summarized below. In all cases the concentration of ferrocene and ferricyanide was maintained at 2 mM.

1. An ethanol/water (60 % ethanol) solution of ferrocene and ferricyanide was scanned continuously between -0.1 V and + 0.7 V vs Ag/AgCl reference electrode with 0.2 M LiClO₄ as the supporting electrolyte. As shown in Figure 12 (a) both ferrocene \( E^0 = + 0.4 \) V and ferricyanide \( E^0 = + 0.2 \) V are unaffected by the scan treatment and demonstrate quasi reversible electrochemical behaviour.
Figure 12. Voltammograms for the interaction of ferricinium with ferricyanide ions. (a) C-V of 2 mM potassium ferricyanide and 2 mM ferrocene. Supporting electrolyte, 0.2 M LiClO₄ in an ethanol/water (60 % ethanol) solution. Peaks 1 and 2 are due to the reduction of ferricinium and ferricyanide ions respectively. Scan rate = 50 mV/sec. (b) C-V in 0.2 M KNO₃ after the electrochemical treatment illustrated in (a). Scan rate = 5 mV/sec.
However the formation of a product at an intermediate potential ($E^0 = +0.3$ V) is indicated by the appearance of a new peak which grows in magnitude on successive scans. Figure 12 (b) shows the voltammogram of the same film after washing with triply distilled water and in the presence of a non-electroactive aqueous electrolyte (0.2 M KNO$_3$). The shape of the voltammogram is indicative of a surface confined species with a zero peak-to-peak separation at low scan rates and at low coverages. Figure (13) shows the scan rate dependency of the voltammogram and a plot of $i_p$ vs $v$ (scan rate) is linear at low scan rates (Figure 14). At high scan rate the scan rate dependency approaches the behaviour observed for diffusion limited process ($i_p \sim v^{1/2}$). The peak to peak separation also increases at high scan rates since for a diffusion limited process all redox molecules will not be in equilibrium with a particular electrode potential.

Only about 1% of the electroactivity is lost when these films were potential cycled repeatedly (between -0.2 V and +0.8 V) for a period of one hour at a scan rate of 50 mV/sec (125 cycles). However, for freshly prepared films of low coverages (< 50 monolayers) the electroactivity was lost when held at negative potentials (less than -0.4 V) for a few minutes. A broad featureless anodic wave was observed at +1.0 V vs Ag/AgCl, however not much cathodic activity
Figure 13. The dependence of peak current on scan rate for the ferricinium-ferricyanide film in 0.2 M KNO₃.
Figure 14. Plot of peak current ($i_p$) vs scan rate (mV/sec) for the Fe$^{2+}$-fericyanide film. Data was obtained from Figure 13.
was seen in this region (irreversible electroactivity). Aged films and films subjected to several potential cycles showed reversible behaviour in this potential region. The position of these peaks is slightly dependent on the pH of the electrolyte. A negative shift of about 75 mV is observed for voltammograms in 0.1 M nitric acid solutions when compared with 0.2 M KNO$_3$ solution. The growth of the film could be controlled by varying the number of scans. The oxidized film is light blue in color and the reduced form is colorless. The maximum electrochemical activity calculated by integrating the current peaks is about 1x10$$^-8$$ moles/cm$^2$. Figure 15 shows the scanning electron micrograph of a film deposited by this method and the exposed substrate in the middle is a scratch made intentionally on the surface of the film in order to estimate a thickness of the film. The SEM photographs reveal an amorphous structure which is covering the entire Au MPOTE surface.

2. The film could also be grown by electrolyzing the same solution under anodic galvanostatic conditions at a current density of about 50 uA/cm$^2$. The electrochemical properties of this layer are similar to the previously described potentiostatically grown film. The deposition could be controlled by varying the time of electrolysis,
Figure 15. Scanning electron micrograph (SEM) of a Fc⁻⁻ferricyanide film deposited on a Au-MPOTE electrode by the potential scan treatment illustrated in Figure 12 (a). The fracture in the middle is a scratch made on the film intentionally.
however a maximum thickness is achieved after about 10 minutes of electrolysis.

3. The film could be deposited by evaporating drops of the ferrocene-ferricyanide solution (described earlier) on the Au MPOTE surface. The electroactivity however, is limited to only a few (10-50) monolayers and a larger irreversible anodic activity is observed at positive potentials [+1.0 V, (Figure-16)]. The ethanol/water solution of ferrocene and ferricyanide was found to be stable for at least one day.

Au/GaPc-Cl/Ferricinium-Ferricyanide Film/0.2 M KNO₃

The second deposition method described above was found to be more suitable for phthalocyanine electrodes since the scan treatment was found to be destructive when applied to these Pc electrodes. The solvent was presaturated with phthalocyanine to minimize dissolution of the film and the constant-current deposition was carried out under illumination from the back side of the cell. SEM photographs reveal an ordered layered structure for freshly deposited Fc⁺-ferricyanide films which were not subjected to aqueous electrolysis (Figure 17). A large portion of
Figure 16. C-V of a ferricinium-ferricyanide film formed on a Au-MPOTE electrode by drop evaporating an ethanol/water (60% ethanol) solution of ferrocene (2 mM) and potassium ferricyanide (2 mM). Scan rate = 50 mV/sec. Supporting electrolyte, 0.2 M KNO₃.
Figure 17. SEM of a Au/GaPc-Cl electrode modified with the ferricinium-ferricyanide deposit. The deposition was performed by the galvanostatic method and was not subjected to any potential scans in aqueous media.
the Pc electrode surface was left uncovered. Two types of Pc films were used for voltammetric analysis.

The first type of electrode showed a negative photopotential when compared with the $E^0$ of solution ferricyanide/ferrocyanide couple on Au MPOTE electrode. Figure (18) shows the light activated voltammogram of this electrode modified with the Fc$^+$-ferricyanide film. As seen in the voltammogram the modified electroactive overlayer too shows a negative photopotential (-150 mV) and the peak to peak separation of the anodic and cathodic peaks (40 mV) is less than that expected for a diffusion limited process. Since the dark current is negligible the electroactivity is entirely due to a photoelectrochemical reaction.

2. The other electrode chosen was left exposed to the atmosphere for several months before the modification treatment and as expected showed a positive photopotential (+200 mV) with the ferricyanide/ferrocyanide couple. This is believed to be due to p-type behaviour induced by interaction with atmospheric oxygen (30). Figure (19) is the light activated voltammogram of the same electrode modified with an overlayer of the ferricinium-ferricyanide film. The positive photo potential (+250 mV) is again observed and the shape of the voltammogram is similar to the film in case 1.
Figure 18. C-V (under light and dark conditions) of a Au/GaPc-Cl electrode modified with an overlayer of the Fc⁺-ferricyanide film. The layer was deposited under illumination by the galvanostatic method. Scan rate = 50 mV/sec. Supporting electrolyte, 0.2 M KNO₃. The Pc electrode showed a negative photopotential with respect to the ferri/ferrocyanide couple prior to modification.
Figure 19. Voltammogram of a Au/GaPc-Cl (O₂ doped) / Fc⁺-ferricyanide layer/KNO₃ electrode system. Same conditions as in Figure 18 except in this case the Pc electrode showed a positive photopotential with respect to the ferri/ferro-cyanide couple prior to modification. Scan rate = 10 mV/sec.
This system could be viewed as an electrochemical analog of the photoconductor in an electrophotographic device. The Pc acts as the charge generation layer and the electroactive overlayer is analogous to the charge transport layer. The electric field required for charge injection is provided by the space charge region of the semiconductor electrode. The small peak-to-peak separation observed for the light activated voltammogram is an indication of excellent charge injection efficiency from the Pc into the overlayer. The apparent limitation in covering the entire Pc film may be due to the limited number of photoactive sites present on the surface. The choice of an ethanol/water mixture as the solvent for deposition is advantageous, since passivation of the photoactive sites is observed when water is used as the solvent for the same electrochemical treatment.

The Proposed Mechanism of Reaction Between Fc⁺ and Ferricyanide

Ferrocene is a stable organometallic complex in which all the coordination sites offered by the cyclopentadienyl (Cp) rings are saturated. The ferricinium ion, which is formed by the removal of an electron from ferrocene is relatively unstable since it is coordinatively unsaturated. The Cp rings in the ferricinium ion are more ionic in character and hence is more susceptible to cleavage of the
ligands or reduction to form the more stable ferrocene. However several stable ferricinium salts have been synthesized and are well characterized (61-65). They include $\text{Fc}^+ \text{BF}_4^-$, $\text{Fc}^+ \text{I}_3^-$, $\text{Fc}^+ \text{FeCl}_4^-$ and $(\text{Fc}^+)_2 \text{MoO}_4^{2-}$. Since the formation of the electroactive $\text{Fc}^+$-ferricyanide film occurs only under oxidative conditions the reaction of ferricyanide ions could occur with ferricinium ions. The immediate conclusion which would be predicted from this reaction is the formation of a ferricinium salt with the ferricyanide anion. The deposition of ferricinium salts of large anions from low dielectric solvents has been postulated recently by Murray et al. (66) to explain the passivating behaviour of certain microelectrodes. For freshly deposited low coverage films the electrochemical data supports this argument. As shown in Figure 16 the reversible peaks at $E^0 = +0.3$ V vs Ag/AgCl could be attributed to the surface-anchored ferricyanide/ferrocyanide redox couple and no activity is observed in the region of ferrocene electroactivity ($E^0 = +0.4-0.6$ V). However, the broad irreversible anodic wave at $+1.0$ V is characteristic of trapped ferricinium ions on electrode surfaces and in contact with aqueous medium as observed for PVF films (Chapter 3). The shift to more positive potentials is indicative of unstable ferricinium ions with considerable
ionic character. Similar waves are observed for 1,1'-diacetyl ferrocene which is unstable due to the electron withdrawing acetyl groups. The ferricyanide electroactivity is lost if the modified electrode is held at negative potentials which implies a limitation imposed on the reduction process by the binding of ferricyanide with ferricinium ions. The loss of electroactivity can be attributed to the release of negatively charged ferricyanide or ferrocyanide ions from the neutral ferrocene upon reduction.

The complexing ability of ferricyanide ions with positive ions via the cyanide ligand is well known. Examples include derivatization of Ni electrodes by oxidation in the presence of ferricyanide (67) and charge transfer interaction with positively charged polyelectrolytes (15,60). Due to this ability of the cyanide ligand to complex with ferric ion we should expect a redistribution of charges in the ferricinium ion with the ferric ion back donating electrons to the Cp ligands causing them to be ionic in nature. We can view this as a competition for electron donation between the cyanide and Cp ligands to the ferricinium, ferric ion. In aqueous media such processes would cause dissolution of the Cp anions and the formation of a ferri-ferrocyanide (Prussian Blue) complex. Aged films and films subjected to several
potential cycles show electrochemical behaviour similar to that reported for Prussian Blue (PB) films (39,68,69). The development of a reduction peak (reversibility) at +1.0 V and the stability of the electroactive peak at +0.3 V, even if held at negative potentials, is an indication of the removal of the influence of the Cp ligands to form a PB-type film. The aged films do not show an intense blue color as PB films which may suggest a slightly different composition. The reversible electrochemical activity observed at +1.0 V in PB films is attributed to the oxidation of Prussian Blue \([K^+Fe^{3+}Fe^{2+}(CN)_6]\) to Berlin Green \([Fe^{3+}Fe^{3+}(CN)_6]\). In summary, the following mechanism is postulated (Figure 20) for the interaction of ferricinium with ferricyanide ion.

The oxidation of ferrocene generates ferricinium ion (step a) which forms an insoluble and unstable salt with the negatively charged ferricyanide ion (step b). The expulsion of ferricyanide or ferrocyanide when held at negative potentials (reduction to generate ferrocene) is evidence for this intermediate (step c). In the presence of water or when subjected to several potential cycles the cyanide ligand complexes with the ferric ion of \(Fe^{3+}\) to cause dissolution of the Cp rings (step d) and form the ferri-ferricyanide (Berlin Green) complex, which could be reduced to Prussian Blue. Prussian Blue is a highly ordered
Figure 20. Possible reaction pathways for the electrochemical reaction between ferricinium and ferricyanide ions in aqueous media.
polymeric compound with alternate ferric and ferrous ions coordinated with cyanide ligands. Evidence for the formation of Prussian Blue by the reaction between ferricinium ion with ferricyanide was obtained in attempts to isolate the ferricinium-ferricyanide complex. Ferricinium ion was generated in aqueous media by dissolving ferrocene in an oxidizing agent such as concentrated sulfuric acid. Potassium ferricyanide was added to this solution after dilution, and the blue precipitate was filtered, washed with ethanol (to remove traces of ferrocene) and triply distilled water. The IR spectra of this compound is shown in Figure 21 (a) and is compared with the IR spectrum of Prussian Blue (Figure 21 b). The C-N stretching peak is at 2080 cm\(^{-1}\) for both compounds. If the compound synthesized is a ferricinium complex the band would be at a different position compared to Prussian Blue. The bands characteristic of ferricinium salts (64) were absent in the spectrum which also suggests the dissolution of the Cp rings caused by complexation with the cyanide ligands.

The deposition of PB films on GaPc-Cl electrodes by previously reported methods (39, 68) was found to produce a featureless photoelectrochemical activity probably due to the instability of the electrolyte solution caused by a rapid reaction rate. The solution used which contained
Figure 21. The C-N stretching band of, (a) PB produced by reacting ferric and ferrocyanide ions and (b) the product isolated by reacting ferricinium with ferricyanide ions in aqueous media.
equal molar ferric ions and ferricyanide ions was found to be unstable and caused adsorption of the PB on the walls of the electrochemical cell. The deposition of similar electroactive films by the interaction of ferricinium and ferricyanide is more suitable for this purpose mainly due to the slow controlled deposition and the use of a low dielectric solvent. Therefore, despite the decomposition of ferricinium ions in aqueous medium this method is a unique technique for the deposition of electroactive ferricyanide ions on Pc electrode surfaces.

The interaction of PVF with ferricyanide is more complex since most of the ferrocene activity could be revived by holding at negative potentials for films which have been stored in a desiccator for several days. However some of the ferricyanide activity is still retained indicating this electroactivity is due to a permanent complexed ion. Since the Cp rings are held together by the vinyl groups the removal of the ligands would be thermodynamically more unfavourable compared to the ferricinium monomer. The negative shift of the ferrocene oxidation peak in dried films suggests an ion exchange type interaction similar to that reported by Wrighton et al. for cobaltaceniura polymers (36). Similar results have been observed by Martin et al. (70) with a vinylferrocene-styrenesulfonate copolymer. They postulated a change in the
chemical microenvironment around a fraction of the ferrocene groups when \(-\text{SO}_3^-\) is incorporated. Polymers with a high \(\text{SO}_3^-\) content showed a new peak at +0.15 V vs SCE similar to that observed for PVF films loaded with ferricyanide ions. The multiple peaks observed in dried PVF-ferricyanide films (Figure 11) suggests ferrocene in two different energetic environments coexisting within the polymer structure. Peak a could be attributed to oxidation of vinylferrocene in a free state and peak c is probably due the oxidation of an ion pair formed by an ionic interaction between ferricinium and ferricyanide or ferrocyanide ions. Peak b is probably due to the oxidation of ferrocyanide associated with ferricinium ions or due to isolated pockets of trapped Prussian Blue complex. The loss of ferrocene activity on continuous scanning can be attributed to inclusion of the aqueous solvent and ferricyanide within the polymer matrix.

**Electrochemical Deposition of Passivating Polyanilines on Au MPOTE Surfaces**

The diffusion of electroactive ions through pores on phthalocyanine modified electrodes is detrimental when these electrodes are subjected to an electrochemical deposition treatment to overlay an electroactive film or when used in solar cell applications. Blocking these exposed sites by electroinactive polyphenols have been tried by our research
group, but due to the limited solubility of phenol in neutral or acidic electrolytes an alternate method was investigated.

Aniline and substituted anilines could be electropolymerized on metal electrode surfaces by anodic potential treatments (71-74). The polymerization of anilines and para-substituted anilines proceeds by head to tail coupling of monomeric aniline units via a radical mechanism (71). These films are electroactive and are generally conductive. Other mechanisms such as the oxidative decomposition of substituted anilines to quinoid compounds have been postulated (75).

Anilines substituted in the meta position were examined for electropolymerization of resistive poly-anilines since the meta substituted polymeric units would have fewer resonance structural forms than their para-substituted analogs. This would make the polymer to be less conjugated causing them to exhibit lower electrical conductivity. M-aminophenol (2 mM, supporting electrolyte 0.2 M KHP-pH=4) was cycled continuously between 0.0 and +1.0 V vs Ag/AgCl reference electrode (Figure 22). The initial scan showed an irreversible anodic wave which shifted towards more positive potentials on subsequent scans and after about 8 potential cyclic scans the electroactivity in this potential region was almost absent. This is
Figure 22. Passivation of Au-MPOTE by meta linked polyanilines. (a) Voltammograms (potential cycles 1-8) of a Au-MPOTE electrode in the presence of m-aminophenol (2 mM) and 0.2 M KHP. Scan rate = 50 mV/sec. (b) C-V of Au/potassium ferricyanide, 0.2 M KHP after passivation. Scan rate = 50 mV/sec.
indicative of the formation of a resistive film which is confirmed by the blocking ability (absence of electrochemical activity) of these films towards the ferricyanide/ferrocyanide redox couple (Figures 22 b and c). The electroinactive and resistive nature of meta-linked polyanilines have been noted recently by other authors as well (71,73). This method could also be applied to passivate the dark currents in porous phthalocyanine modified electrodes, however a loss in anodic photocurrent is observed which indicates the partial passivation of photoactive sites. A much better method is to use diamino-benzene (o-phenylenediamine) as the monomer and employ the same electrochemical technique to block the exposed Au sites on Pc modified electrodes. Di-aminobenzene has been used by Bard et al to eliminate dark currents in n-WSe₂ semiconductor photoelectrodes (76). The molecular nature of this resistive film is yet to be investigated.
CHAPTER 4

ELECTROCATALYTIC APPLICATIONS

Introduction

One of the major goals in modifying metals with a polymer overlayer is to develop a catalyst to speed up sluggish organic reactions, the primary advantage being the large amount of catalytic centers which could be immobilized within a polymer matrix. The $E^0$ of ferricyanide/-ferrocyanide and ferrocene/ferricinium redox couples are suitably placed for the electrocatalytic oxidation of biomolecules such as ascorbic acid which show a large overpotential for oxidation at metal electrodes (Figure 23 B). Two types of modified electrode systems were utilized as models to study this mediation reaction.

Electrocatalytic Oxidation of Ascorbic Acid Mediated by Ferricinium-Ferricyanide Films

Ferricyanide /ferrocyanide incorporated into PVF by the continuous potential cycling method did not show mediation of the oxidation of ascorbic acid. This might be due to the catalytic centers being distributed in isolated sites on the surface of PVF and not uniformly and widely spaced. In order to cause a more uniform distribution of the ferricyanide catalytic centers both PVF and ferricyanide
Figure 23. Catalytic oxidation of ascorbic acid mediated by a Au/PVF-ferricyanide electrode. (A) Voltammogram of a Au-MPOTE/PVF-ferricyanide film deposited by drop evaporating a DMF solution saturated with PVF and potassium ferricyanide. (B) C-V of Au-MPOTE/ascorbic acid (2 mM). (C) C-V (initial scan) of the modified electrode in ascorbic acid (2 mM). In all cases, Scan rate = 50 mV/sec and the supporting electrolyte was 0.2 M KNO$_3$. 
were predisolved in a suitable solvent such as DMF and drop evaporated on a Au MPOTE electrode. Figure 23 (A) shows the voltammogram of this modified electrode in 0.2 M KNO₃ solution. The amount of electroactive ions calculated by integrating the anodic peak is about \(1 \times 10^{-9}\) mol/cm². Figure 23 (B) is the C-V of the unmodified electrode in the presence of 2 mM ascorbic acid in and evidently shows a large overpotential for oxidation. Figure 23 (C) is the voltammogram after modification and in contact with 2 mM ascorbic acid. The oxidation current shows about a four fold increase at the expense of the reduction current. This indicates a mediation process in which the ferricyanide ions acts as an oxidizing agent by mediating the oxidation of ascorbic acid at more negative potentials (at the \(E^0\) of the ferri/ferrocyanide couple) when compared to the unmodified electrode. Since this causes a rereduction of ferricyanide to ferrocyanide a corresponding loss in the reduction current is observed.

**Rotating Disk Electrode (RDE) Studies of Electrocatalysis of Ascorbic acid**

Chapter 1 explains the theory involved in using RDE to estimate the kinetic parameters of electrocatalytic mediation reactions. An ethanol/water (60 %) solution containing both ferrocene (2 mM) and ferricyanide (2 mM) was drop evaporated on the solid Au disk electrode to produce
a very thin coating of the ferricinium-ferricyanide film. This approach was utilized since the method explained in the previous paragraph did not show reproducible results.

A definite pattern of electrochemical behaviour emerged for the oxidation of ascorbic acid after performing several trials using the modified RDE. The catalytic peak currents at + 0.3 V (increase in the anodic limiting current) was observed only at very low rotation rates (less than 500 rpm). Above this rotation rate the catalytic effect shifted towards more positive potentials and the limiting current was observed at + 1.0 V. This limiting current increased with rotation rate and data was obtained for every 500 rpm increase in the rotation rate up to 4000 rpm. The solution used was a 2 mM ascorbic acid in 0.2 M KNO₃. In the absence of the redox film (bare Au) the anodic current observed in this region (+ 1.0 V) was much less and showed only a very small increase with rotation rate which indicates that the apparent increase in the limiting current (at + 1.0 V) in the presence of the ferricinium-ferricyanide overlayer is mostly due to a catalytic effect. The limiting currents for the mediation process were calculated by subtracting the background current obtained in the absence of the redox film. The observed behaviour is similar to that reported by Oyama and Anson for the oxidation of Fe²⁺ by IrCl₆³⁻ bound to a
polyvinyl pyridine coated graphite electrode (45). At low rotation rates the current is controlled by the Levich flux (delivery of ascorbic acid to the surface catalytic sites of the film). At high rotation rates the Levich flux is large therefore more ascorbic acid molecules are available than the catalytic centers present and hence a much slower catalytic step limits the rate of reaction. The dependency of the limiting current ($i_L$) on the rotation rate ($w$) is now given by the Koutecky-Levich Equation (Equation 7). As shown in Figure-24 the plot of $i_L^{-1}$ vs $w^{-1/2}$ is linear (as expected from the Koutecky-Levich equation) only above 2500 rpm. The intercept is equal to $nF\alpha_k C_s$ where $A$ is the area of the electrode, $C$ is the amount of electroactive ions (moles/cm$^2$), $C_s$ is the bulk concentration of ascorbic acid (2 mM) and $n=1$ for the ferri/ferrocyanide electrochemical reaction. A problem encountered in calculating the rate constant ($k$) is in estimating the amount of immobilized electroactive ions involved in the catalytic process. The contribution due to diffusion through pinholes and the through the film is ignored in deriving the Koutecky-Levich equation which could also contribute to error. The film is less strongly held to the Au-RDE than on a Au-MPOTE electrode which could cause a loss of electroactivity if the experiment was to be extended for longer periods. Despite all these limitations a an
Figure 24. Koutecky-Levich plot for the oxidation of ascorbic acid mediated by the $\text{Fc}^+\text{-ferricyanide}$ film. Concentration of ascorbic acid = 2 mM. Supporting electrolyte used to obtain data was 0.2 M KNO$_3$. The film was deposited by drop evaporating a saturated ethanol/water solution of ferrocene and potassium ferricyanide on a solid Au disk electrode.
approximate value for the rate constant was calculated from
the inverse Levich plot. Assuming all sites are involved in
the catalytic process we have, \( n = 5 \times 10^{-10} \text{ moles/cm}^2 \),
\( A = 0.196 \text{ cm}^2 \), \( C_s = 2 \times 10^{-3} \text{ M} \) and intercept
(Figure 24) = \( 2 \times 10^3 \text{ A}^{-1} \). The rate constant for the
mediation reaction \( (k) \) was calculated to be \( 2.55 \times 10^4 \text{ M}^{-1}\text{s}^{-1} \) which was comparable to previously reported
values on other modified electrodes (46).

**Au/GaPc-Cl/PVF/Ascorbic Acid: Oxidation of Ascorbic Acid Mediated by Trapped Ferricinium Ions**

Chapter 3 describes a method to irreversibly oxidize ferrocene (in PVF) by inducing p-type behaviour in Au/GaPc-Cl electrodes. The charge trapped as ferricinium ions could be discharged by either promoting electrons into the conduction band by illumination or by holding the electrode at negative potentials under dark conditions. Another method of causing the discharge would be to expose the electrode to an electroactive reducing agent. This approach is of interest in the development of chemical sensors. The use of a semiconductor bilayer system is advantageous in minimizing leakage currents due to the absence of minority carriers in the dark. The trapping of ferricinium ions has been observed in polymer bilayer electrodes as well (77). Here the redox energy levels of
the inner polymer film is such that reduction of the outer PVF film is thermodynamically unfavourable.

Figure 25 shows the C-V of a PVF modified GaPc-Cl electrode in 0.2 M KNO₃ electrolyte. The amount of electroactive ferrocene molecules calculated by integrating the wave due to the initial scan (scan 1) is equal to about \(1 \times 10^{-8}\) mol/cm². The electroactivity diminished on subsequent potential cycles (waves 2, 3 and 4). Most of the electroactivity could be revived by illuminating the electrode when held at -0.2 V vs Ag/AgCl for 3 minutes (wave 5). This is attributed to the irreversible oxidation of ferrocene by trapped holes induced by the deposition treatment. A complete explanation for this behaviour is given in Chapter 3. The effect due to illumination could be duplicated in the presence of electroactive molecules such as ascorbic acid. Here, the oxidation is mediated at +1.0 V vs Ag/AgCl by trapped ferricinium ions. In order to test the feasibility of using this bilayer system as a possible chemical sensor the following experiment was performed.

The potential was cycled between 0.0 and +1.1 V vs Ag/AgCl until the ferrocene electroactivity was almost eliminated (wave A - Figure 26). The cell was then filled with ascorbic acid at various concentrations and a C-V was performed each time between 0.0 and 1.2 V vs Ag/AgCl (waves B, C, D, E, F - Table 1). The potential was held at 0.0 V
Figure 25. C-V of Au/GaPc-Cl/PVF/0.2 M KNO₃. Waves 1-4 are due to the first 4 scans performed under dark conditions. The next scan (wave 5) was performed after holding the potential at -0.2 V for 3 minutes under illumination (BS). Scan rate = 50 mV/sec.
Figure 26. Effect of added ascorbic acid on the voltammetric response of the oxidation of PVF on a Au/GaPc-Cl electrode. (A) 0.2 M KNO₃ (blank) (B) 1x10⁻⁴ M. (C) 2x10⁻⁴ M. (D) 4x10⁻⁴ M. (E) 6x10⁻⁴ M. (F) 1x10⁻³ M. (G) Au/ascorbic acid (1 mM). Supporting electrolyte, 0.2 M KNO₃. Scan rate 50 mV/sec. Waves A-F were performed on the same electrode used in Figure 25.
for 15 seconds before performing each potential scan in order to allow time for equilibration. Between each filling of the cell with the ascorbic acid solution the electrode was cycled in 0.2 M KNO₃ until the electroactivity was reduced to that shown in wave A of Figure 26. This was done to ensure similar conditions before contact with the different concentrations of ascorbic acid. As shown in Figure 26 the peak currents increased with molarity for concentrations ranging between 1x10⁻⁴ M and 1x10⁻³ M. Wave G of Figure 26 shows the C-V of ascorbic acid (mM) in contact with bare Au MPOTE electrode and when compared to wave F the current at +1.0 V is negligible. Figure 27 (a) illustrates the catalytic mediation scheme for the oxidation of ascorbic acid. In order for this electrode to be used for practical purposes this catalytic cycle should be repeated several times. The peak current and concentration values are tabulated in Table 1 and a plot of peak current vs concentration is linear between 2 to 8 x 10⁻⁴ M (Figure 27 b), however flattens out at higher concentrations.

The loss of response at higher concentrations could be attributed to the participation of only a fraction of ferrocene molecules as catalytic centers. This would impose a limitation for higher fluxes of ascorbic acid molecules. It should be possible to extend the linear dynamic range to lower concentrations by allowing longer times for
Figure 27. (a) Catalytic cycle for the oxidation of ascorbic acid mediated by Au/GaPc-Cl (p-type)/PVF electrode. (b) Plot of peak current vs concentration of ascorbic acid for data obtained from Figure 26.
### TABLE 1

Data for calibration graph for the catalytic oxidation of ascorbic acid by trapped ferricinium ions.

<table>
<thead>
<tr>
<th>Wave (Figure 26)</th>
<th>Concentration: $x 10^{-4}$ M</th>
<th>Peak current: uA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1.0</td>
<td>75</td>
</tr>
<tr>
<td>C</td>
<td>2.0</td>
<td>135</td>
</tr>
<tr>
<td>D</td>
<td>4.0</td>
<td>195</td>
</tr>
<tr>
<td>E</td>
<td>6.0</td>
<td>230</td>
</tr>
<tr>
<td>F</td>
<td>10.0</td>
<td>280</td>
</tr>
</tbody>
</table>
equilibration to take place. Stirring the solution is a possible approach to achieve this objective. The upper limit of the linear range depends on the amount of electroactive ferrocene molecules present initially. This imposes a limitation on reproducibility since the electroactivity of ferrocene is partially lost after several potential cycles. A method to quickly revive the lost electroactivity should be found in order to overcome this problem. To increase the current response and hence the detection limit a semiconductor which exhibits more p-type character should be tried. Attempts to overlay PVF on Au/TiOPc electrodes ended in failure due to the higher solubility of TiOPc in toluene.

During the time scale of the potential scan (t sec) the diffusion layer would have expanded to a distance \((2Dt)^{1/2}\) cm from the electrode surface, where \(D\) is the diffusion coefficient of ascorbic acid in aqueous media \((\text{cm}^2/\text{sec})\). This corresponds to a volume \(V = Ax(2Dt)^{1/2}\), where \(A\) = area of electrode \((\text{cm}^2)\). If \(C_s\) is the concentration of ascorbic acid \((\text{moles/lit})\) the moles of ascorbic acid oxidized in time \(t\) \((n_t) = VxC_s \times 10^3\). Substituting the experimental values for \(C_s = 1\times10^{-4}\) M \(t = 15\) sec, \(D = 5.7\times10^{-6} \text{ cm}^2/\text{sec}\) and \(A = 1 \text{ cm}^2\) we have, \(n_t = 1.9\times10^{-3}\) moles. The amount of electroactive ferrocene = \(n_{FC} = 1\times10^{-8}\) moles/\(\text{cm}^2\) and
\( n_{Fc} : n_t = 5.2 \times 10^{-4} \) i.e only a fraction of ascorbic acid molecules were successful in discharging the trapped Fc\(^+\) ions. The amount of electroactive ferrocene calculated by integrating wave A of Figure 26 was \( 3 \times 10^{-9} \) moles/cm\(^2\) which implies that not all ferrocene molecules participated in the catalytic process. This fraction would be even less if some of the catalytic centers underwent repeated catalytic cycles. A minimum detectable concentration calculated by assuming that all electroactive ferrocene molecules participated in the catalytic process and using the equation derived above, was equal to \( 5.4 \times 10^{-10} \) M. However at low concentrations the flux of ascorbic acid molecules would be less and hence a lower probability of causing a catalytic cycle. Therefore the above equation has to be modified by including a probability function which is dependent on the concentration (or flux) and also a turnover rate for the catalytic centers to get more reasonable values. Leakage currents would be a factor for longer periods of equilibration.
CHAPTER 5

ADSORPTION OF ELECTROACTIVE AND ELECTROINACTIVE IONS ON Au-MPOTE SURFACES

Introduction

The Au-MPOTE surface shows unique surface properties and offers adsorption sites for ions such as iodide, Cl\(^-\) and SO\(_4\)^{2-}. Electroactive ions such as anthraquinone and ferricyanide also showed adsorption. Adsorption generally occurs when the electrode is poised at anodic potentials or when scanned through the Au oxidation potential region. Such adsorbed ions could alter the photoelectrochemical properties of Pc modified Au-MPOTE electrodes.

**Au/ Hydroquinone /Benzoquinone: Effect of Adsorbed Iodide Ions on Reaction Rate**

The H\(_2\)Q / BQ redox couple shows an irreversible voltammogram with a peak separation exceeding 200 mV when in contact with a Au electrode. This behaviour could be attributed to adsorbed impurity ions such as Cl\(^-\) from the reference electrode and anions from the supporting electrolyte. The electrode could be activated towards H\(_2\)Q / BQ couple by continuous cycling between 0 and + ve 1.5 V vs Ag/AgCl reference electrode. Figure 28 (a) shows the voltammogram for the oxidation of Au-MPOTE in 0.1 M H\(_2\)SO\(_4\). The anodic wave at +1.15 V is due to the
Figure 28. Effect of cleaning (with ethanol) and anodic treatment on the voltammetric response of the oxidation of Au-MPOTE. (a) C-V of a Au-MPOTE electrode in 0.1 M H₂SO₄ (0-1.6 V) prior to any cleaning treatments. (b) C-V of this electrode after ultrasonication in absolute ethanol for 10 minutes. (c) C-V of this Au-MPOTE electrode after the treatment described in (b) and then potentiostating at +1.0 V for 5 minutes in 0.1 M H₂SO₄. Scan rate = 50 mV/sec for all cases.
oxidation of Au to oxides or hydroxides (78) and the
cathodic peak at 0.95 V is the reduction of the oxides or
hydroxides to Au. Continuous cycling in this region
apparently causes desorption of the adsorbed impurity ions
and hence causes the H_2Q / BQ electroactivity to be
reversible. The sensitivity of the H_2Q / BQ couple
towards adsorbed ions was utilized in studying the
adsorption of iodide ions. The adsorption of iodide ions on
Pt electrode surfaces has been studied by Hubbard et al.
(79) and has been shown to retard the electrolysis rate.
Figure (29) shows the effect of added I^- on the oxidation
of a 1 mM H_2Q solution. Figure 29 (wave 1) is the
voltammogram of H_2Q after the activation treatment
described above (peak potential seperation = 50 mV). Iodide
was added incrementally (while continuously scanning through
the Au oxidation region) to this solution, starting at
2 x 10^-5 M until a concentration of 1 x 10^-4 M was
reached (waves # 2, 3, 4 of Figure 29). At this point the
peak current of the reversible wave decreased and the peak
current of a new irreversible wave increased to detectable
levels. Even though the electrode was continuously scanned
through positive potentials (0 - 1.5 V) the conversion of
the electrode to the inactive state was completed (waves
#4, 5, 6, 7 of Figure 29). The passivation is entirely due
to iodide ions since under similar conditions and in the
Figure 29. Effect of added I⁻ on the voltammetric response of the oxidation of 1x10⁻⁴ M H₂O₂ in 0.2 M KHP (pH=4) electrolyte. Scan rate = 50 mV/sec. Upper scans - peaks 1, 2, 3, 4 are for the scans associated with concentrations of I⁻ of 2x10⁻⁵ M, 4x10⁻⁵ M, 6x10⁻⁵ M and 8x10⁻⁵ M respectively. Lower scans - peak 4 is reproduced from above, and peaks 5, 6 and 7 are for successive scans after #4, when the I⁻ concentration was increased to 1x10⁻⁴ M and held at that level.
absence of iodide ions the reversibility of the $H_2O/BQ$ could be maintained. Weaver et al. used surface-enhanced Raman spectroscopy to study the adsorption of iodide ions on Au electrodes and postulated the following pathway (80).

$$2I^- + I^- \text{(ads)} - 2e \rightarrow I_3^- \text{(ads)} \tag{rxn \ I}$$  

$$2I^- + I_3^- \text{(ads)} - 2e \rightarrow I_5^- \text{(ads)} \tag{rxn \ II}$$ and/or 

$$2I^- + I^- \text{(ads)} - 2e \rightarrow I_2 \ldots I^- \text{(ads)} \tag{rxn \ III}$$

These steps could be followed by dissociation of both $I_5^-$ (ads) and $I_2 \ldots I^-$ (ads) to $I_3^-$ and $I^-$ respectively. However each of these steps could involve several microscopic steps and the above given steps could be an over simplified mechanism of the overall process.

Au/ Ferricyanide/Ferrocyanide: Decomposition of Ferricyanide Induced by Anodic Dissolution of Au

The adsorption of the ferricyanide/ferrocyanide couple was studied in the Au oxidation potential region. Figure 30 (a) shows the voltammogram of a Au-MPOTE electrode when subjected to a continuous scan treatment through the Au oxidation region in the presence of 2 mM ferricyanide solution. The growth of a new peak is observed at $+0.3 \text{ V}$ vs Ag/AgCl which is retained after the electrode is washed
with distilled water and analysed in the presence of 0.2 M KNO₃ (Figure 30 b). The electrochemical behaviour of this product is characteristic of Prussian Blue films and IR spectroscopic studies done recently has confirmed the product to be Prussian Blue (81). The proposed mechanism was based on the removal of cyanide ligands from ferricyanide by Au surface sites to form a Au-CN complex. The ferric ion formed by this decomposition reaction could then react with ferrocyanide to form a PB film. The dissolution of Au as Au(CN)₂⁻ when subjected to anodic potentials is well known (82). This would create more free Au surface sites which would cause further decomposition of ferricyanide according to the above mentioned mechanism.

Effect of Anodic Treatment on the Electrochemical / Photoelectrochemical Properties of Au-MPOTE and GaPc-Cl Electrodes

Anodic treatment causes adsorption of negatively charged or electronegative oxygen atoms on Au electrode surfaces (78). The formation of such an adlayer was achieved by holding the Au-MPOTE electrode in 0.1 N sulfuric acid at positive potentials (+ ve 1.0 vs Ag/AgCl reference electrode) for about 3-5 minutes. Since this potential is well removed from the bulk Au oxidation region we would expect the adsorption to be via an electrostatic interaction of negatively charged oxygen atoms on sulfate ions and the
Figure 30. Decomposition of ferricyanide under anodic potential treatment. (a) C-V of a Au-MPOTE electrode subjected to a continuous potential cyclic treatment through the Au oxidation region and in the presence of 2 mM potassium ferricyanide and 0.2 M KNO$_3$. (b) C-V in 0.2 M KNO$_3$ after the electrochemical treatment described in (a). Scan rate = 50 mV/sec.
oxygen atom of water molecule with the Au surface (78). In order to investigate the effect of this adlayer on the oxidation potential of Au the following experiments was performed.

An electrode left exposed to atmospheric conditions for several months was analysed in the Au oxidation/reduction potential region prior to any cleaning treatments (Figure 28 a). The oxidation wave for bulk Au occurs at +1.15 V vs Ag/AgCl reference electrode. After cleaning the electrode surface by ultrasonication in absolute ethanol for about ten minutes followed by rinsing with triply distilled water the oxidation wave shifts to +1.5 V (Figure 28 b). When this same electrode was held at +1.0 V in sulfuric acid (0.1 N) to cause adsorption of negatively charged and electronegative ions, the oxidation wave shifted back to the original position (Figure 28 c). The formation of the adlayer evidently shifts the oxidation wave to more cathodic potentials. Similar results have been observed for electrodes exposed to 1.5 kV Ar ion beams and for electrodes exposed with oxygen RF plasmas (83). The additional peak at the shoulder of the reduction wave in Figure 28 (c) is also observed in Ar ion treated electrodes which indicates a similar surface reorganization in both cases. Electrodes exposed to atmospheric conditions for several months (uncleaned electrodes) also show similar
electrochemical behaviour probably due to interaction with oxygen and water molecules to cause partial oxidation of the Au surface.

Previous work done in our research group indicates that phthalocyanine (GaPc-Cl) sublimed on uncleaned electrodes shows a positive photopotential when compared to films grown on electrodes cleaned with absolute ethanol followed by deionized water. Based on the results above an experiment was performed to test the effect of anodic treatment on the photoelectrochemical properties of GaPc-Cl electrodes.

A Au / GaPc-Cl electrode $E^0_{\text{photo}}$ Ferri/ferrocyanide = + 0.2 V, Figure 31 a) was held at + 1.0 V vs Ag/AgCl reference electrode for 5 minutes in 0.1 N sulfuric acid solution under dark conditions. After this treatment a positive shift in the photo potential was observed ($E^0 = 0.38$ V, Figure 31 b). The dark current in both cases was negligible compared to the photo current, however in certain cases the anodic treatment caused partial dissolution of the Pc to cause an increase of dark current due to reaction at exposed Au. The same results could also be obtained under anodic galvanostatic (25 uA/cm$^2$) conditions.

Based on the above results a complete explanation is not possible. However the following possibilities arise.
(a) Electrodes subjected to anodic treatment, exposed to Ar
Figure 31. Effect of anodic treatment on a Au/GaPc-Cl photoelectrode. (a) C-V under illumination (BS) in 2 mM potassium ferricyanide. (b) C-V (BS illumination) of this electrode after potentiostating at +1.0 V under dark conditions in 0.1 M H_2SO_4. Supporting electrolyte was 0.2 M KNO_3 and the Scan rate = 50 mV/sec for both cases.
ions, RF oxygen plasma and atmosphere (for long periods) shows similar electrochemical effects. This could result due to partial oxidation of the Au surface (formation of an adlayer) by interaction with oxygen and other oxygen containing ions or molecules. This explanation assumes that the Pc film has large enough pores to permit the diffusion of oxygen, water and sulfate ions to interact with the Au surface. This is a reasonable expectation since the redox couples such as ferricyanide/ferrocyanide are larger in size compared to these ions thus making the Pc film to be relatively porous to the smaller ions or molecules. If this explanation is correct it should be possible to reverse the $E^\text{photo}_0$ of the Pc electrode by reductive removal of the adlayer (other than treatment with ethanol). Attempts to reverse the $E^0$ by electrochemical reduction was met with only limited success.

(b) The above mentioned treatments could also cause reorganization of the MPOTE surface to cause functional groups from the polyester back bone to protrude out. These functional groups could cause a redistribution of charges within the Pc film to cause more p-type behaviour.

**Adsorption of Anthraquinone Sulfonate (AQ-SO$_3^-$) on Au-MPOTE Electrode by Anodic Treatment?**

Catalytic Reduction of Oxygen

The electrocatalytic reduction of oxygen by quinoid compounds have been of particular interest (84,85). The
2-electron reduction of oxygen to hydrogen peroxide and the 4-electron reduction to water generally occurs at large negative overpotentials. Due to the importance of this reaction in fuel cell applications many attempts have been made to catalytically reduce oxygen (86), particularly the 4-electron reduction process. Hydrogen peroxide is also an important oxidant from an industrial point of view. Derivatives of anthraquinone (AQ) after reduction to their dihydro form (AQH$_2$) are known to reduce oxygen to hydrogen peroxide (84) and is also an industrial procedure for the production of hydrogen peroxide.

The adsorption of quinoid compounds on Pt electrodes has been extensively studied by Hubbard et al. (87-90). The derivatization of the Au-MPOTE by AQ was achieved by holding the electrode at +1.0 V vs Ag/AgCl for about 5 minutes in a 0.05 M sulfuric acid solution saturated with the sodium salt of AQ-sulfonic acid. After this treatment the voltammogram was performed in 0.2 M KNO$_3$ without removal of oxygen and is shown in Figure 32 (a), after 5 potential cycles. The initial scan showed a comparatively large cathodic wave which could be attributed to the reduction of oxygen. On subsequent scans the voltammogram approached reversibility. In the absence of adsorbed AQ negligible currents were observed in this potential region. The large reduction wave observed during the initial potential scan
could be attributed to the reduction of oxygen mediated by adsorbed AQ. Photoelectrochemical approaches have been attempted in order to shift the reduction to more positive potentials, i.e. closer to the thermodynamic value (85). The same anodic potential treatment was performed on a Au/GaPc-Cl electrodes by illuminating from the backside of the cell. The dark and light activated voltammograms of the Pc electrode after this anodic treatment in 0.2 M KNO₃ is shown in Figure 32 (b). The reduction process begins at + 0.2 V (under illumination) which is about + 0.4 V more positive when compared with the bare Au electrode.

The predominant product formed by the reduction of oxygen by AQH₂ is known to be hydrogen peroxide (85). The chemical nature of the adsorbed AQ on Au-MPOTE electrode is speculative at the moment however two possibilities exist.

(1) A polymeric coating is generated similar to the poly(naphthoquinone) modified Au and Pt electrodes reported by Dubois et al. (91). This modification was achieved by placing the potential at positive values and the polymeric coating showed catalytic behaviour towards the reduction of oxygen. The polymerization however, occurred via -OH groups attached to the naphthoquinone molecule which is not present in the AQ derivative used in this experiment.

(2) A monolayer of AQ molecules formed on the electrode surface by adsorption via the SO₃⁻ functional group
Figure 32. Adsorption of AQ on Au-MPOTE and the catalytic reduction of O\textsubscript{2}. (a) Voltammogram (sixth cycle) of a Au\textsuperscript{2+}-MPOTE electrode after potentiostating at +1.0 V in a saturated solution of AQ-SO\textsubscript{3} in 0.05 M H\textsubscript{2}SO\textsubscript{4}. (b) and (c) are voltammograms of a Au/GaPc-Cl electrode under light and dark conditions respectively after performing the anodic treatment described in (a). Supporting electrolyte was 0.2 M KNO\textsubscript{3} and scan rate = 50 mV/sec in all cases.
attached to the AQ molecule, which is similar to the adsorption of $\text{SO}_4^-$ described earlier.

The scan rate dependency of the peak currents is similar to a diffusion limited process even at low scan rates. The electroactivity was stable for at least 20 potential cycles if the same electrolyte was used, but is lost if washed with water. The $E^0$ of the adsorbed AQ / AQH$_2$ redox couple ($-0.2\,\text{V}$) is much more positive than the $E^0$ of solution AQ / AQH$_2$ couple ($E^0 = -0.5\,\text{V}$). The reason for this large positive shift in potential is unclear at present.
CHAPTER 6

CONCLUSIONS

The method developed to deposit the electroactive ferricyanide/ferrocyanide film is unique to Au / GaPc-Cl electrode surfaces due to several reasons. The ethanol/water solvent used for the deposition of Fc\(^+\)-ferricyanide films apparently prevents the passivation of photoactive sites when constant current or constant potential treatments are used. This method could also be viewed as a method to protect the photoelectrode surface. Apart from the deposition of PB films few other methods have been developed for the deposition of electroactive films from aqueous media. Although the electrochemical properties of the ferricinium-ferricyanide films are similar to the PB films, the slow rate of deposition and the stability of the electrolyte solution allows a better control of the deposition process. The interaction of PVF with ferricyanide ions also raises some interesting questions regarding the nature of the trapped ferricyanide or ferrocyanide ions. A method to release the trapped anions within the PVF matrix upon electrochemical reduction could lead to useful practical applications.

From the results obtained it is apparent that the
efficiency of charge transfer from the Pc to the electroactive overlayer is comparable if not better than for a solution redox species. This result, although positive has some limitations for the development of a multilayered solid state device. A method has to be developed to cover the entire Pc surface with an electroactive film. Blocking the exposed Pc surface by an electroinactive polymer could be one method to overcome this problem. This would not affect the photoactive sites since it would already be covered by the ferricinium-ferricyanide film. Attempts to modify the Pc surface with a metal overlayer was not successful due to the ability of metal atoms to penetrate the Pc film. Conducting polymers such as polypyrrole could be substituted for the metal overlayer. Attempts to sublime Pc on a Au-MPOTE electrode modified with an electroactive and conducting polyaniline film met with limited success due to the movement of counter ions through pores in the Pc film to cause large dark currents. Perhaps the biggest breakthrough in such a project would be to develop a method to electrochemically deposit photoconductor systems showing similar properties, since such a method would allow us to easily control the electronic properties of the Pc. Phthalocyanines should be made more soluble in a suitable solvent to achieve this objective.
The mediated oxidation of ascorbic acid by trapped ferricinium ions on a Au / GaPc-Cl / PVF electrode is a promising result and such examples have not been reported previously. However other redox couples should be tried since the charge due to ferricinium ion has a tendency to decay if kept for long periods.
REFERENCES


