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Studies of Oxygen Reduction on
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ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL STUDIES OF OXYGEN REDUCTION ON METAL PHTHALOCYANINES AND PORPHYRINS

By

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ABSTRACT

ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL STUDIES OF OXYGEN REDUCTION ON METAL PHTHALOCYANINES AND PORPHYRINS

By

Gary Alan Deborski

The study of macrocyclic metal chelates as electrocatalysts for the reduction of oxygen has been an active research area for some years. In several recent studies, increases in the rate of oxygen reduction occurring at illuminated metal phthalocyanine electrodes have been reported.

The reduction of oxygen and the influence of visible light on the reaction were studied on monolayer films of various macrocyclic chelates deposited on pyrolitic graphite and SnO_2 electrodes. A series of metal phthalocyanines and iron porphyrins were studied, including some novel cofacial diporphyrins.

Linear sweep, cyclic and differential pulse voltammetry were used to measure the activities for oxygen reduction in 0.1 N KOH and pH 7 phosphate buffer.

A reversible redox process was found to be associated with catalytic oxygen reduction at iron phthalocyanine.

Light in the visible region promotes the reaction as evidenced by higher current densities. The spectral dependence of this effect was measured for iron phthalocyanine.

DEDICATION

To my loving wife Mary and
our boys Christopher and Corey

ACKNOWLEDGMENTS

I wish to thank my family for their patience and understanding. I also thank my mother and father, Mr. and Mrs. Leo F. Deborski, for their guidance.

I also acknowledge Dr. Neal Armstrong, Dr. Chris Chang and Dr. James Harrison for their encouragement and support.

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CHAPTER I

INTRODUCTION

A. Oxygen Reduction, Electrochemistry and Photoelectrochemistry

Oxygen reduction, either

$$O_2 + 4H^+ + 4e^- = 2H_2O \quad E° = + 1.23 \qquad (I)$$

in acidic solution, or

$$O_2 + 2H_2O + 4e^- = 4OH^- \quad E° = + 0.40 \qquad (II)$$

in alkaline solution, is of central importance in electrochemical energy conversion. At present, most of the energy used by man comes from the burning of fossil fuels, although nuclear sources are becoming more common and greater emphasis is being placed on geothermal and solar energy. Concerns about the effects of carbon dioxide, sulfur dioxides and particulate emissions on the quality of the environment and the final realization that oil and coal are not in unlimited supply have intensified the search for more efficient production of energy. As Bockris and Reddy(1) have pointed out, electrochemical methods of producing energy offer a minimum of double the efficiency of conventional combustion processed due to the intrinsic efficiency loss in heat engines in accordance with Carnot's theorem. Fuel cells have been widely studied(2-6) as a means of efficiently producing direct current power from a variety of fuels. The majority of these fuel cell systems use oxygen, either in purified form or from the air directly, as the cathodic oxidant. The exchange current density, i_o, of the oxygen reduction reaction has been determined(1) to be about 10^{-10} amp cm^{-2} on platinum in either acidic or alkaline solution. This indicates that oxygen reduction is a relatively slow reaction compared to other common electrochemical processes. When practical current densities are passed, a large overpotential is usually observed and the search for electrocatalysts to lower this overpotential has been a major research topic.

An electrocatalyst may be defined as a substance which accelerates the rate of an electrochemical reaction while not being consumed in the overall reaction. Just as the heterogeneous catalyst provides a reaction site in a chemical process, the electrode serves as the reaction site in an electrodic process, that is it catalyzes charge transfer reactions. From the Arrhenius equation,

$$V = ATe^{-\Delta G^{\circ\neq}/RT}$$

where A is a collection of constants, $\Delta G^{\circ\neq}$ is the activation energy, R is the gas constant and T the temperature, the rate, V, of a heterogeneous chemical reaction is dependent on the temperature. The Butler-Volmer equation,

$$V = ATe^{-\Delta G^{\circ\neq}/RT}e^{-\alpha F\Delta\phi/RT}$$

where A, $\Delta G^{\circ\neq}$, R and T have the same meanings as before and α is the transfer coefficient, F is the Faraday constant and $\Delta\phi$ is a potential term, shows that the rate, V, of an electrochemical reaction is dependent on both temperature and potential. The more active electrocatalyst then results in a faster rate (higher current density) at a constant overpotential or, conversely, a lower overpotential when compared at a constant current density.

Platinum is generally considered to be the best catalyst for oxygen reduction and has been widely studied.(7-10) Platinum and the other noble metals are expensive and in scarce supply which has prompted the search for less expensive and more readily available catalyst materials. Silver,(11) tungsten bronzes,(12) tungsten carbide(13) and various metal oxides(14-16) have been investigated as catalysts for the electroreduction of oxygen. Jasinski(17,18) found an organometallic compound, cobalt phthalocyanine, to be an active catalyst when used in an oxygen cathode.

Considerable difficulty has been encountered in evaluating the mechanism of oxygen reduction even on a relatively well defined surface such as platinum. Substrate changes occur in the potential range in which the reaction occurs(5) and these greatly complicate the determination of the mechanism. Generally two views exist as to the mechanism of oxygen reduction at electrode surfaces. These views deal with the presence of peroxide as an intermediate in the reaction. In many cases peroxide is detected during the reduction of oxygen. This had been taken as evidence for a mechanism involving first the reduction of oxygen to peroxide (III) followed by the reduction of peroxide to water (IV).

$$O_2 + 2H^+ + 2e^- = H_2O_2 \qquad E° = +\ 0.68 \qquad (III)$$

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O \qquad E° = +\ 1.78 \qquad (IV)$$

Damjanovic, Genshaw and Bockris(19-22) have pointed out that since the standard potential of reaction (III) is 0.68, in regions cathodic of this value it may be possible to have the four-electron process (I) operating in parallel to the two-electron reduction of O_2 to H_2O_2.

The presence of H_2O_2, then, would not imply that it was produced as an intermediate in the four-electron process. These same authors have used the rotating ring-disk electrode to establish a distinction between H_2O_2 produced due to reaction (III) and that produced as an intermediate in the four-electron path. Their conclusions were based on the absence of current at the ring electrode which was held at a potential sufficient to oxidize any H_2O_2 formed at the platinum disk at a limiting current density. In purified sulfuric acid solution, oxygen is apparently reduced directly to water in a four electron process with no peroxide intermediate, but in solutions that had not been rigorously purified, oxygen is reduced to H_2O and H_2O_2 in parallel reactions. In alkaline solutions the parallel reactions also appear to occur with peroxide formed as a true intermediate even in purified solution.

Sawyer and Seo(23) have explained both pathways in terms of a one-electron mechanism whereby oxygen is electrochemically reduced to superoxide ion,

$$O_2 + e^- = O_2^- \qquad E° = -0.33V \qquad \text{(V)}$$

followed by chemical reactions from the following series.

$$H^+ + O_2^- \rightleftarrows HO \qquad pK_a = 4.88 \qquad \text{(VI)}$$

$$2O_2^- + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^- \qquad k_1 < 100M^{-1}s^{-1} \qquad \text{(VII)}$$

$$O_2^- + HO_2 + H_2O \rightarrow H_2O_2 + O_2 + OH^- \qquad k_2 = 8.5 \times 10^7 \qquad \text{(VIII)}$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \quad k_3 = 7.6 \times 10^5 \qquad \text{(IX)}$$

The net reaction is the same as (III) in acid and (X) in alkaline solution.

$$O_2 + H_2O + 2e^- = HO_2^- + OH^- \qquad E° = -0.08 \qquad \text{(X)}$$

This path is claimed to account for the apparent two-electron stoichiometry and the presence of hydrogen peroxide while avoiding multi-electron transfer or unstable reactant species. Evidence given in support of this proposal includes data on polarographic oxygen reduction in dimethyl sulfoxide-water mixtures. Below $\sim$8 vol % water, oxygen is reduced in a reversible one-electron process. Above 10% water the electron per oxygen molecule ratio increases with a maximum value of 2 observed at 35% water and the reaction becomes irreversible.

The nature of oxygen reduction on metal chelates such as the phthalocyanines and porphyrins is considerably more complex. The central metal ion has a pronounced effect on the activity for oxygen reduction.(24-26) It has generally been found that the iron and cobalt complexes are superior to those of nickel, copper, zinc, etc.

Jahnke et al.(27) have investigated the suitability of various types of carbon as substrate materials with iron phthalocyanine as the catalyst. Their results show that the specific surface area and electrical conductivity of the support are only minor factors in the activity for oxygen reduction. The nature of the carbon surface was found to have a much more significant impact. Alkaline surface groups were deemed necessary for the chelate to have a catalytic effect. Mössbauer studies were cited which indicated strong interaction between the phthalocyanine complex and the alkaline groups on the carbon surface.

Beck(28) has proposed a redox mechanism for the chelate catalyzed oxygen cathode. The described mechanism has a potential determining step which regenerates the reduced form of the catalyst. The following steps with iron phthalocyanine (FePc) are suggested:

$$\mathrm{Fe^{II}Pc} + \mathrm{O_2} \rightleftarrows [\overset{\delta+}{\mathrm{FePc}}\cdots\cdots\overset{\delta-}{\mathrm{O_2}}] \tag{XI}$$

$$[\overset{\delta+}{\mathrm{FePc}}\cdots\cdots\overset{\delta-}{\mathrm{O_2}}] + \mathrm{H^+} \rightarrow [\mathrm{Fe^{III}Pc}\cdots\cdots\mathrm{O_2H}]^+ \tag{XII}$$

$$[\mathrm{Fe^{III}Pc}\cdots\cdots\mathrm{O_2H}]^+ + \mathrm{H^+} + 2e^- = \mathrm{Fe^{II}Pc} + \mathrm{H_2O_2} \tag{XIII}$$

$$\mathrm{H_2O_2} \xrightarrow[\text{catalase action}]{\text{FePc}} \mathrm{H_2O} + \tfrac{1}{2}\mathrm{O_2} \tag{XIV}$$

The oxygen is first coordinated to the metal center of the complex (XI). This is followed by the proton-assisted chemical reduction of the oxygen molecule which yields the chelate, in the oxidized form, coordinated with a radical HO_2 (XII). Then, in the potential determining step (XIII), this complex is electrochemically reduced to give the reduced form of the catalyst and H_2O_2. The peroxide is catalytically decomposed as in (XIV). Beck has interpreted the higher activities observed with cobalt and iron as the central metal as being due to their ability to donate an electron in a reaction like (XII). Kuwana et al.(29) have reported on a similar catalytic scheme for water-soluble iron tetra-(4-N-methylpiridyl) porphyrin pentachloride ($Fe^{III}TMP^{+5}5Cl^-$). Their experimental results are consistent with a mechanism in which the porphyrin is electrochemically reduced (XV) with a subsequent proton-assisted chemical reduction of oxygen (XVI).

$$Fe^{III}TMP^{+5} + e^- = Fe^{II}TMP^{+4} \qquad (XV)$$

$$Fe^{II}TMP^{+4} + \tfrac{1}{2}O_2 + H^+ \rightarrow Fe^{III}TMP^{+5} + \tfrac{1}{2}H_2O_2 \qquad (XVI)$$

Alt et al.(30) attempted to explain the electrocatalytic activity of macrocyclic chelates by a model for oxygen adsorption based on simple MO considerations. They have theorized that oxygen reduction is favored by partial electron transfer from the metal to the antibonding π^* orbitals of oxygen during formation of the chelate-oxygen adsorption complex. By comparison with the π-complexes of ethylene and based on the symmetry of the various metal d-orbitals, they have assumed that this partial electron transfer is favored by filled d_{xz} and d_{yz} orbitals and vacant d_{z2} orbitals.

As mentioned previously, the economics of fossil fuels, their limited supply and the pollution problems associated with their combustion have, in recent years, resulted in an accelerated search for alternative means of producing useful forms of energy. In addition to electrochemical energy conversion, another major area of investigation has been utilization of solar energy. The use of the sun's energy has been studied from two different viewpoints; either concentrating the thermal energy for use in space or process heating or converting the energy directly to electrical energy with a photovoltaic device such as a silicon solar cell. The photodecomposition of water at semiconductor electrodes to oxygen in an anodic process and hydrogen in a cathodic process has also been studied as a means of capturing the energy available in solar radiation.(31,32) The combination of the anodic photodecomposition of water to oxygen and the fuel cell process of cathodic oxygen reduction can be envisioned as another type of photovoltaic device for the utilization of solar energy. Along these lines, recent studies(33-35) have reported the enhancement of photocurrents at semiconductor electrodes with adsorbed or covalently attached dye molecules. Acceleration of the rate of oxygen reduction on metal phthalocyanines with illumination has also recently been reported.(36,37)

Excited molecules generated by absorption of light have significantly different redox properties compared to the ground state.(38,39) When in contact with an electrode, electron transfer is the most prominent reaction of molecules in the excited state.(40,41) Photoconduction and the generation of photopotentials in dyestuffs, including the phthalocyanines and porphyrins, are well known and have been widely studied. For many years inconsistencies in the combustion have, in recent years, resulted in an accelerated search for alternative means of producing useful forms of energy. In addition to electrochemical energy conversion, another major area of investigation has been utilization of solar energy. The use of the sun's energy has been studied from two different viewpoints; either concentrating the thermal energy for use in space or process heating or converting the energy directly to electrical energy with a photovoltaic device such as a silicon solar cell. The photodecomposition of water at semiconductor electrodes to oxygen in an anodic process and hydrogen in a cathodic process has also been studied as a means of capturing the energy available in solar radiation.(31,32) The combination of the anodic photodecomposition of water to oxygen and the fuel cell process of cathodic oxygen reduction can be envisioned as another type of photovoltaic device for the utilization of solar energy. Along these lines, recent studies(33-35) have reported the enhancement of photocurrents at semiconductor electrodes with adsorbed or covalently attached dye molecules. Acceleration of the rate of oxygen reduction on metal phthalocyanines with illumination has also recently been reported.(36,37)

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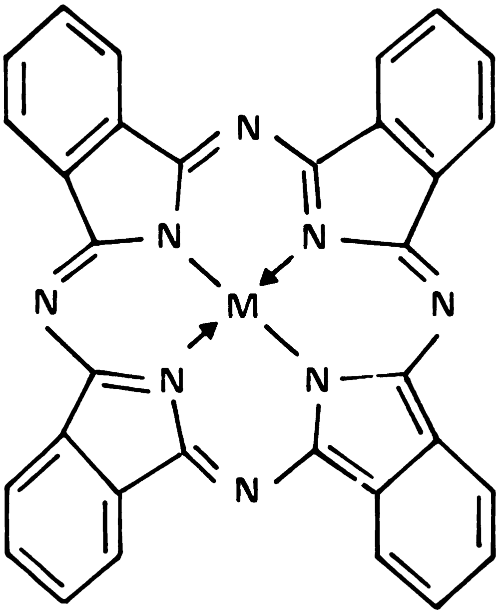
Recently, Meshitsuka and Tamaru(36) have measured the spectral distribution of a number of photoelectrochemical reactions occurring at metal phthalocyanine electrodes. Their results indicate that the maximum rate for oxidation reactions occurs at the peak of an absorption band at <u>ca</u>. 610 nm which has been assigned(43) to a π-π^* transition of the phthalocyanine ring. The maximum for reduction, including oxygen reduction, was found to correspond to a shoulder of this band occurring near 580 nm which has been assigned(44) to a n-π^* transition of the macrocycle. They have explained these observations as being due to photo-generation of charge carriers in the thin phthalocyanine films. Alferov and Sevast'yanov(37) have also reported enhanced rates of oxygen reduction on thin layers of phthalocyanines when illuminated with light in the visible region.

B. <u>Phthalocyanines and Porphyrins</u>

Phthalocyanine is a large macrocyclic chelate having the structure shown in Figure 1. The two central amine protons can be replaced by



Metal Phthalocyanine

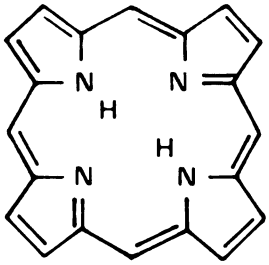
M = Fe, Co, Ni, Cu, Mn . . . .

Figure 1

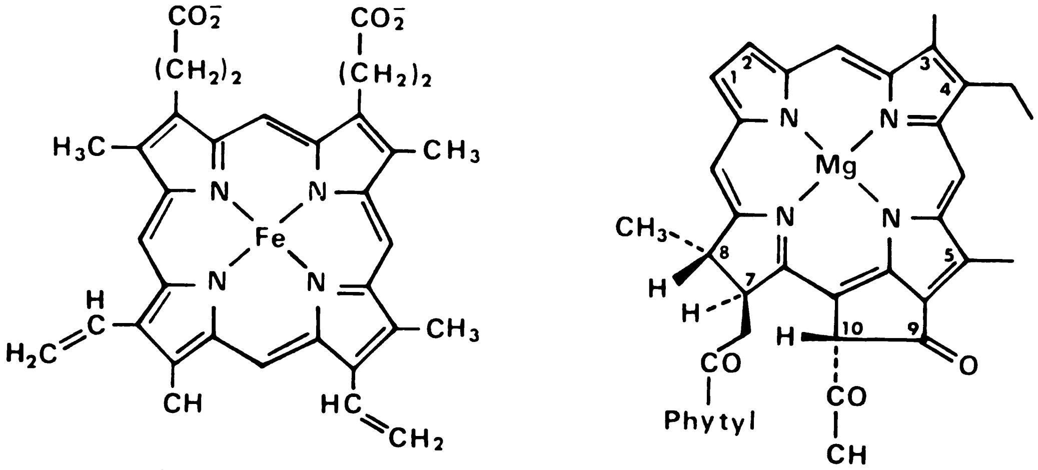
metal ions to give the metal phthalocyanines. More than forty metal phthalocyanines are known.(45) The highly conjugated ring system absorbs strongly in the visible region with extinction coefficients in the range of 3,000 $M^{-1}cm^{-1}$ to 220,000 $M^{-1}cm^{-1}$.(45) The strongest absorption band occurs in the 600 nm - 750 nm region giving these compounds intense blue or green colors. The metal phthalocyanines, most notably the copper complex, have been widely used as pigments. Soluble forms, for use as dyes, have been prepared(45,46) by the replacement of some of the peripheral ring protons with sulfonic or carboxyclic acid groups.

The metal porphyrins are another class of similar macrocycles. The parent compound, porphine, is shown in Figure 2a. A significant difference between the phthalocyanines and porphyrins is the bridge between the pyrole groupings. The nitrogen bridges of the phthalocyanine system do not allow substitution at this point which can affect the catalytic activity and stability through electron shifting. Porphyrin compounds are abundant in living organisms where they play primary roles in the life process. These are typified by the iron containing heme group (Figure 2b) and the magnesium complexes of the chlorophylls (Figure 2c).

Recently, the preparation of a number of cofacial diporphyrins has been reported.(47,48) Because of the parallel configuration of the two porphyrin rings (see Figure 3), these materials should have very interesting properties. They may serve as synthetic models for the reaction center in the photosynthesis process.(48) The distance



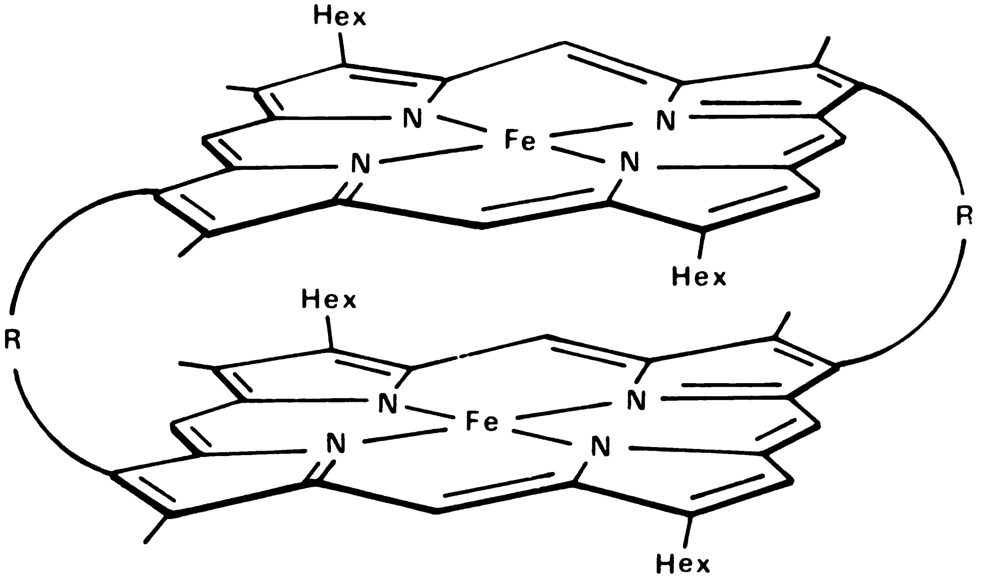
(a) Porphine



(b) The Heme Group

(c) Chlorophyll - a

Figure 2



Fe - Fe - 7, R = -$CH_2CH_2CON(n\text{-}Bu)CH_2CH_2CH_2$-

Fe - Fe - 6, R = -$CH_2CON(n\text{-}Bu)CH_2CH_2CH_2$-

Fe - Fe - 5, R = -$CH_2CON(n\text{-}Bu)CH_2CH_2$-

Structure of the Cofacial Iron Diporphyrins

Figure 3

between the two porphyrin rings will clearly affect the properties, such as the ability to bind molecular oxygen. Oxygen binding has been observed with a dicobalt porphyrin.(49) The oxygen forms a μ-peroxo [Co-O_2-Co] complex which was detected via e.s.r. Chang(48) has synthesized a series of these diporphyrins with interplanar distances ranging from 4.2 Å to 6.4 Å. The variation of electrocatalytic activity with the change in interplanar spacing may provide useful information about the nature of oxygen adsorption and reduction by metal chelates.

A number of reactions involving the phthalocyanines show amazing similarities to processes based on their naturally occurring counterparts. The iron proteins, hemoglobin, myoglobin and the cytochromes, take part in oxygen-transport and storage as well as electron transfer. Iron phthalocyanine has been shown(50,51) to be an effective catalyst for oxygen reduction which requires oxygen adsorption and transfer of electrons. Meshitsuka et al.(52) have found that the phthalocyanine complexes of cobalt and nickel are active electrocatalysts for the reduction of carbon dioxide which is analogous to the photosynthetic reduction of carbon dioxide by chlorophyll. Catalase-like activity in the decomposition of hydrogen peroxide by iron phthalocyanine is well known.(45)

The reduction potentials of a number of metal phthalocyanines have been measured at a dropping mercury electrode in dimethylformamide with tetra-n-propylammonium perchlorate as the supporting electrolyte.(53) Reduction of metal-free, magnesium, zinc, copper and nickel phthalocyanines was found to occur by electron addition to the ring system. Reduction of cobalt phthalocyanine takes place by formation of a cobalt (I) species. Results for iron phthalocyanine were not as definitive but were consistent with reduction proceeding through the metal center at some stage.

A great deal of research has been done concerning the use of metal phthalocyanines and porphyrins as electrocatalysts for oxygen reduction.(50,51,54-56) Several authors have tried to correlate various structural parameters with electrocatalytic activity. Appleby *et al*.(57) have shown a relation between the spectroscopic properties and catalytic activity in iron phthalocyanines. Correlations have also been found with oxidation potentials,(25) activity toward dehydrogenation reactions and magnetic moments.(25,55)

This research was directed at the study of oxygen reduction occurring at a number of macrocyclic metal chelates. One objective of this study was to measure the activity toward oxygen reduction of essentially monolayer levels of a series of metal phthalocyanines and iron porphyrins. Further, study of the basic electrochemical processes of these metal complexes in the absence of oxygen were investigated as a means of probing the pathway by which oxygen reduction occurs.

Additionally, the manner in which visible light, incident upon these monolayer deposits of metal macrocycles, affects the course of the reaction was studied with a view toward better understanding of this important reaction.

C. Electrode Preparation

The principle material used as a substrate in this research was pyrolitic graphite. A few measurements were made with polycrystalline tin oxide as the substrate.

Pyrolitic graphite has been used for voltammetry in aqueous solutions for a number of years.(58,59) Wax impregnated pyrolitic graphite has found use in anodic stripping voltammetry(59) where reproducibility superior to wax impregnated spectroscopic graphite was found. Recently, the electrochemical behavior of several compounds irreversibly adsorbed on pyrolitic graphite electrodes has been studied.(60)

Pyrolitic graphite is deposited when low molecular weight hydrocarbons are pyrolyzed at low pressures (25-150 mmHg) in the temperature range of 1700-2500°C.(61) The graphite crystallites are deposited with their basal planes parallel to the surface upon which the deposition occurs. The resulting structure has some very unusual properties which make pyrolitic graphite quite different from conventional graphites.

Pyrolitic graphite is quite dense and may approach the theoretical figure for single crystal graphite.(61) It is also extremely anisotropic in nature, with high strength properties in a direction parallel to the basal planes. The material also shows high electrical and thermal conductivity in this direction. In the direction perpendicular to the basal planes, the strength of the structure is much lower and the material is virtually an electrical and thermal insulator. Because it is almost totally impermeable to gases even at elevated temperatures and has a higher degree of resistance to oxidation than conventional graphite, pyrolitic graphite has been considered for use in nuclear reactors, as a coating for missile nose cones and for construction of nozzle inserts for rocket motors.(61)

The resistance to oxidation, reproducibility and convenience of use of pyrolitic graphite make it a very useful electrode material for studying electrochemical reactions.

Tin oxide vapor deposited on glass or quartz has been used as an electrode material in electrochemical spectroscopy.(59) The most useful characteristic of these electrodes is their optical transparency and, in recent years, tin oxide electrodes have been employed as optically transparent electrodes in spectroelectrochemical and photoelectrochemical measurements.(62,63)

Tin oxide electrodes are prepared by pyrolitic decomposition of volatile tin compounds, such as $SnCl_4$, onto glass or quartz substrates. To increase the conductivity a dopant, usually antimony, is added with the result that the tin oxide has n-type semiconductor properties.

The surface of the tin oxide is chemically active due to the presence of amphoteric Sn-OH groups. Covalent attachment of electrochemically active compounds to the surface of tin oxide electrodes has been studied.(34,35,64) The electrochemical behavior of silane modified SnO_2 electrodes has been investigated by Murray and co-workers.(64,65) The electrochemical, photoelectrochemical and surface properties of a number of organic and organometallic dyes adsorbed or covalently attached to SnO_2 electrode have been studied as possible systems for capturing solar energy.(33)

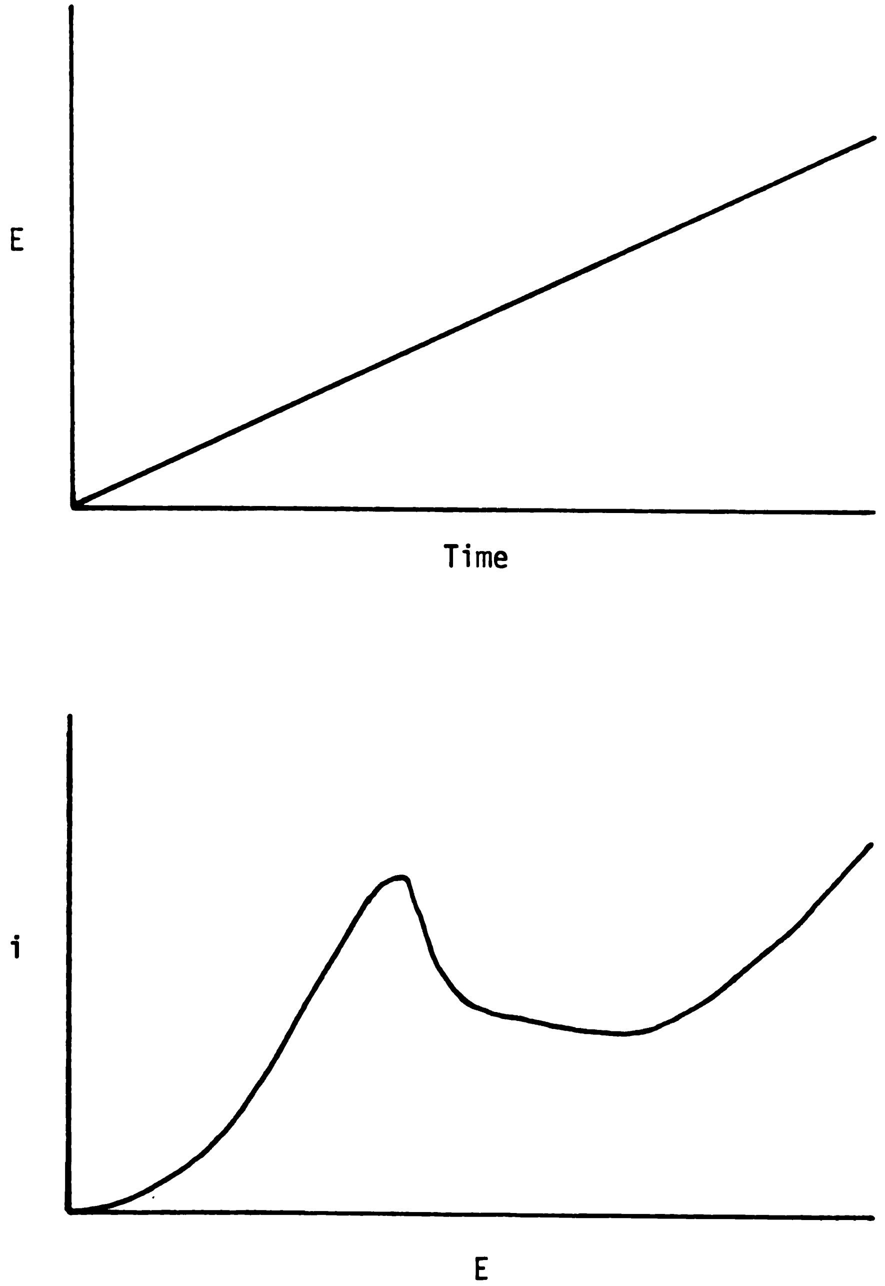
D. Electrochemical Methods

Several different electrochemical methods were used to analyze various aspects of the electrochemistry and photoelectrochemistry of the phthalocyanines and porphyrins.

The methods used to evaluate the activity of the macrocycles toward oxygen reduction were linear sweep and cyclic voltammetry and differential pulse, linear sweep voltammetry.

In linear sweep voltammetry, a linear voltage ramp is applied to the electrode and the resulting current is recorded versus potential. The current observed may be composed of two components, the current due to charging of the capacitance of the electrical double layer and that due to any Faradaic process which occurs in the potential region being scanned. A graphic portrayal of the perturbation applied and a typical response curve are shown in Figure 4.

The differential pulse method was developed(66,67) as a means of increasing the sensitivity of polarographic analysis. This technique has also been used effectively in conjunction with anodic stripping voltammetry for determination of sub-ppb levels of heavy metals.(68)



Potential Ramp and Current-Voltage Curve, Linear Sweep Voltammetry

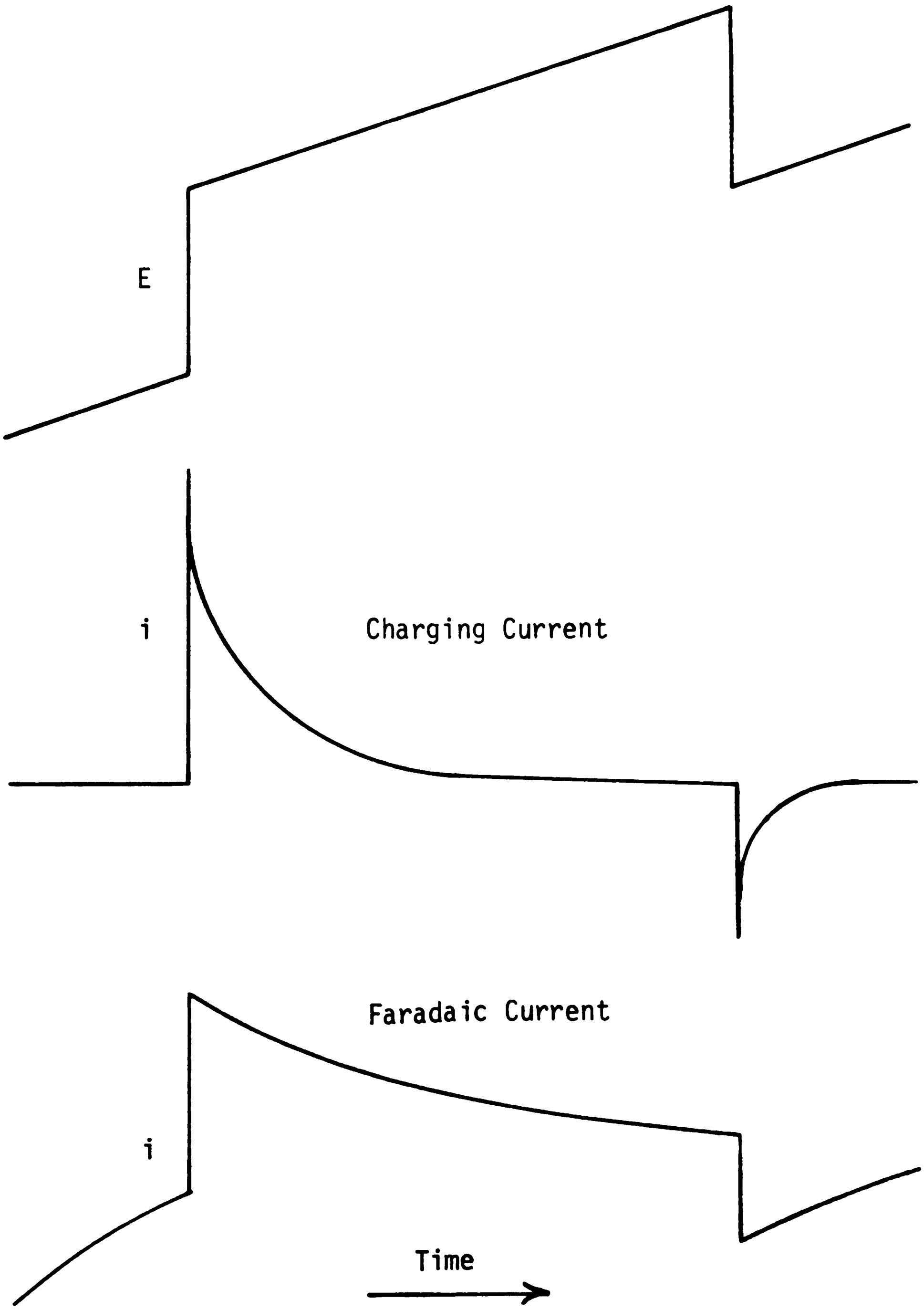
Figure 4

The differential pulse excitation consists of a slow linear potential ramp upon which is superimposed a small amplitude square wave pulse. The basis of the method is the time dependence of the components at the current.(67) The time response of the current components during one pulse are shown diagrammatically in Figure 5. The current due to the charging of the double layer decays to negligibly small values within a few milliseconds of application of the pulse. If a Faradaic reaction is occurring in this potential region, there will be a current component associated with it as well. According to the Cottrel equation,

$$i = \frac{n\ F\ A\ C\ D^{\frac{1}{2}}}{\pi^{\frac{1}{2}}\ \ t^{\frac{1}{2}}}$$

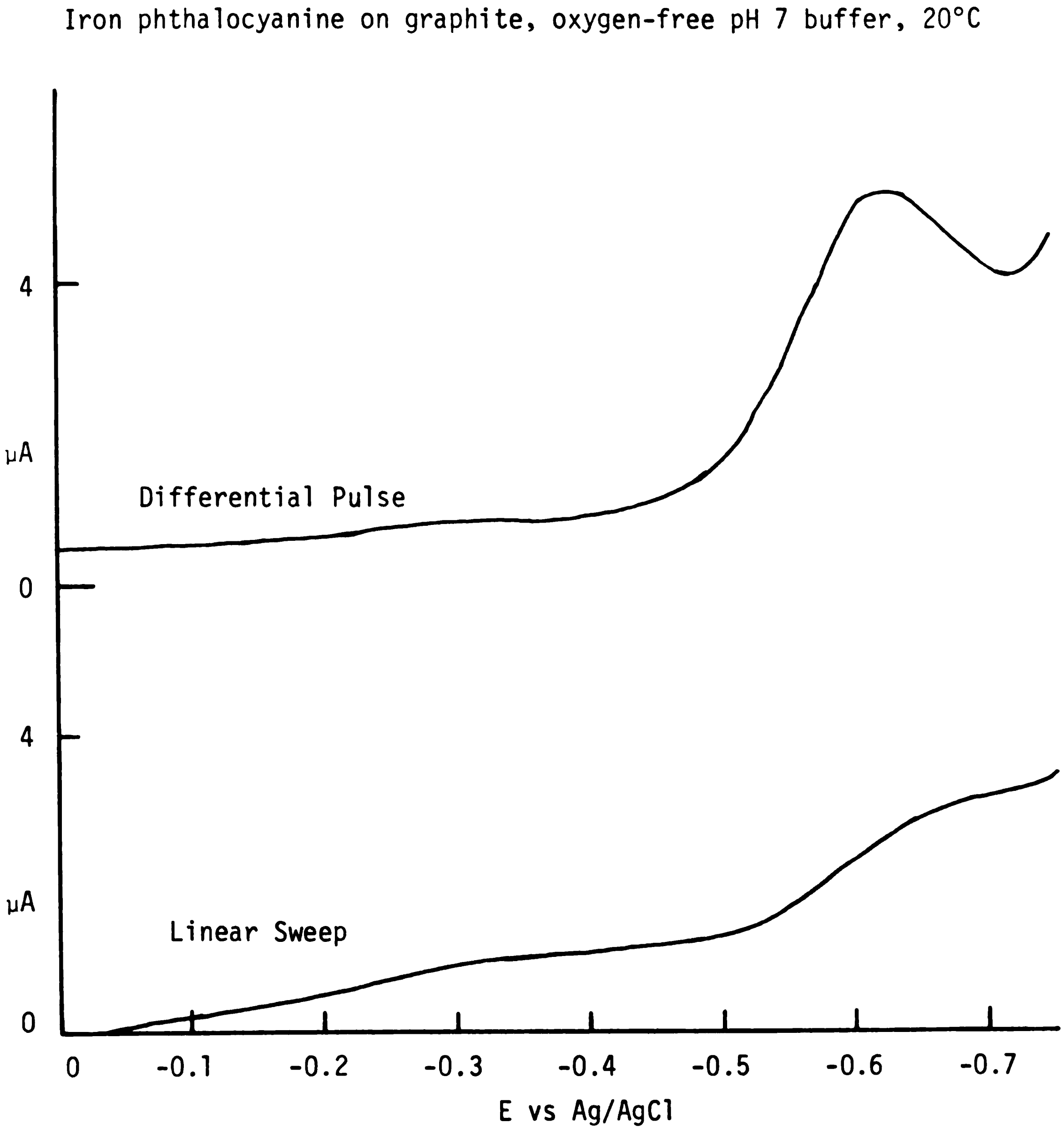
the Faradaic current will decay inversely as $t^{\frac{1}{2}}$. By selecting the points at which the current is sampled, the charging current contribution can be nearly eliminated. Thus, the current is measured just prior to each pulse and just prior to its removal and the difference (hence the name - differential pulse) between these two values is what is followed versus potential.

A comparison of the current-potential curves obtained with both methods is presented in Figure 6. The curves shown are successive scans in the cathodic direction on a pyrolitic graphite electrode onto which has been deposited a layer of iron phthalocyanine on the order of a monolayer thick. The current maximum occurring at <u>ca</u> -0.62 V vs. Ag/AgCl is a reduction occurring at the macrocycle. In the linear



Current-Time Responses to a Voltage Pulse

Figure 5



Comparison of Linear Sweep and Differential Pulse Voltammetry

Figure 6

sweep voltammetric scan, this peak appears as a low, broad, ill defined hump due to the effects of the charging current. In contrast, the differential pulse scan gives a much more well defined maximum from which the peak potential can easily be determined.

Brown, Koval and Anson(60) have pointed out that it is surprising that differential pulse voltammetric methods have proved so useful in measurements of reactions involving adsorbed reactants. The oxidation or reduction of an adsorbed species is the same type effect as the charging of a pseudo-capacitance and should be discriminated against by the differential pulse method. The utility of this technique for studying surface species is in fact dependent on the presence of uncompensated solution resistance. It appears that, within certain ranges of surface concentration and uncompensated resistance, the differential pulse method can be used to provide quantitative as well as qualitative information about the electrochemistry of surface species with increased sensitivity over the methods currently employed.

Cyclic voltammetry was used to study redox processes of the thin layers of metal complexes deposited on graphite electrodes in deoxygenated solutions. By scanning with oxygen-free solutions and then after electrochemically injecting small amounts of oxygen, information about the influence of the redox process on oxygen reduction could be obtained.

Some aspects of the photoelectrochemistry of oxygen reduction were studied using chronoamperometry. This method utilizes a step of the potential of the working electrode to a value sufficiently cathodic to produce diffusion controlled conditions with the oxygen concentration at the electrode surface at zero. The diffusion controlled rate of the reaction can then be followed by measurement of the current-time response curves.

E. Conclusion

Some aspects of oxygen reduction and theories as to the mechanism through which it occurs have been presented. The study of oxygen reduction on metal macrocycles, such as the phthalocyanines and porphyrins, has been quite an active research area. A relatively new and much less explored area is the effect of light on this important electrochemical reaction. The object of this research has been to study oxygen reduction at monolayers of metal phthalocyanines and porphyrins and to investigate the effects of illumination on the reaction. Since the metal macrocycles are deeply colored, with intense absorptions in the visible region, and many of them are known to catalyze the electroreduction of molecular oxygen, the perturbation to the electronic structure of these compounds produced by illumination could reasonably be expected to result in a change in the nature of the oxygen reduction reaction occurring at these materials. Studies of the effects of illumination on oxygen reduction, particularly determining which excitations affect the reaction, may possibly lead to a better understanding of the mechanism of oxygen reduction and could be useful in developing devices capable of converting sunlight directly into electrical energy.

CHAPTER II

EXPERIMENTAL

A. Catalyst Deposition

To obtain loadings of the phthalocyanine and porphyrin materials on the substrate which approximated monolayer coverage, deposition was done from solution. With a molecular area of ca. 100 square Å(45,69) and an electrode area of 1.27 cm^2, monolayer coverage corresponds to 2 X 10^{-10} moles of the phthalocyanine or porphyrin. The porphyrins were deposited by spreading 20 μl of a 10^{-5} molar solution in dichloromethane on the substrate using a microliter syringe. The solvent was evaporated and the last traces removed by a brief period under vacuum. The phthalocyanines posed somewhat of a problem, however, since they are insoluble (or nearly so) in most common solvents. Some of the metal phthalocyanines have slight solubility in 1-chloronaphthalene, pyridine or quinoline.(45) It was desired to avoid use of these solvents if possible because, in some instances, strongly coordinated solvent adducts are known to form.(70) Adequate solubility was found in methanol to allow deposition of the compounds studied. Saturated solutions were used as the stock solutions because they made reproduction of the deposition solutions simple.

The methanolic solutions of the phthalocyanines were prepared by adding a large excess (>100 fold) of the chelate to a small volume of methanol with vigorous stirring. After stirring for 30 min., the excess phthalocyanine was filtered out using a fine glass fritted filtering funnel. These solutions have a tendency to precipitate on standing, a common occurrence with the phthalocyanines in many solvents,(45) and were freshly prepared just prior to each use. To determine the volume of solution necessary to deposit monolayer levels of the metal complexes, the concentrations of the saturated solutions were determined. A measured aliquot of the freshly prepared methanol solution was gently heated to drive off the solvent. The residue was dissolved in a minimal volume of concentrated sulfuric acid and the chelate was decomposed by adding concentrated nitric acid followed by gentle heating. This solution was diluted to a known volume with distilled water and analyzed for the appropriate metal using a Varian Techtron Model 1200 Atomic Absorption Spectrophotometer. The results of these analyses (see Table 1) show that the concentrations varied from a low of 2.1 X 10^{-5} molar for copper phthalocyanine to a high of 4.1 X 10^{-4} molar for nickel phthalocyanine.

B. Electrochemical Measurements

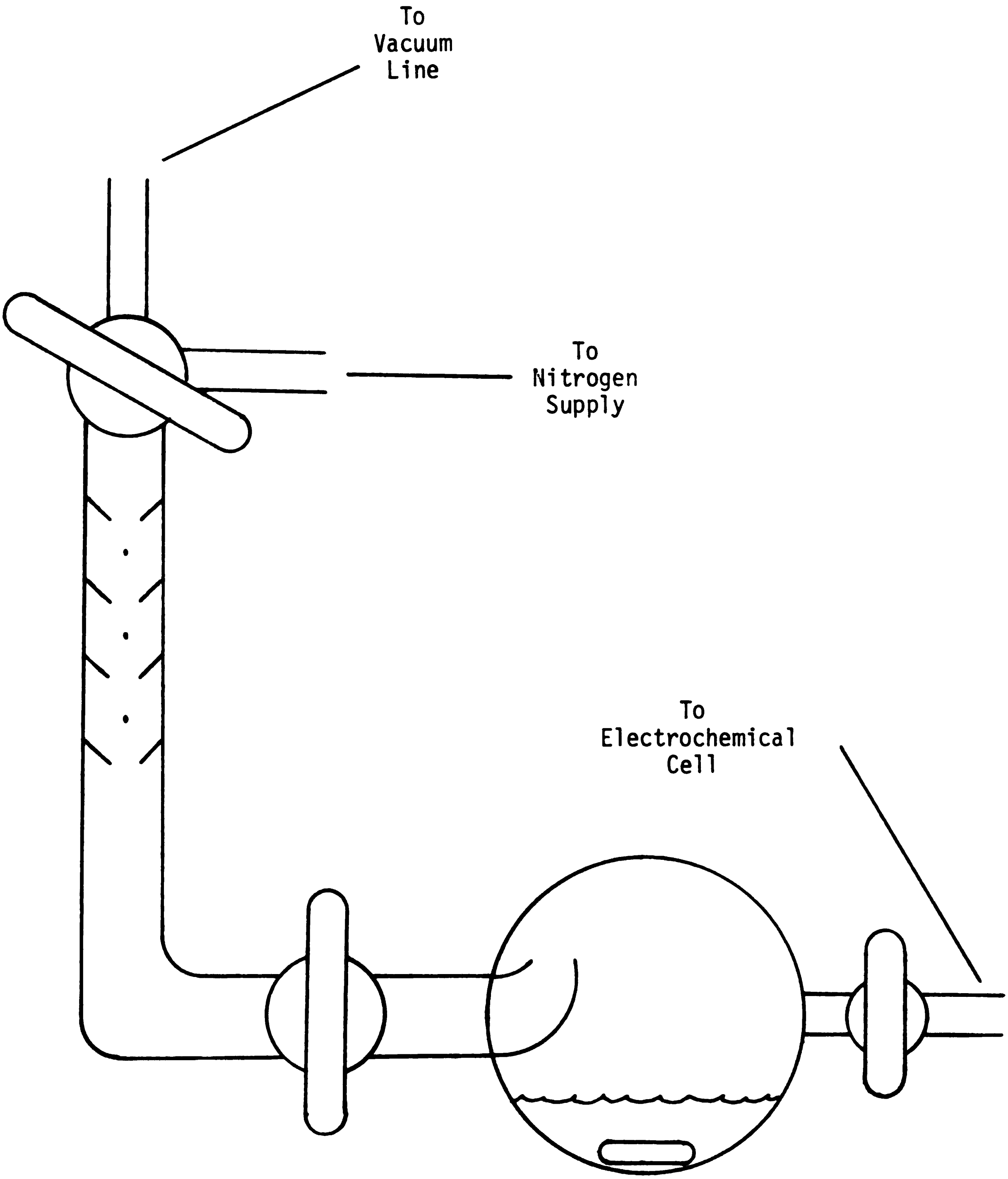
The potentiostat used for cyclic voltammetry, linear sweep voltammetry and chronoamperometry was a Princeton Applied Research (Princeton, New Jersey) Model 173 equipped with a digital coulometer. Potential ramps were supplied by a PAR Model 175 programmer. Differential pulse, linear sweep voltammetry was accomplished using a PAR Model 174 polarographic analyzer. All results were recorded on a Houston Instruments (Houston, Texas) Model 2000 x-y recorder.

In order to investigate the redox behavior of the metal chelates, it was necessary to use deoxygenated solutions. In solutions containing dissolved oxygen, the current due to oxygen reduction obscures the current due to other Faradaic processes occurring at the electrode. Electrolyte solutions were deoxygenated using the apparatus shown in Figure 7. A degassing bulb was constructed of Pyrex.® Solutions were

Table 1

Concentrations of Saturated Solutions of Metal Phthalocyanines in Methanol

MnPc	$2.6\text{x}10^{-4}$M
FePc	$4.8\text{x}10^{-5}$M
CoPc	$3.0\text{x}10^{-5}$M
NiPc	$4.1\text{x}10^{-4}$M
CuPc	$2.1\text{x}10^{-5}$M
ZnPc	$3.8\text{x}10^{-4}$M



Apparatus for Degassing Solutions

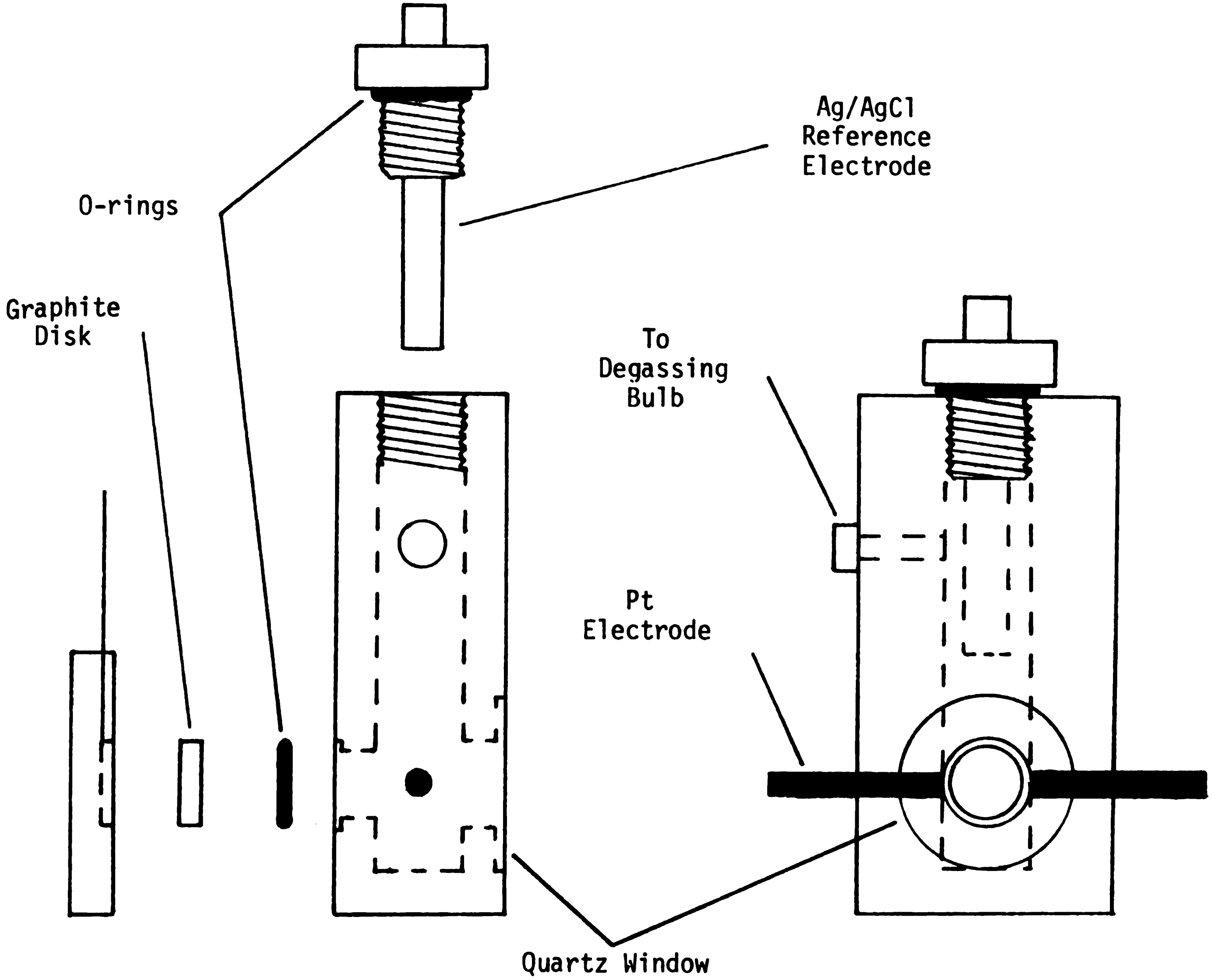
Figure 7

degassed in vacuo with stirring for five minutes, then flushed with nitrogen which had been purified by passage over hot copper wool. Those steps were repeated several times. Introduction of the deoxygenated solution into the electrochemical cell was accomplished by evacuating the cell and forcing in the liquid with a slight overpressure of nitrogen.

Oxygen saturated solutions were prepared by gently bubbling with oxygen from a cylinder for 30 minutes. Small controlled injections of oxygen were made electrochemically using a second platinum electrode (see below), the amount being measured by the number of coulombs passed.

C. Electrochemical Cell

The basic cell for electrochemical and photoelectrochemical measurements was constructed of Lucite® and is shown in Figure 8. The graphite disc working electrode was sealed to the cell body by a Viton® o-ring and held in place by a Lucite® backing plate which bolted to the cell body. Electrical contact was made through a circular piece of nickel foil and nickel wire lead which fit into recessed areas in the backing plate. The reference electrode was constructed of a Pyrex® tube with a thirsty quartz frit (Corning Glassworks, Corning, New York) sealed to it with heat shrinkable tubing. A silver wire, which had been anodically coated with AgCl,(59) immersed in a saturated potassium chloride solution served as the Ag/AgCl reference electrode. This assembly was mounted in a threaded cap with epoxy resin. The cap was also fitted with an o-ring which provided a gas/liquid seal. Two #10



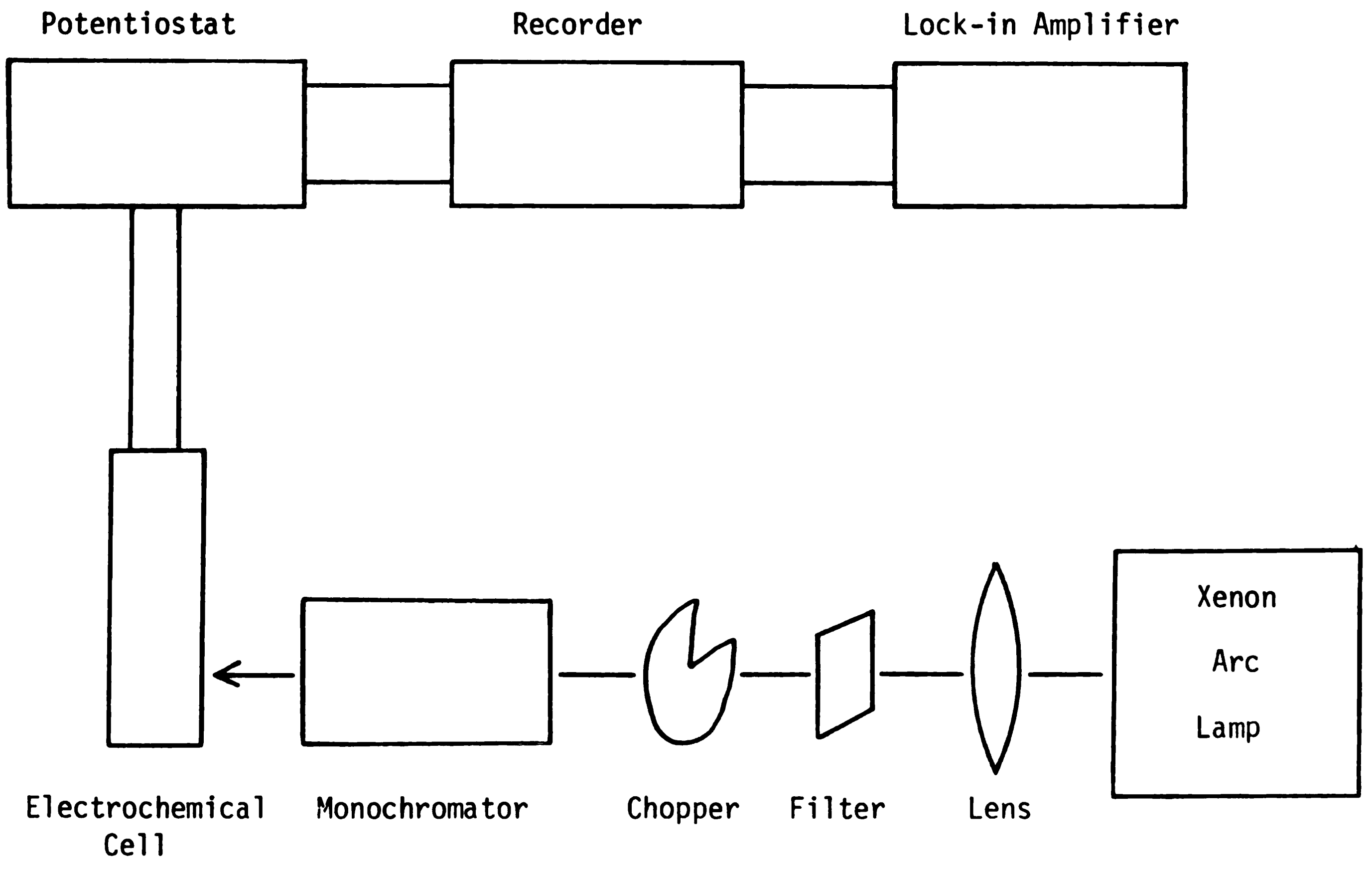
Electrochemical Cell

Figure 8

guage platinum wires were sealed through the sides of the cell. One was used as the auxilliary electrode in the electrochemical measurements. The second platinum electrode was used to generate controlled oxygen concentrations in the cell by anodic decomposition of the solvent water. The oxygen concentration could be controlled by the number of coulombs passed as measured with the digital coulometer. Connection to the degassing bulb (Figure 7) was made through a Teflon® lined micro-valve (The Hamilton Co., Reno, Nevada).

D. Photoelectrochemical Measurements

The cell used for electrochemical measurements, Figure 8, was also fitted with a quartz window to permit entry of a light beam during the electrolysis. The apparatus used for the photoelectrochemical studies is shown schematically in Figure 9. The light source consisted of an Electra Powerpac Corp. power supply and an Oriel lamp housing with a 450 watt xenon-arc lamp. The light beam was passed through a six inch water filter and an infrared interference filter to minimize thermal effects. The wavelength of the light reaching the surface of the working electrode was controlled either by a series of long pass filters (Oriel) or by an Oriel monochromator. The photocurrent was measured either directly as the difference in current output of the potentiostat between dark and illuminated, or by using a PAR Model 126 lock-in amplifier as a phase sensitive monitor which was triggered by a chopper in the light beam operating at 13 hertz. All photocurrents were measured with the working electrode poised at a potential sufficiently cathodic to insure diffusion controlled conditions as determined from current-voltage curves. To eliminate stray interfering



Schematic Diagram of Apparatus for Photoelectrochemical Measurements

Figure 9

signals, the electrochemical cell was enclosed in a grounded woven wire cage during the measurements.

E. Materials and Reagents

Carbon electrodes were employed as support for the phthalocyanines and porphyrins studied as electrocatalysts for the reduction of oxygen. These were obtained from Ultra Carbon Corp. (Bay City, Michigan) and were in the form of 0.5 inch diameter discs of microcrystalline electrographite with a vapor deposited coating of pyrolitic graphite (∿1000 μm thickness). These discs were approximately 0.125 inch in thickness. Before use, the graphite electrodes were pretreated by extraction with toluene. The extraction was carried out in a standard Soxhlet apparatus using anhydrous toluene for a minimum of two hours. To insure removal of any residual solvent, the discs were stored *in vacuo* overnight prior to use.

A small number of experiments were done with metal chelates supported on conductive tin oxide glass plates. Vapor deposited tin oxide on glass was obtained from Pittsburgh Plate Glass (Pittsburgh, Pennsylvania). The SnO_2 films were approximately 4000-7000 Å thick on the glass support.

The phthalocyanine complexes (Pc) of Mn, Fe, Co, Ni, Cu and Zn were purchased from Eastman Kodak (Rochester, New York) and were used as received. Iron (III) tetraphenylporphyrin chloride (Fe(III)TPPCl), iron (III) octaethylporphyrin chloride (Fe(III)OEPCl) and the three iron (III) cofacial diporphyrins (Fe-Fe-5, Fe-Fe-6 and Fe-Fe-7) were prepared in Professor Chang's laboratory and supplied by him for this study.(48)

The methanol (Fischer) and dichloromethane (Drake) used for catalyst deposition and the toluene (Drake) used for extraction of the graphite electrodes were used as supplied without further purification.

All aqueous solutions were prepared in distilled water which had passed through a Milli Pore Milli-Q® system containing an anion exchange resin, a cation exchange resin and an activated charcoal bed. The alkaline electrolyte was prepared from reagent grade potassium hydroxide. Reagent grade sodium hydroxide and potassium dihydrogen phosphate were used to prepare the pH 7 buffer solutions.

CHAPTER III

RESULTS AND DISCUSSION

A. Oxygen Reduction on Metal Phthalocyanines

There have been a number of studies of oxygen reduction occurring at metal phthalocyanines.(17,18,24-30,51,52,54-56) One factor which is cited as having an effect on the activity for oxygen reduction is the nature of the surface of the support material.(27) To begin the study of oxygen reduction by monolayer levels of the metal phthalocyanines supported on pyrolitic graphite, the relative activities of the complexes of Mn, Fe, Co, Ni, Cu and Zn were determined. A comparison of the linear sweep voltammograms of these metal derivatives in oxygen saturated 0.1 N KOH is shown in Figure 10. A similar comparison is shown in Figure 11 for the differential pulse voltammograms in oxygen saturated pH 7 phosphate buffer. As these comparisons show, there are variations in the activity with central metal atom and the ordering varies somewhat with the change in pH. A better comparison can be drawn if the activities for oxygen reduction are quantified. Electrocatalysts can be compared by comparing the potential at which the reaction occurs at a constant current density. For a reduction, the less cathodic the potential, the more active the electrocatalyst. The activities of the metal phthalocyanines are shown in Table 2 for both electrolytes. From this listing, the order of catalytic activity observed for the metal phthalocyanines is

$$\mathrm{Fe}>\mathrm{Mn}>\mathrm{Co}\approx\mathrm{Zn}>\mathrm{Ni}>\mathrm{Cu}$$

in 0.1 N KOH, and

$$\mathrm{Co}>\mathrm{Fe}>\mathrm{Mn}\approx\mathrm{Ni}\approx\mathrm{Zn}>\mathrm{Cu}$$

in pH 7 phosphate buffer. This ordering of activities can be compared with the results of other studies.(25,28,30) in which it has been

Linear sweep voltammograms. Oxygen Reduction on metal phthalocyanines
Oxygen saturated 0.1 N KOH, 25°C, 20 mV/sec.

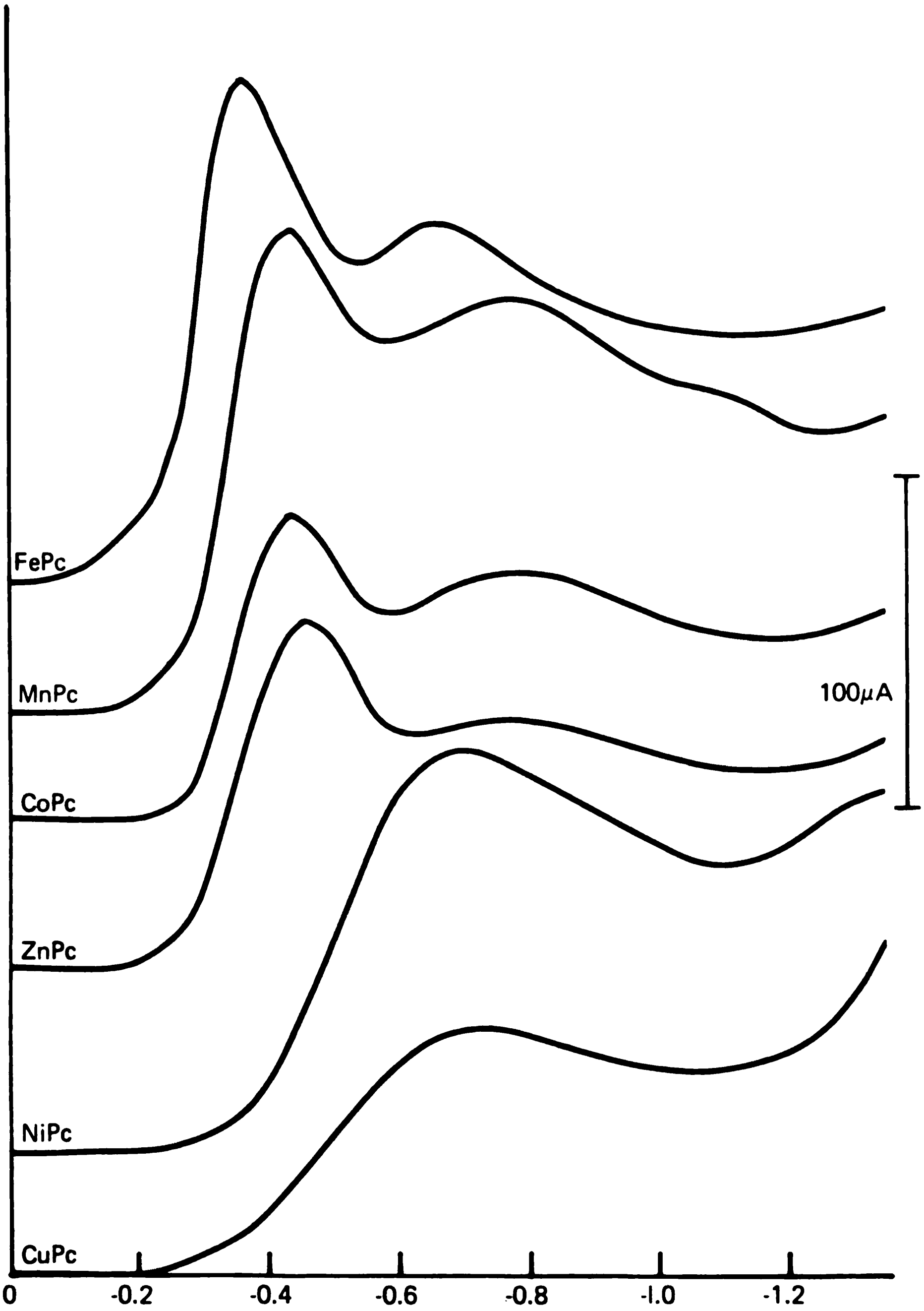
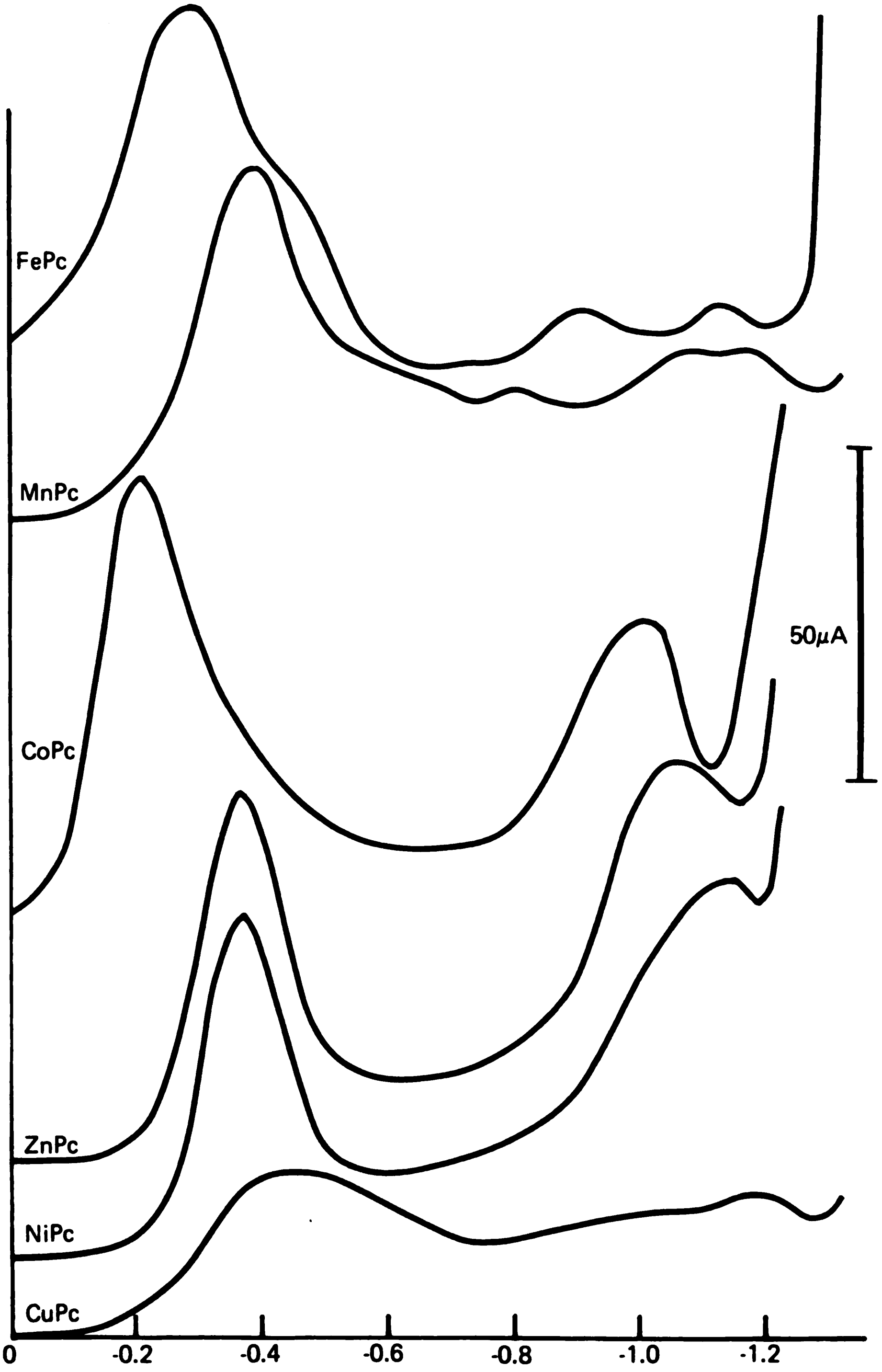


Figure 10

Differential pulse voltammograms.
Oxygen Reduction on metal phthalocyanines
Oxygen saturated phosphate buffer (pH 7), 25°C, 5 mV/sec.



E vs Ag/AgCl

Figure 11

Table 2

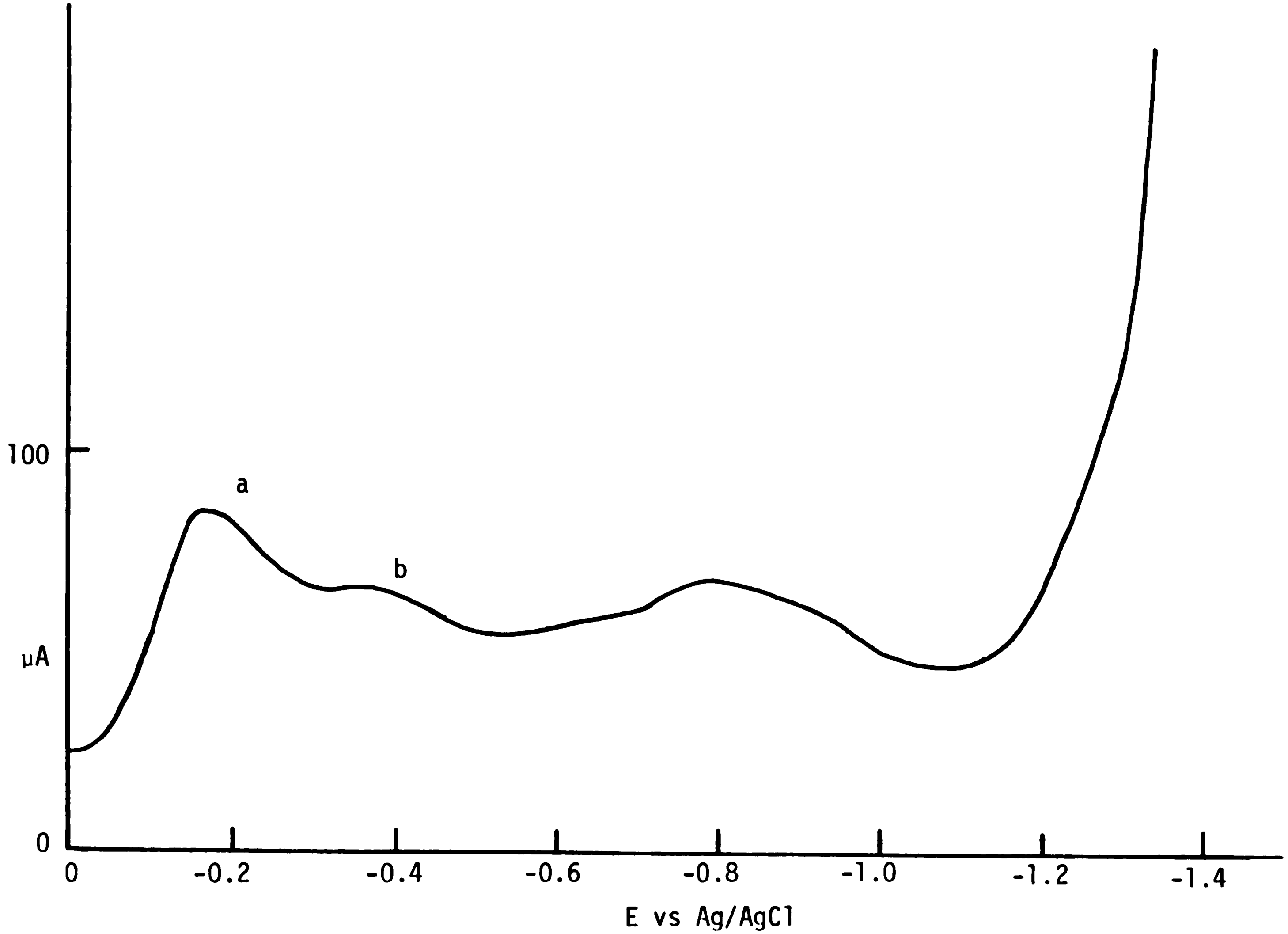
Activities of the Metal Phthalocyanines
for Oxygen Reduction

	E vs Ag/AgCl	
	0.1 N KOH @ 100μA/cm^2	pH 7 @ 50μA/cm^2
MnPc	-0.33	-0.32
FePc	-0.29	-0.18
CoPc	-0.37	-0.14
NiPc	-0.51	-0.32
CuPc	-0.63	--
ZnPc	-0.37	-0.32

observed that the activity of the iron and cobalt complexes is higher than that of the nickel and copper complexes.

Beck(28) explained these relative activities as being due to a "redox" mechanism in which the availability of a second valence state in the metal favors oxygen reduction. Randin(25) has interpreted the differences in activities with central metal through correlations between the electrochemical activity and oxidation potential, magnetic properties and gas phase chemical catalytic activity. Alt and co-workers(30) have theorized that the electrochemical activity arises due to the ability to bond molecular oxygen and have developed an explanation based on the interaction of the π^* anti-bonding orbitals of oxygen and vacant $d_z{}^2$ orbitals of the metal in the phthalocyanine complex.

Beyer and von Sturm(71) investigated the reduction of oxygen at a dropping mercury electrode in a methanol solution which was 0.1 N in LiOH and contained dissolved iron phthalocyanine. The square wave polarogram shown in their paper is quite similar to the differential pulse voltammogram of oxygen reduction at an iron phthalocyanine monolayer in 0.1 N KOH observed in this study, Figure 12. The initial, sharply rising peak, quite similar to peak a in Figure 12, was attributed to the reduction of oxygen to superoxide ion. The second peak, similar to peak b in Figure 12, was assigned to the further reduction of superoxide and, if water were present, the formation of H_2O_2. Such reactions would tie in with the mechanism proposed by Sawyer(23) and it has been suggested(23) that superoxide may be



Differential Pulse Voltammogram. Iron phthalocyanine, oxygen saturated 0.1 N KOH, 24°C, 5 mV/sec.

Figure 12

observable in a strongly alkaline aqueous media.

B. Oxygen Reduction on Iron Porphyrins

The activities for oxygen reduction on the iron porphyrins were determined as for the phthalocyanines. The linear sweep voltammograms recorded in 0.1 N KOH are shown in Figure 13. The activities (see Table 3) are in all cases lower than iron phthalocyanine in the same electrolyte. The iron octaethylporphyrin and the diporphyrin Fe-Fe-6 do have activity comparable to cobalt phthalocyanine. The greater activity exhibited by Fe-Fe-6 compared to either Fe-Fe-5 or Fe-Fe-7 suggests that the interplanar spacing may be optimum for oxygen binding in this complex. In the neutral phosphate buffer, Figure 14 and Table 3, much larger variations in activity are seen. The iron octaethylporphyrin has a very high activity, even surpassing that of iron phthalocyanine. In contrast, on the tetraphenylporphyrin complex, oxygen reduction occurs several hundred millivolts more cathodic and the peak current is very low. These effects may be due to steric factors, with the bulky phenyl groups preventing good contact with the supporting electrode and resulting in a hindrance to the electron transfer step. An interesting pH effect is also seen in the diporphyrin materials. In the alkaline solution of pH ∿13, the iron diporphyrins have activities for oxygen reduction comparable to the monomeric octaethyl- and tetraphenylporphyrins. At pH 7, however, the diporphyrins show much lower activity with the reduction potential at 50 $\mu A/cm^2$ occurring 0.5-0.6 V cathodic of the potential observed with the octaethylporphyrin. This is somewhat akin to the pH dependence, called the Bohr effect, of oxygen binding seen in hemoglobin which binds

Linear sweep voltammograms. Oxygen Reduction on metal porphyrins
Oxygen saturated 0.1 N KOH, 25°C, 20 mV/sec.

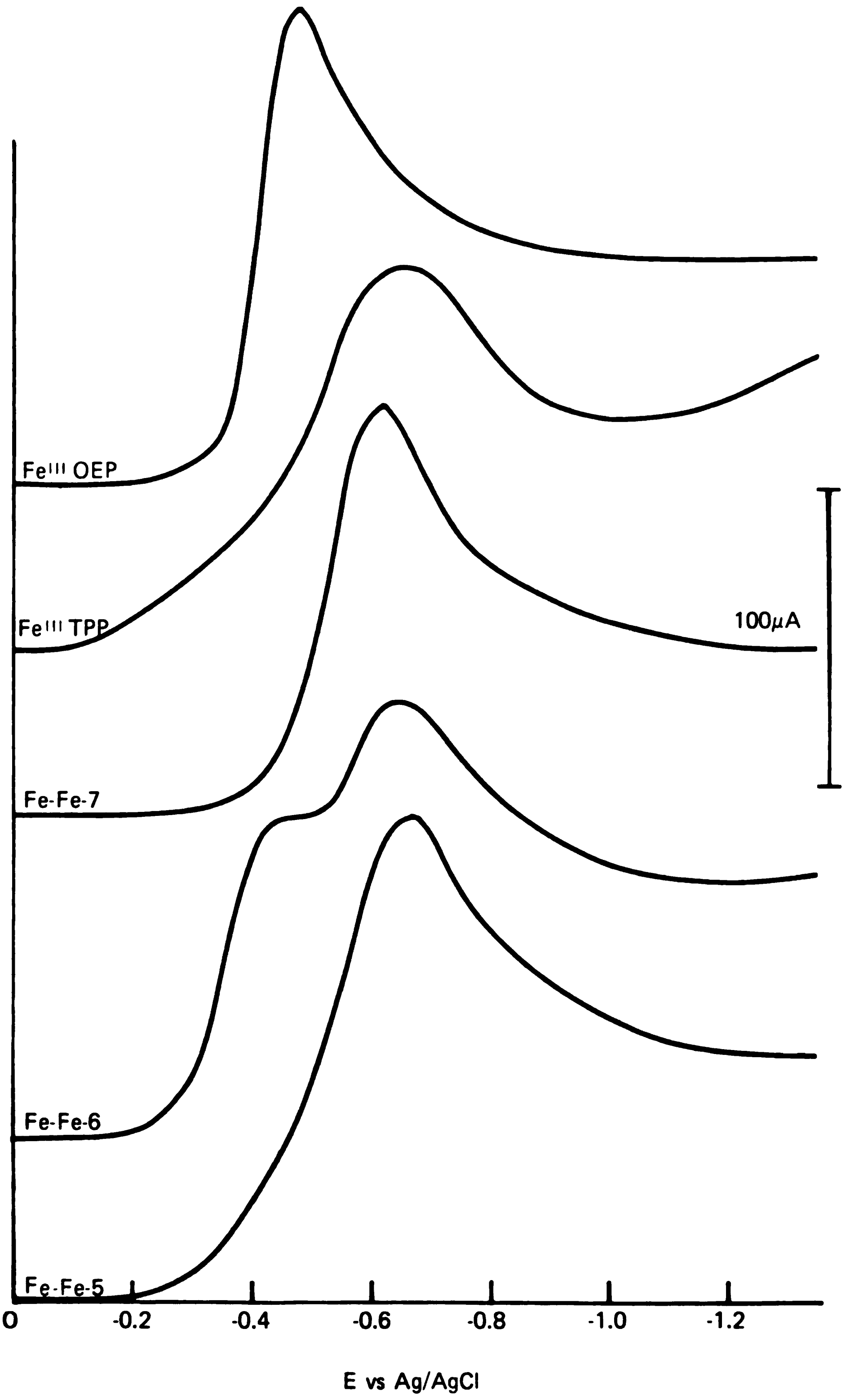


Figure 13

Differential pulse voltammograms. Oxygen Reduction on Metal Porphyrins
Oxygen saturated phosphate buffer (pH 7), 25°C, 5 mV/sec.

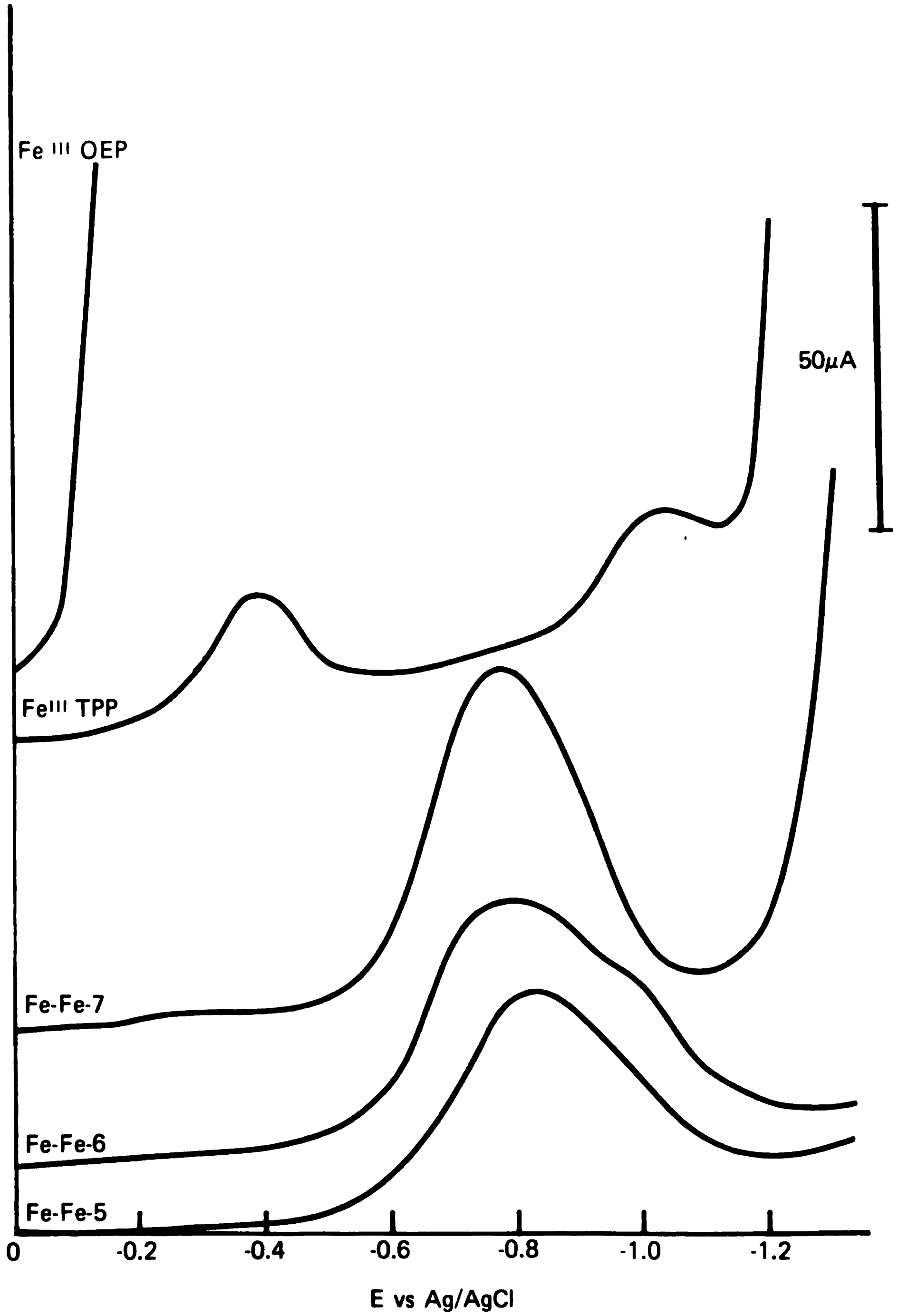


Figure 14

Table 3

Activities of the Iron Porphyrins for Oxygen Reduction

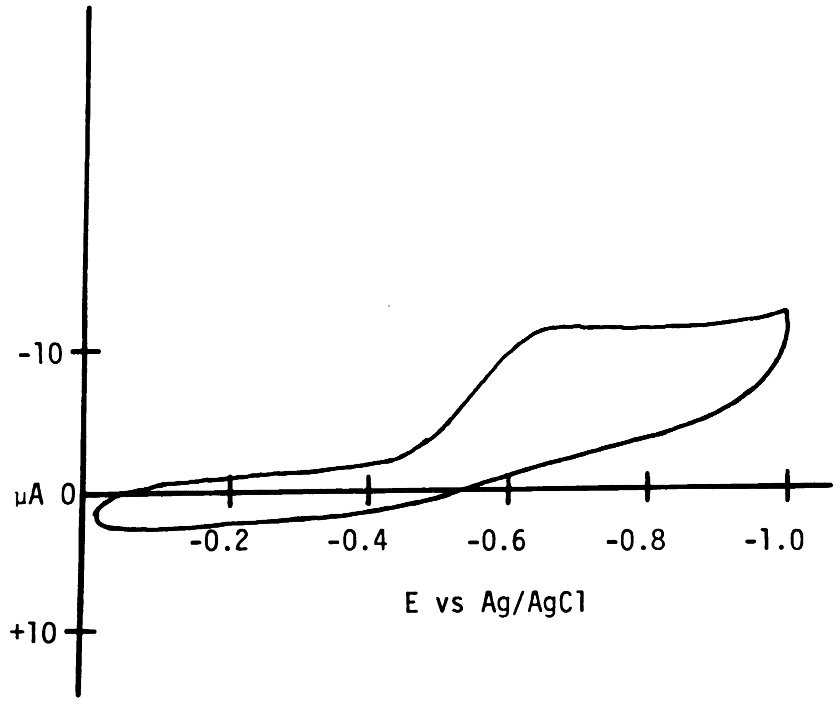
	E vs Ag/AgCl	
	0.1 N KOH @ 100μA/cm^2	pH 7 @ 50μA/cm^2
Fe(III)OEPCl	-0.39	-0.10
Fe(III)TPPCl	-0.49	--
Fe-Fe-5	-0.49	-0.77
Fe-Fe-6	-0.37	-0.70
Fe-Fe-7	-0.52	-0.66

oxygen better at higher pH.(72)

C. Electrochemistry in Deoxygenated Solution

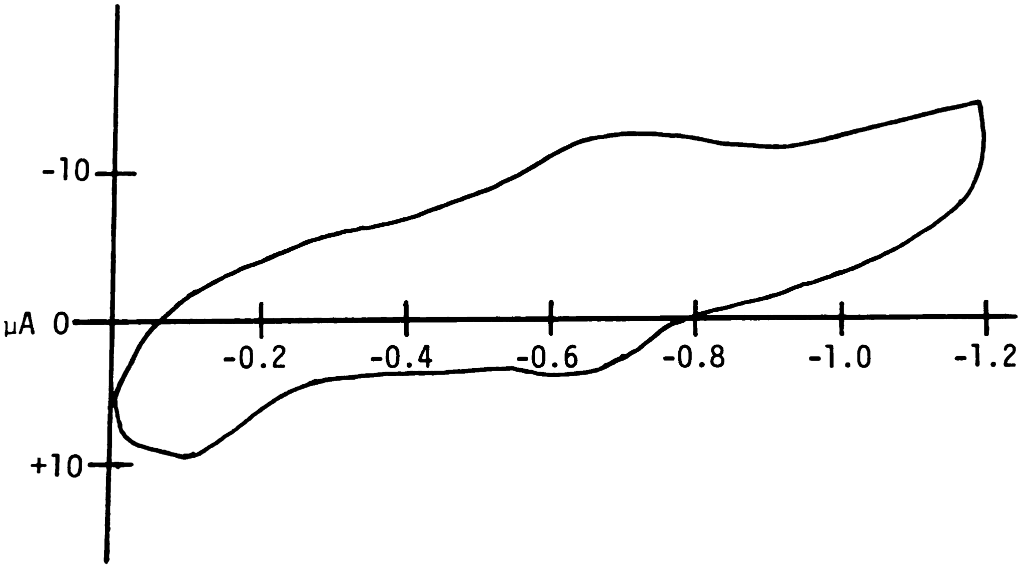
Solutions were deoxygenated using the apparatus and procedure described above and the redox behavior of the metal chelates was investigated using cyclic voltammetry. All the materials studied, both phthalocyanines and porphyrins, were found to exhibit a reduction wave in the vicinity of -0.6 V vs Ag/AgCl. In all cases, except one, this proved to be an irreversible process with no oxidation wave appearing on the reverse scan. Such behavior is shown in the cyclic voltammogram, Figure 15, for the diporphyrin Fe-Fe-7. The only material for which a reversible redox couple was observed was iron phthalocyanine. In both 0.1 N KOH and the pH 7 buffer, iron phthalocyanine exhibited reversible redox behavior at a potential of -0.65 V vs Ag/AgCl. The potential observed for a given chelate on several different electrodes could vary as much as 30 millivolts and the curves shown in Figure 6 are also due to this redox process. The form of the cyclic voltammogram, Figure 16, is typical of an electrochemical reaction involving an absorbed layer.(60) The position of the peaks remained constant at scan rates from 20 mV/sec to 1000 mV/sec, the latter approaching the response capabilities of the x-y recorder used. This indicates that the observed process is fast with respect to the available measuring methods.

The observed redox couple could correspond to electron addition/abstraction involving either the phthalocyanine ring or the iron in the complex. Clack, Hush and Woolsey(53) have indicated that



Cyclic Voltammogram. Fe-Fe-7, Oxygen-free
0.1 N KOH, 24°C, 500 mV/sec.

Figure 15



Cyclic Voltammogram. Iron phthalocyanine, oxygen-free 0.1 N KOH, 24°C, 500 mV/sec.

Figure 16

measurements they have made are consistent with a reduction proceeding through a change in the metal valence in iron phthalocyanine. Davis and Martin(73) have observed a reversible couple for a water soluble iron porphyrin occurring at nearly the same potential as that in this study. They attributed this reversible behavior to the reaction

$$\text{Fe(III) porphyrin} + e^- = \text{Fe(II) porphyrin}$$

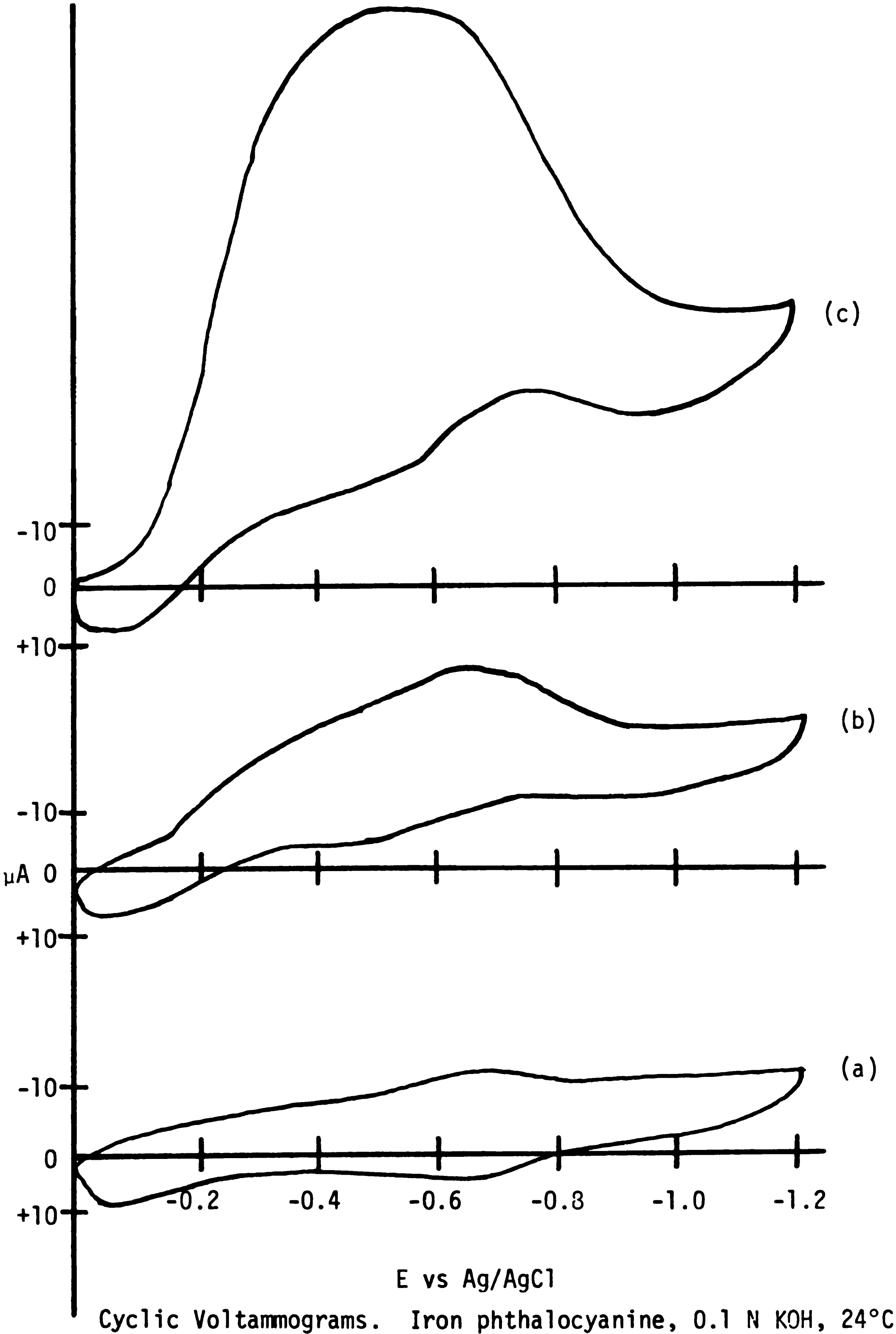
From these studies it appears likely that the reaction occurring is

$$\text{Fe(III)Pc} + e^- = \text{Fe(II)Pc}$$

but from the cyclic voltammogram alone it is not possible to establish this unambiguously.

To determine if the observed redox reaction plays a role in oxygen reduction occurring at iron phthalocyanine, cyclic voltammetry was again employed, in conjunction with small, incremental additions of oxygen to the system. Figure 17a is the cyclic voltammogram of iron phthalocyanine in oxygen-free 0.1 N KOH. After the addition, electrochemically, of sufficient oxygen to make the solution concentration 2 μM, Figure 17b, the reduction peak current is significantly increased while a coupled oxidation peak is no longer observed. When the solution is made 20 μM in oxygen, Figure 17c, the reduction peak is greatly increased and now an anodic shift of the peak becomes apparent.

Beck(28) reported similar behavior for cobalt dibenzotetrazannulene and iron phthalocyanine in 4.5 N H_2SO_4. The mechanism proposed to explain these observations was dubbed "redox catalysis" and is exemplified by reactions XI through XIV. This reaction scheme is claimed to account for the shift of the peak to values more positive



Cyclic Voltammograms. Iron phthalocyanine, 0.1 N KOH, 24°C, 500 mV/sec., (a) oxygen-free, (b) 2 μM oxygen, (c) 20 μM oxygen.

Figure 17

than the redox couple and the influence exerted by the substrate through variation of electron density at the metal center.

Kuwana *et al.*(29) have also reported the contribution to oxygen reduction of a reversible redox couple for a water soluble iron porphyrin. Their results show that the potential of oxygen reduction was governed by the potential of the redox couple with no anodic shift in the presence of oxygen. The experimental observations were said to be completely explained by an *ec catalytic* scheme represented by reactions XV and XVI.

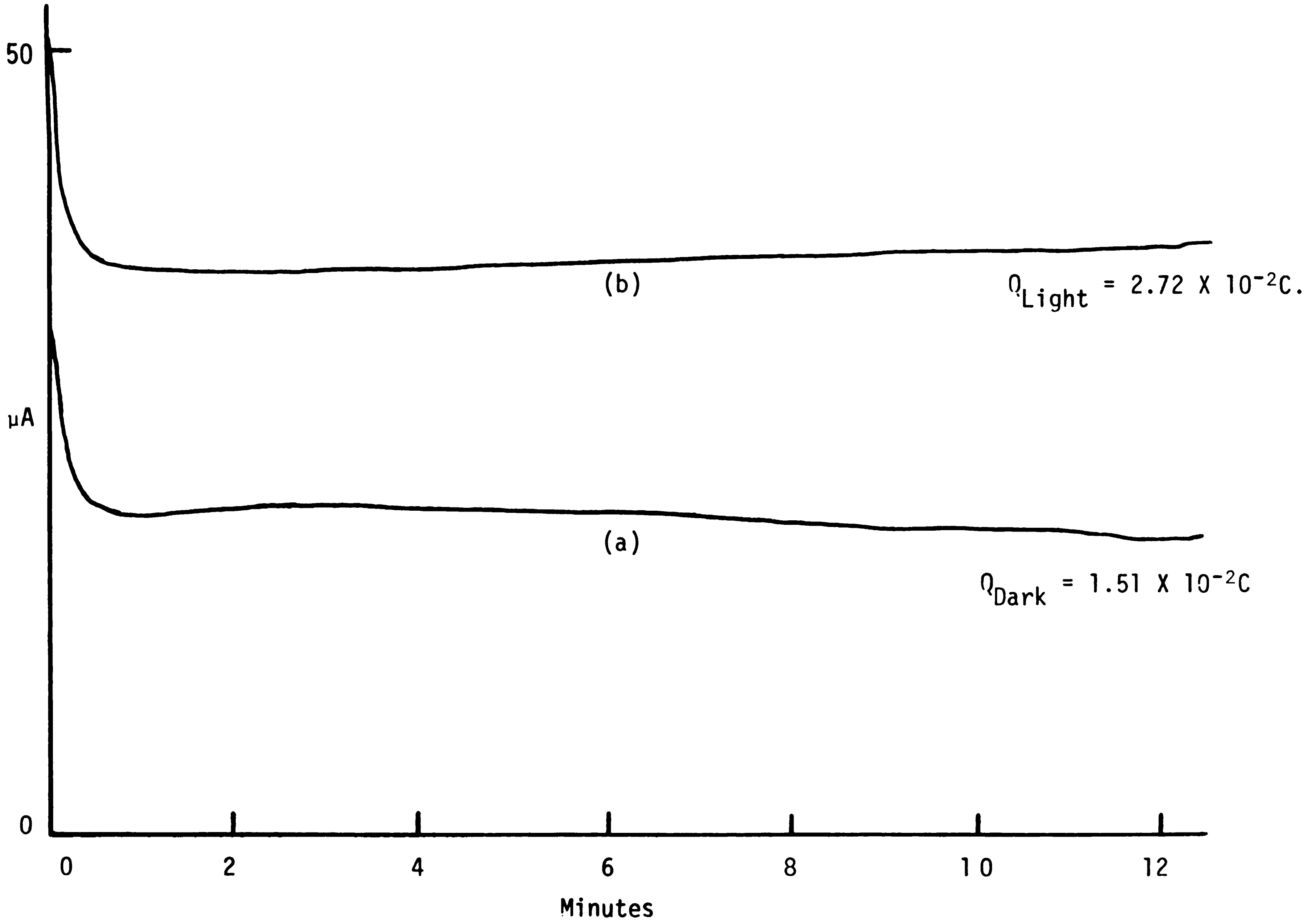
The basic differences between these two mechanisms lie in whether or not a coordinated oxygen species is reduced in the electrochemical step and the apparently homogeneous reaction proposed by Kuwana as the oxygen reduction step.

It is not possible to determine if either of these pathways is operable with iron phthalocyanine solely on the basis of the cyclic voltammetric behavior, although it is apparent that the reversible redox couple of the iron phthalocyanine is intimately involved in the mechanism of oxygen reduction occurring at this macrocycle.

A determination of the mechanism of oxygen reduction would involve use of the rotating ring-disk electrode and possibly the digital simultation techniques as discussed by Bard and co-workers.(74-76)

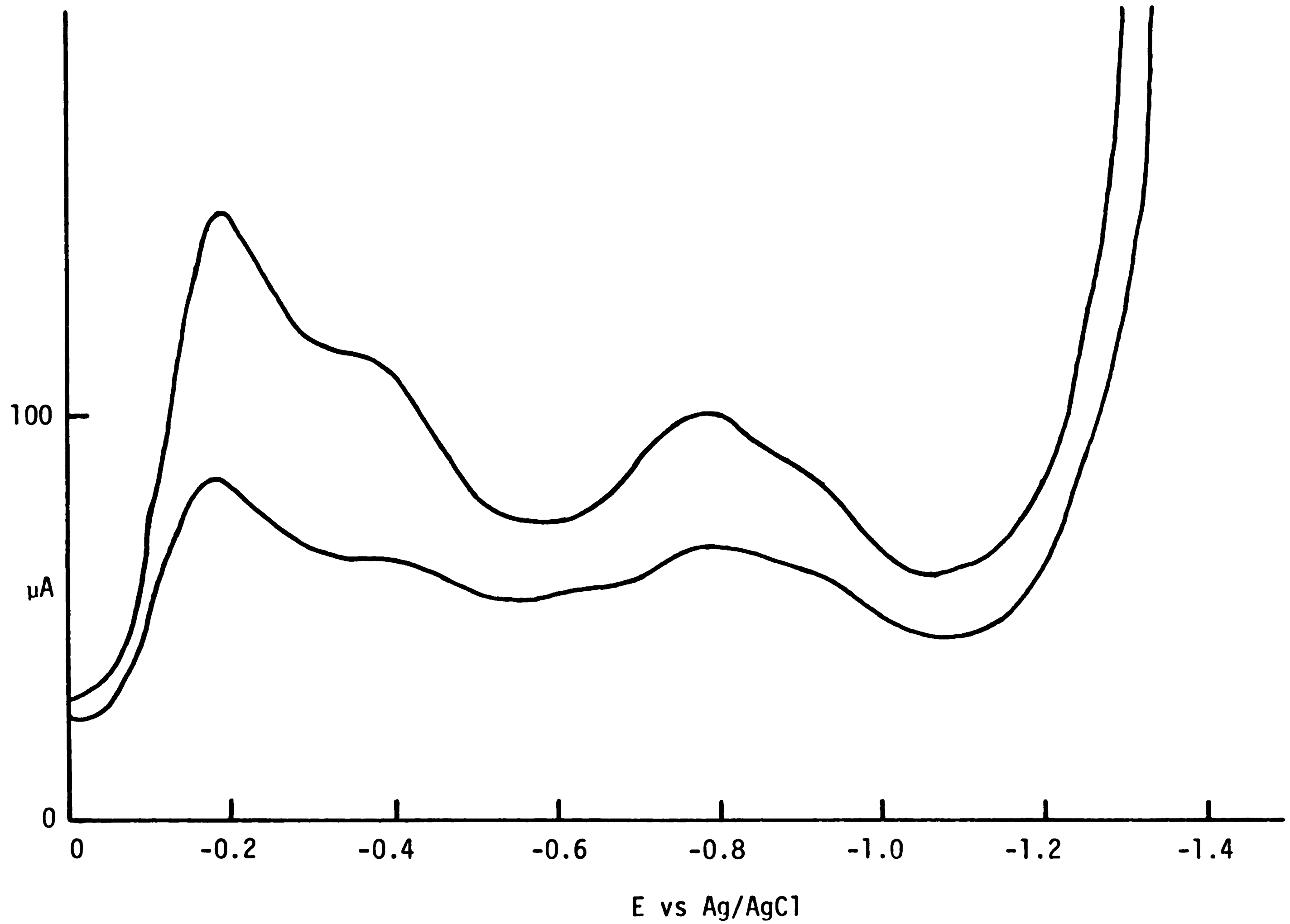
D. The Effects of Illumination on Oxygen Reduction at Metal Chelates

Oxygen reduction during illumination was studied on monolayers of iron and cobalt phthalocyanine and iron octaethylporphyrin. The initial investigation of the effects of illumination was done by recording chronoamperometric curves of chelate covered electrodes in oxygen saturated solutions. The potential was stepped from open circuit to a value beyond the peak potential as observed in Figures 10, 11, 13 and 14 and the current-time curves were recorded. A comparison of such curves recorded in darkness and illuminated is shown in Figure 18 for an iron phthalocyanine monolayer on pyrolitic graphite. Reference to this figure shows that the steady state current density has nearly doubled due to the light. Measurement of the total charge, Q, passed during the recording of each curve using a digital coulometer allows an accurate evaluation of the observed effect. For monolayers of iron phthalocyanine, cobalt phthalocyanine and iron octaethylporphyrin, the ratio Q_{light}/Q_{dark} was 1.8, 1.7 and 1.8 respectively. These observations led to speculation that illumination brought about a change in the mechanism of oxygen reduction, perhaps going from a two electron process to a four electron process, the results of other experiments, however, make this hypothesis unlikely. For example, differential pulse voltammetric curves, Figure 19, show that, while the current density is increased, the peak potentials remain essentially unaltered upon illumination. Some shift of the voltammetric peaks would be expected if a change in the mechanism had occurred. Another observation showed that increased surface coverage resulted in a greater increase in the illuminated current density, e.g. at a loading equivalent to five monolayers, iron octaethylporphyrin exhibited a



Chronoamperemetric curves. Iron phthalocyanine, oxygen-saturated pH 7 buffer, 24°C, Ez -0.30 V vs Ag/AgCl, (a) Dark, (b) Illuminated

Figure 18



Differential Pulse Voltammograms. Iron phthalocyanine, oxygen-saturated 0.1 N KOH, 24°C, 5 mV/sec., (a) Dark, (b) Illuminated

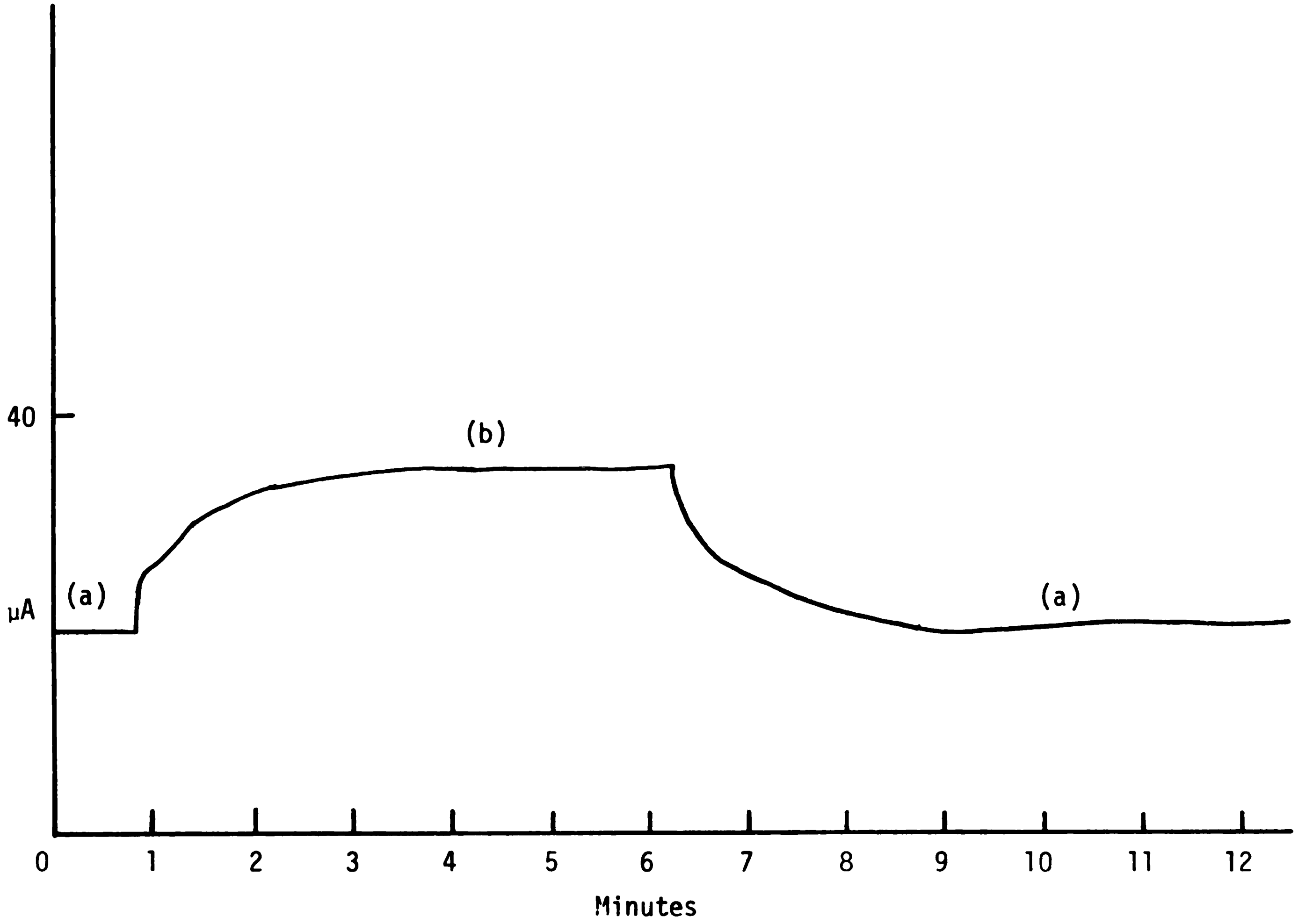
Figure 19

Q_{light}/Q_{dark} of 3.48. These points indicate that the initially observed approximate doubling of current was somewhat fortuitous and probably not indicative of a change in the mechanism of oxygen reduction.

To investigate the time response of the current due to oxygen reduction when illuminated, the electrode was poised at a potential beyond the peak potential and the current allowed to come to a steady state in the dark. A current-time curve, such as Figure 20, was recorded as the electrode was illuminated. These results show that the rise in the current can take on the order of two to three minutes before a steady value is reached. The decay of current when the light path is blocked was also quite slow. Similar current-time curves were observed for cobalt phthalocyanine and iron octaethylporphyrin.

The slow response shown by the metal chelates supported on graphite made it impossible to use both a monochromator and a lock-in amplifier to measure the wavelength dependence of this effect. The decrease in intensity due to the monochromator plus the response time which was long with respect to the cycle time of the 13 Hz light chopper used as a trigger for the lock-in amplifier, made the photocurrent too low to reliably measure. It was, however, possible to evaluate the wavelength dependence to a degree through use of a series of long pass filters.

Filters LP39, LP47, LP54, LP63 and LP70 which block out wavelengths below 390, 470, 540, 630 and 700 nm respectively, were used. The



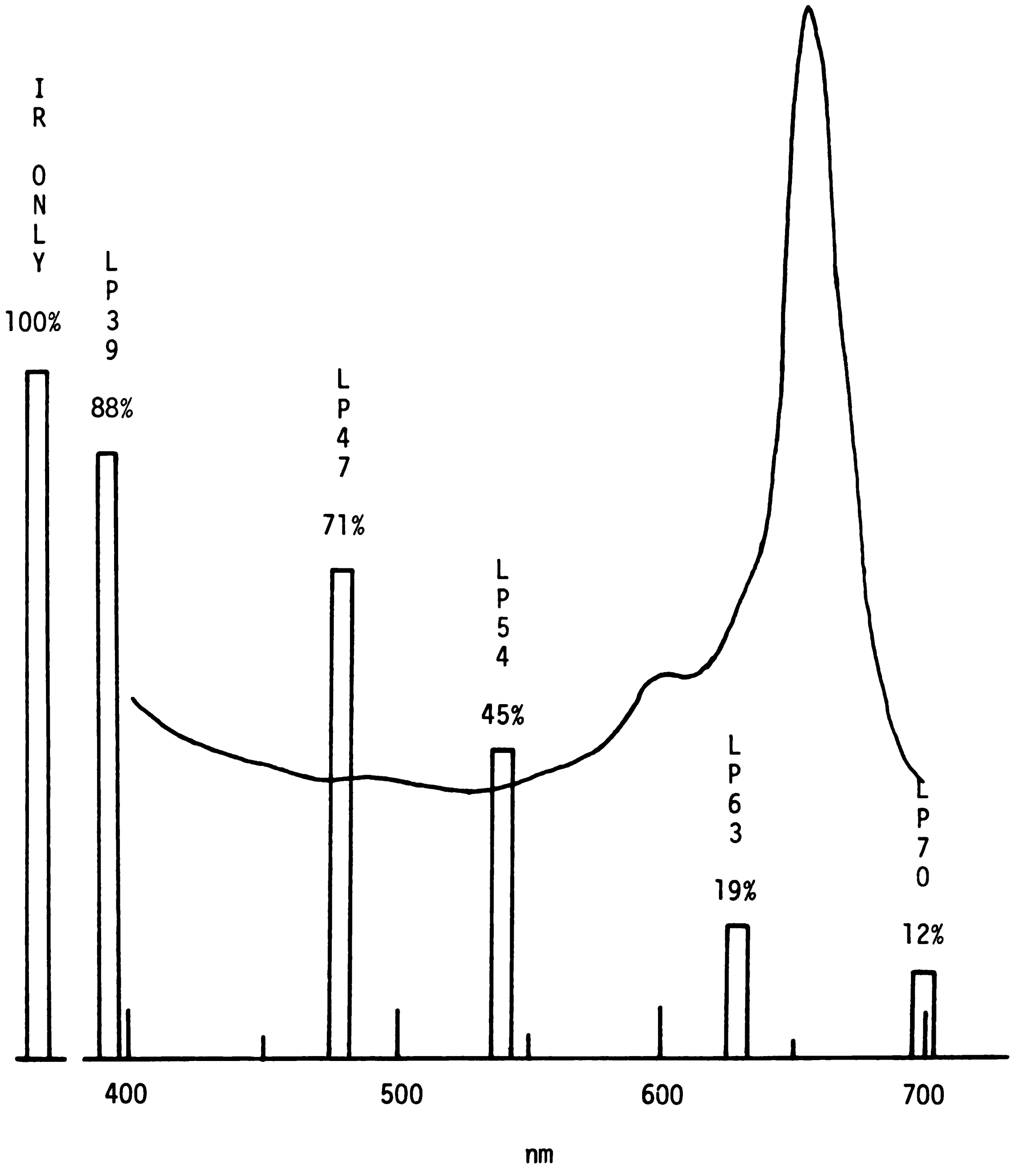
Chronoamperemetric Curve. Iron Phthalocyanine on Graphite, Oxygen-Saturated pH 7 Buffer, 24°C, E = -0.30 V vs Ag/AgCl, (a) Dark, (b) Illuminated.

Figure 20

results are portrayed in Figure 21. The current measurements using the lock-in amplifier and the various long pass filters have been normalized with the measurement made using only the infrared filter being set equal to 100%. The currents obtained with the various filters are plotted as the bars in Figure 21. The solid curve is a solution spectrum of iron phthalocyanine in methanol. There are measureable decreases in the photocurrent at wavelengths quite far from the absorption maximum in the solution spectrum, but the largest effect coincides, at least qualitatively, with the maximum absorption peak.

A number of measurements were also made using conductive tin oxide on glass as the supporting electrode. Tin oxide plates with a sublimed coating of iron phthalocyanine were prepared by C. Linkous and supplied by him for this study. The thickness of the iron phthalocyanine deposit was estimated at ca. 100 monolayers.(77) With the electrode held at -0.30 V vs Ag/AgCl, the rise in current upon illumination, Figure 22, is much faster than that observed for iron phthalocyanine monolayers deposited on pyrolitic graphite. On SnO_2, the steady state current in the light is roughly five times the dark current. The differences in behavior between the sublimed deposit on SnO_2 and the solution deposited material on graphite are probably due to the surface properties of the different substrates.(27) It is also possible that differences in orientation of the chelate molecules or the different thicknesses of the deposit affect the behavior when illuminated.

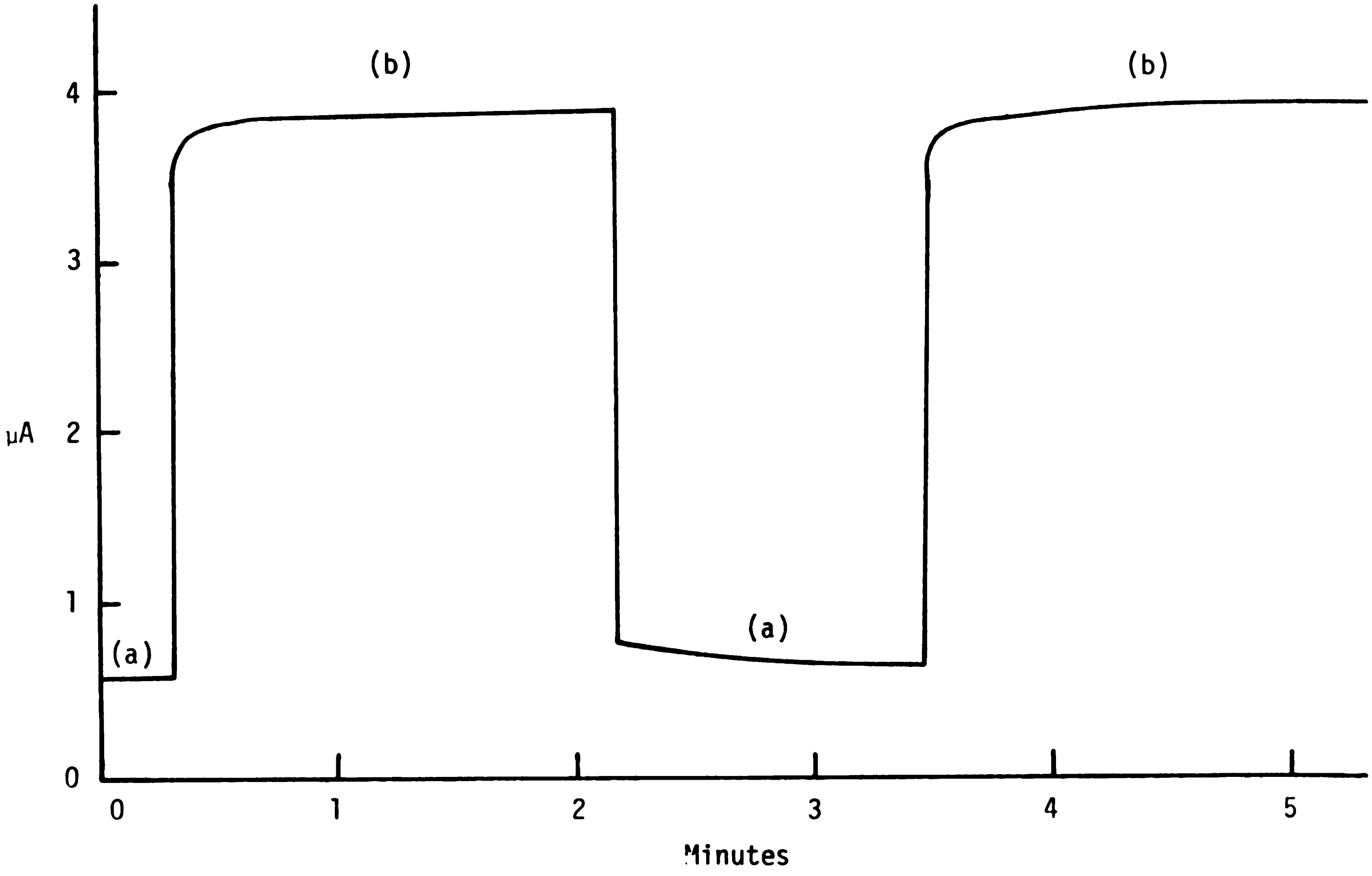
With a more rapid response to illumination, a more accurate determination of the wavelength dependence could be made using both the



Wavelength Dependence, Iron Phthalocyanine

on Graphite, Oxygen Saturated pH 7 Buffer, $24^{\circ}C$

Figure 21



Chrono amperometric curve. Iron phthalocyanine on SnO_2, oxygen-saturated pH 7 buffer, 24°C, E -0.30 V vs Ag/AgCl, (a) Dark, (b) Illuminated

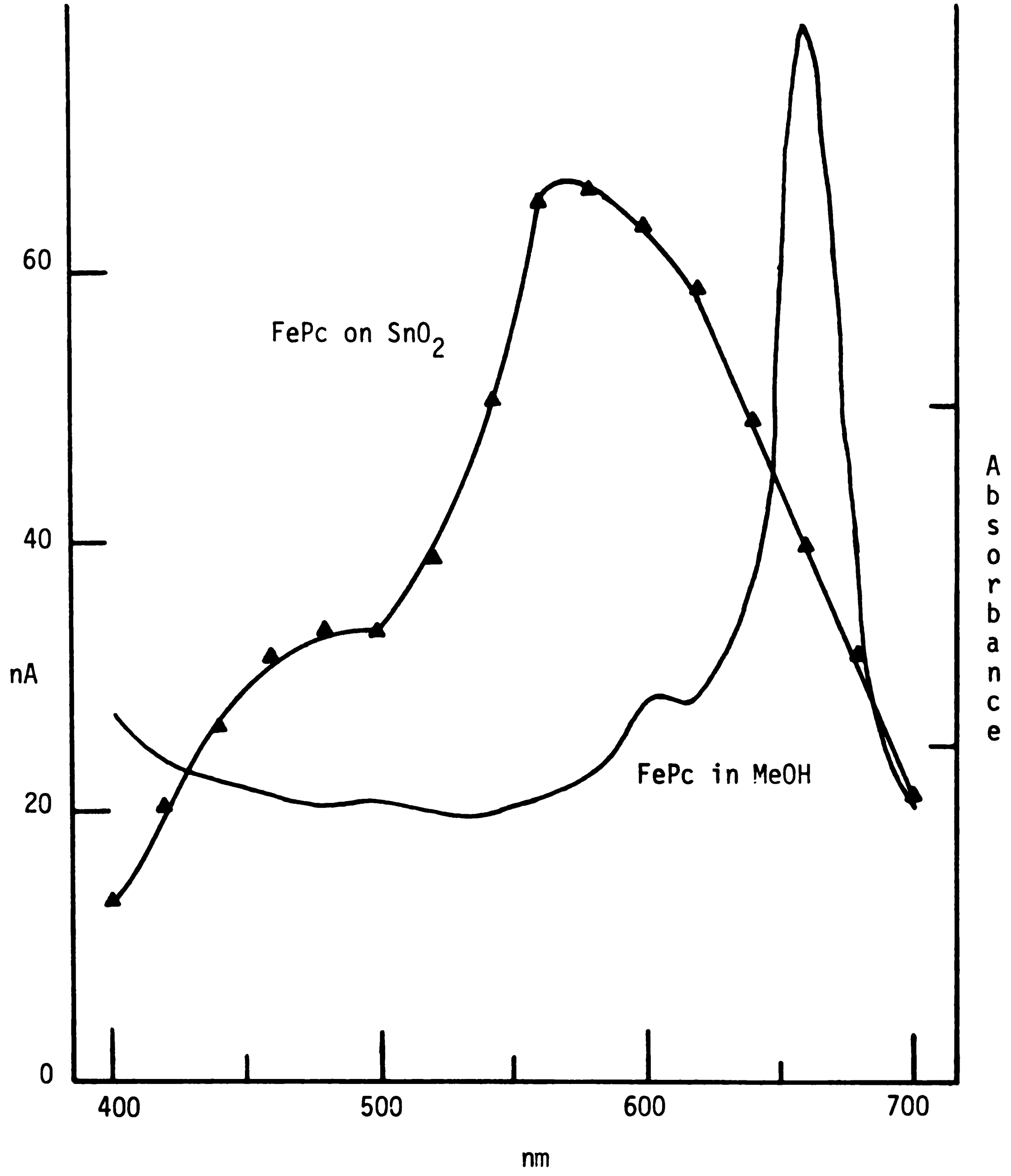
Figure 22

lock-in amplifier and a monochromator. The results of such a determination are shown in Figure 23. An absorption spectrum of iron phthalocyanine in methanol (axis at the right) is compared with the current output of the lock-in amplifier (axis at the left). The maximum current was found at 580 nm while the absorption maximum occurs near 660 nm. The current maximum corresponds more closely to a shoulder on the primary absorption peak which occurs at 600 nm.

Both absorptions are due to transitions of the phthalocyanine ring, the 660 nm peak is the result of a π-π^* transition(43) and the 600 nm peak arises due to an n-π^* transition.(44) The results reported here follow quite closely those reported by Meshitsuka and Tamaru(36) who attributed the contribution of the n-π^* excitation to an increase in the number of charge carriers in phthalocyanine films brought about by this transition. This theory would be consistent with an increase in the rate of electron transfer with no alteration in the potential of the reduction process, and would explain the behavior as shown in Figure 19.

E. Conclusion-Suggestions for Further Work

This research has shown that oxygen reduction can be effectively catalyzed by monolayer levels of macrocyclic metal chelates. A series of cofacial iron diporphyrins were shown to catalyze oxygen reduction, with the interplanar spacing and the electrolyte pH affecting the relative activity.



Wavelength Dependence, Iron Phthalocyanine on SnO_2, Oxygen Saturated pH 7 Buffer, 24°C

Figure 23

Illumination was shown to enhance the rate of oxygen reduction, with the degree of enhancement being dependent on the thickness of the chelate layer and the substrate onto which it is deposited. The wavelength of maximum current for iron phthalocyanine on SnO_2 was found to coincide with an n-π^* transition of the macrocyclic ring.

This research opens the way for more work in this area which can be directed at certain specific objectives. A determination of the mechanism by which oxygen is reduced at these metal macrocycles should be available through use of a rotating ring-disk electrode system. In addition, valuable information about the nature of the reaction can be obtained through use of the digital simulation techniques available.(74-76) A rotating ring-disk apparatus which allows entry of a light beam(78-80) could also be used to clarify the way in which incident light accelerates the reaction. The use of a pulsed dye laser would permit greater intensities and therefore facilitate the measurement of wavelength dependence. The measurement of the wavelength dependence of the current due to oxygen reduction over substances, like the metal porphyrins, which have significantly different absorption spectra than the phthalocyanines should yield information about which electronic states of these molecules are involved in oxygen binding and reduction.

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