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Photoelectrochemical Characterization of the Passive Films on Iron and Nickel

By

Stanley Mark Wilhelm

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree

Doctor of Philosophy

Approved, Thesis Committee:

Norman Hackerman, President
John L. Margrave, Professor of Chemistry
Franz Brotzen, Professor of Materials Science

Houston, Texas
May, 1979
Abstract

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The semiconducting properties of the passive films on iron and nickel have been established through capacitance, photocurrent and kinetic measurements. The passive films on iron and nickel are n-type and p-type oxide semiconductors respectively. Extrinsic conduction in the passive films is due to non-stoichiometry. Ferrous ions in the iron film act as donors in producing n-type conductivity and Ni$^{3+}$ acceptor ions in the nickel passive film give rise to p-type conductivity. The band gaps of the anodic films on iron (2.0eV) and nickel (3.3eV) are close to those expected for Fe$_2$O$_3$ and NiO.

Passivation occurs by the formation of a barrier oxide which is photoconductive and partially present even during active dissolution of the metals. Electrochemical oxidation and reduction of ionic species in solution can be correlated with the electronic structure of the passive films.
Acknowledgments

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Chapter I

Introduction

When iron metal is placed in concentrated nitric acid, a reaction takes place on the surface which terminates after several seconds. Although thermodynamically unstable the iron does not appear to react further. In this condition the iron is said to be passive and its behavior is attributed to an alteration of the metal surface. The same condition can be produced by anodic polarization in an electrochemical cell.

A general definition of passivity is advanced by H.H. Uhlig (1):

1. "A metal is passive if it substantially resists corrosion in a given environment resulting from marked anodic polarization."

2. "A metal is passive if it substantially resists corrosion despite a marked thermodynamic tendency to react."

Iron and nickel are passive by either definition. Definition 2 also applies to metals which, although in an active state, do not dissolve because of thick barrier films which form on the surface from corrosion products.

The traditional definition of passivity is limited to metals at which the active and passive surface cannot be distinguished visually. Fe, Cr and Ni are the best examples and it is with these metals that the phenomenon of passivity is most commonly associated. Iron is unique among metals which passivate in that the process of passivation is seemingly reversible. Under certain conditions, iron can oscillate between an active and passive condition with a period on the order of several seconds.
The thermodynamic stability of iron as a function of pH is illustrated in Fig. 1. The Pourbaix diagram (2) describes the equilibrium between a metal and its ions. Line A represents the equilibrium

\[ \text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2e^- \]  \[ \text{[1]} \]

for a concentration of ferrous ions of \(10^{-6}\) M. Below this line iron is thermodynamically stable. Line B denotes the equilibrium between divalent iron ions in solution and insoluble corrosion products

\[ 2\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2e^- \]  \[ \text{[2]} \]

Although corrosion is thermodynamically favored above this line, iron does not dissolve due to the formation of an insoluble oxide film on its surface. A similar diagram for nickel (2) is shown in Fig. 2.

Passivity has been the subject of numerous investigations. The first reported study was by J. Keir in England (3). He observed that iron wire remained bright in concentrated nitric acid for several weeks. Subsequent investigations by Schönbein (4) established that low reaction rates for metals in aggressive media were favored by galvanic coupling to metals which enhance a more noble potential.

In 1836, Faraday (5) proposed: "My strong impression is that the surface of the iron is oxidized or that the superficial particles are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation." In this statement, Faraday noted that an oxidative process is a fundamental requirement of passivity. It is likely that the "equivalent of oxidation" that Faraday described would today be called "adsorption". Faraday also demonstrated that passive films were not insulators which is an important and distinguishing property of the
films on iron and nickel.

The modern view of passivity does not differ significantly with Faraday's. There is some disagreement, however, as to the mechanism which leads to passivity. It is therefore necessary to draw a clear distinction between the process "passivation" and the product "a passive film". It has not been established conclusively that the reduction of the corrosion rate during passivation is due to the formation of an oxide film on the surface.

The two theories have been proposed to describe the process of passivation (6). One theory suggests that passivation is due to the formation of an oxide film which inhibits corrosion by reducing ionic conduction. The oxide itself determines the reactivity of the metal towards the environment. An alternate theory proposes that adsorption of oxygen on some oxygen containing species alters the double layer potential and hence retards surface reaction rates.

The oxide film theory is thermodynamic in nature. It assumes that under certain conditions a separate phase can form on the surface and when completely covered, the metal is no longer in physical contact with the aqueous solution. An implicit assumption is that the rate of oxide formation is greater than the rate of oxide dissolution and that oxide formation is energetically favored over metal dissolution. The adsorption theory follows a kinetic derivation in which passivity is described as a steady state condition. During passivation, the driving force for corrosion is reduced through successful competition for active metal sites by oxygen atoms. The rate of metal dissolution is greatly diminished but does not vanish.

The principal point of disagreement in the two theories is in the
Figure 1
Potential versus pH Diagram for Iron
Figure 2
Potential versus pH Diagram for Nickel
chemical step which produces full or complete passivation. The adsorption theory holds that adsorption of a monolayer or less of oxygen is sufficient to prevent dissolution. The oxide film theory suggests that a greater degree of stoichiometry is required and that a separate phase must form, not an adsorbed or chemisorbed layer. Attempts at reconciliation of the two theories are only partially successful even though they point out that a sorbed oxygen atom or oxygen containing molecule is prerequisite to oxide film formation (7). It is generally agreed that with time the passive film thickens and becomes more stoichiometric. The exact chemical and structural composition of static passive films is still unresolved.

Passivity can be induced by a variety of oxidative mechanisms. For the purposes of this thesis, the discussion will be limited to electro-chemical passivation via anodic polarization. The terms "anodic oxide" and "passive film" will be used interchangeably. The electrochemical aspects are best illustrated by a typical current/potential (i-U) curve (Fig. 3).

Metal dissolution occurs in the region AB according to Eq. 1. This portion of the curve is referred to as the active region. If the metal remained active, it would continue to exhibit an exponential i-U relationship and the current would increase in a positive direction (point C). The potential at which formation of insoluble corrosion products becomes thermodynamically possible (point B) is the "Flade Potential" and is characteristic of the initial adsorption of oxygen of the initial formation of an oxide film depending on the theory ascribed to. At point D, the rate of metal dissolution is balanced by the rate of passivation. At point E the inhibition process is complete.
Figure 3
Typical Current versus Potential Curve for a Passive Metal.
The portion of the curve between E and F is the passive region. With it we associate a small residual current \( i_p \) which is usually less than 1 \( \mu A \). At point F oxygen evolution begins, and the portion of the curve anodic to point F is the transpassive region. During the oxidation of water to yield \( O_2 \), the passive film does not participate except as a sink for electrons. This observation was one of the first empirical clues as to the inherent conductivity of passive films.

Electrochemical measurements (8-13) suggest that the passive film on iron consists of two layers, an inner \( Fe_3O_4 \) and an outer \( \gamma Fe_2O_3 \) layer. The thickness of the oxide can be determined by cathodic reduction or anodic changing curves. In general the thickness varies between 10 and 40 \( \AA \) depending on pH and the potential of formation. The rate of film growth has also been studied by electrochemical means (14-16).

Analytical techniques such as electron diffraction (8,17) and Auger Analysis (18) in general support the contention that the film on iron has a crystal structure close to \( \gamma Fe_2O_3 \). These investigations suffer from the fact that the film must be removed from its environment and evacuated for the purpose of analysis. It is not certain that under these conditions the oxide retains the structural properties it possesses in an electrolyte solution.

The results of \textit{in situ} ellipsometry studies (19-21) are consistent with the proposed model of a bilayered oxide of \( Fe_3O_4 \) and \( \gamma Fe_2O_3 \). Sato and Kudo (21) demonstrate that an oxide thickness of 9 \( \AA \) is necessary for complete passivation, thus supporting the oxide film theory. Bockris (19), however, states that a ferrous hydroxide \((Fe(OH)_2)\) film of two monolayers or less is sufficient to cause passivation and that at more anodic potentials the film converts to \( \gamma Fe_2O_3 \).
The structure of the passive film on nickel is somewhat more complicated than that of iron. Several surface oxides (NiO, Ni$_2$O$_3$, NiO$_2$, Ni$_3$O$_4$) and hydroxides (Ni(OH)$_2$, NiOOH) are thermodynamically stable depending on the pH, temperature and electrode potential of the experiment (22-27). In the pH range 6 to 9 Cohen (23-25) proposes NiO as the primary passivating oxide on the basis of electrochemical studies. Bockris (28) from ellipsometric information suggests that a precursor Ni(OH)$_2$ film is converted to a non-stoichiometric oxide (NiO$_{1.7}$) at the Flade potential. Sato and Kudo (29) also propose a NiO passive film from ellipsometric measurements.

It has been suspected for some time that the anodic oxides on iron and nickel are semiconductors (30-34) and that their electrochemical behavior is due, at least in part, to solid state properties. Although there is little direct physical evidence to support this contention, the semiconducting properties of thick anodic oxides (35,36) and thermally grown oxides on iron and nickel (37-40) have been firmly established.

The lack of a direct correlation between the solid state properties of transparent anodic oxides and their electrochemical behavior can be attributed to the fact that they are less than 50 Å thick and exhibit both metallic and semiconducting characteristics. It is also due to the absence of in situ methods of determining the physical properties of the oxides.

One goal of this thesis is to quantitatively establish the semiconducting nature of the passive films on iron and nickel and to correlate the solid state properties with ionic and electronic transport through the oxide. Spectroscopic techniques will be applied to measure the band structure and to monitor changes in physical parameters. The elec-
tronic processes involved in oxidation and reduction of molecules in solution will be examined and correlated with a model of the energy states of the oxides. From the data obtained, fundamental questions regarding the mechanism of passivity and the nature and structure of passive films will be addressed.

A photoelectrochemical technique was used in this investigation. The effect of light on semiconductors is to create electron-hole pairs in the conduction and valence bands respectively. In an electrochemical cell this translates into photovoltages and photocurrents which arise from the separation of charge. The influence of light on passive surfaces was first studied by E.K. Oshe and I.L. Rosenfeld (41-44). They measured changes in electrode potential caused by irradiation of iron electrodes with UV light. A new technique was utilized in this investigation to measure electrode currents which result from illumination. A portion of the text will deal with the technique itself which should prove to be of general use for the characterization of surface films.
Chapter II
Experimental

All solutions were made with triply distilled water \((R>10^6)\). All chemicals were reagent grade or better. The solutions were degassed with purified nitrogen \((99.95\% \text{ N}_2)\) which had passed through a heated \((400^\circ\text{C})\) column of copper turnings to remove traces of oxygen. All glassware was cleaned in alcoholic KOH \((5 \text{ hours})\), a 1:1 mixture of concentrated sulfuric and concentrated nitric acid and thoroughly rinsed with distilled water prior to use. The temperature of all experiments was \(298 \pm 2^\circ\text{K}\).

Aqueous solutions for iron and nickel experiments were \(1\text{M} \text{ in NaNO}_3\) and \(1\text{M} \text{ in Na}_2\text{SO}_4\) respectively unless otherwise noted. For basic solutions \(\text{Na}_2\text{B}_4\text{O}_7\) and \(\text{H}_3\text{BO}_3\) were added in ratios which buffered the solutions to a pH between 6 and 9. The standard buffer solution of pH 8.4 was \(0.075\text{N in H}_3\text{BO}_3\) and \(0.075\text{N in Na}_2\text{B}_4\text{O}_7\). Acidic solutions were unbuffered and contained sulfuric acid \((\text{H}_2\text{SO}_4)\) at a concentration of \(0.01\text{N} \text{ (pH 3.1)}\).

Solutions containing the redox couple were \(1\text{M} \text{ in NaNO}_3\) or \(1\text{M} \text{ in Na}_2\text{SO}_4\) for iron or nickel respectively and were buffered to pH 8.4. The hexacyanoferrate redox couple was \(0.025\text{N in K}_3\text{Fe(CN)}_6\) and \(0.025\text{N in K}_4\text{Fe(CN)}_6\).

Iron and nickel exhibit essentially ideal passive behavior in the borate buffer system over the entire accessible pH range. The buffering ions are not incorporated into the film and do not participate as reactants or intermediates in any electrode reactions \((8,9,23,24)\). The hexacyanoferrate redox couple is stable over the pH range, its redox potential falls within the passive region and its kinetic behavior is a simple one electron exchange. Several authors \((34,45,46)\) have examined the \(\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}\) couple in borate buffer solutions and direct comparisons can be made.
A standard two compartment electrochemical cell was used (Fig. 4). The main compartment incorporated a working electrode, a counter electrode, and a gas inlet. The reference compartment was separated from the main compartment by two glass frits of medium porosity. The counter electrode was platinum gauze and the reference was a saturated calomel electrode (SCE). All electrode potentials are reported versus SCE. In photocurrent experiments, incident light was focused on the electrode surface through an optical quartz window attached to the main compartment. The spectral response of the quartz window is shown in Fig. 5.

Electrodes were prepared from 1cm x 1cm x 2mm pieces of zone refined iron* or high purity nickel (99.99% Ni). One side of each electrode was abraded with successively finer grades of silicon carbide paper, 4/0 emery paper and finally polished to a mirror finish with 0.05 µ aluminum oxide. Some electrodes were not polished with aluminum oxide, rather their surfaces were left abraded in order to increase the surface area. After polishing, a microscopic (500X) examination revealed no impurity particles (SiC, Al₂O₃) on the electrode surface. Roughness factors of 2 and 3 were assumed for the polished and abraded surfaces respectively by comparison of capacitance values. Electrical contact was made to the back side of the electrode by silver epoxy to a nickel wire which was enclosed in a glass tube. The sides and back of the electrode were covered by silicone adhesive (Dow Corning) leaving only a flat 1cm² surface exposed to solution.

The current through the electrochemical cell was measured as a

**Impurities in ppm: C 3.5, O 2.5, N 1.0, Al 2.0, Cu 10.0, Ni 1.00, S 1.00, Ca 5.0**
Figure 4
Electrochemical Cell
function of electrode potential by standard potentiostatic or galvanostatic techniques. The cell potential and current could be changed manually or automatically with a function generator. The current and potential were recorded simultaneously on an X-Y recorder.

In photoelectrochemical experiments, the working electrode was positioned approximately 1cm from an optical quartz window through which light of varying wavelength and/or intensity was focused on the electrode surface. The spectral intensity of the light sources, the efficiency of the monochromator gratings, and the transmission spectra of the quartz window are given in Figs. 5 and 6.

The experimental method for measuring photocurrents (Fig. 7) employs a phase sensitive amplification system. A focused beam of light was periodically chopped (F = 35 Hz) and the corresponding periodic component of the electrode current was selectively amplified. The portion of the current due to light modulation was obtained as the analog output of the lock-in amplifier and displayed on an X-Y recorder. In some experiments the photoresponse was of sufficiently large magnitude to record it directly without phase sensitive amplification.

For spectra normalization, a standard photon flux (I_o) was arbitrarily chosen as the output of the monochromator at 500nm with the 150 W Xenon lamp attached. Relative intensities (I/I_o) for other light sources and/or wavelengths were measured with a photodiode detection system and corrected for detector sensitivity. Photocurrent spectra were normalized to constant photon flux (I_o) using spectral calibration data supplied with the optical components and also with the spectral response obtained from the photodiode detection system. I_o is approximately 1mW/cm^2.

The cell capacitance was measured using an A.C. bridge technique
Figure 5
Spectral Characteristics of the Photocurrent Detection System

A. Efficiency of the monochrometer UV grating.
B. Efficiency of the monochrometer visible grating.
C. Transmission of the optical quartz window.
Figure 6
Spectral Characteristics of the Illumination Sources

A. 150 W Xenon Lamp
B. 50 W Tungsten Lamp
Spectral Irradiance (W/cm² nm)
Figure 7
Photocurrent Detection System
(Fig. 8) (47). An attenuated sinusoidal signal (1000Hz, 5mV) was imposed on the electrochemical cell by a function generator. The series capacitance and resistance could be measured directly by balancing the working electrode against the internal components of the bridge.
Figure 8
Electrode Capacitance Measurement Circuit
Chapter III

Capacitance Measurements

Theory--The electrochemical behavior of semiconductors as opposed to metals may be accounted for by the lower concentration of charge carriers and the discrete electronic structure of the semiconducting materials. Excess charge in a semiconductor electrode in contact with an aqueous electrolyte does not reside only on the surface, but rather extends a considerable distance into the bulk (Fig. 9A). The existence of a space charge region causes the unique electrochemical properties of semiconductor electrodes (48).

It is customary in discussing the electrochemistry of semiconducting materials to greatly simplify the band structure i.e., to assume well-defined parallel energy bands of infinite width. This is a reasonable conceptual simplification for single crystal semiconductors (49). Although the same simplification will be adopted here (Fig. 2B), it should be pointed out that the interaction of electronic energy levels in transition metal oxides does not necessarily give bands in a traditional sense. In fact, some studies (50) suggest that the conductivity of Fe$_2$O$_3$ and NiO differs fundamentally from that of broad band semiconductors. Additional difficulties in precisely defining the electronic structure are introduced by the polycrystalline nature of surface oxides. It will be demonstrated, however, that explanations of the electrochemistry of metal oxides based on a simplified energy level diagram are useful and accurate within proper limits.

The distribution of electrons in the energy levels of a semiconductor can be derived using Fermi-Dirac statistics. For an n-type semiconductor, the concentration of electrons in the conduction band (n$_c$)
Figure 9
The Metal/Oxide/Electrolyte Interface
is given by
\[ n_o = N_c \exp \left( \frac{E_c - E_f}{kT} \right) \] [3]
where \( N_c \) is the density of states in the conduction band. The lower energy limit of the conduction band relative to the Fermi energy is \( E_c \).
The Fermi energy, \( E_f \), is defined as the chemical potential of electrons or in a statistical sense as that energy level for which the probability of occupancy is 1/2. A useful expression for \( E_f \) follows from Eq. [3]:
\[ E_f = E_c - kT \ln N_c/n_o \] [4]

The termination of the semiconductor lattice at its surface distorts the bands (Fig. 2B). This distortion is usually referred to as band bending and it is due to an altered charge distribution at the surface.

By denoting \( E_{C}^s \) and \( E_{V}^s \) as the energy (in eV) of the edges of the conduction and valence bands at the surface, the concentration of electrons at the surface \( (n_s) \) is
\[ n_s = n_o \exp \left( \frac{E_c - E_{C}^s}{kT} \right) \] [5]
and for holes \( (p_s) \) at the surface is
\[ p_s = p_o \exp \left( \frac{E_{V}^s - E_v}{kT} \right) \] [6]

At equilibrium, the Fermi energy in the metal, the Fermi energy in the semiconductor, and the applied electrode potential \( (U) \) must be equal.
The positions of the valence band and conduction band at the surface \( (E_{V}^s, E_{C}^s) \) are fixed relative to the energy levels in the electrolyte. The effect of changing the electrode potential is to move the Fermi energy
upward for cathodic polarization, and downward (on the energy scale of Fig. 2B) for anodic polarization. In Fig. 2B the bands are bent "up" illustrating the case of an exhaustion layer where \( n_s < n_o \).

The potential distribution at the metal/oxide/electrolyte interface (Fig. 2C) is markedly different from the situation at a bare metal electrode. The galvani potential \( (\Psi) \) is the sum of the potential drops across the various interfaces

\[
\Psi = \psi_{m/sc} + \psi_{sc/el} + \psi^o
\]  

[7]

where \( \psi_{m/sc} \) is the potential drop between the metal and semiconductor, \( \psi_{sc/el} \) is the potential difference across the semiconductor electrolyte interface and \( \psi^o \) is a sum of ohmic potential losses.

Since absolute potential differences cannot be measured, an arbitrary zero of potential is defined and changes in electrochemical properties are correlated with changes in the cell potential \( (U) \) measured with changing cell potential. The interfacial potential \( \psi \) can therefore be expressed as

\[
\psi = \psi_{sc} + \psi_h + \text{constant}
\]  

[8]

where \( \psi_{sc} \) and \( \psi_h \) are the potential drops across the space charge region and Helmholtz layer respectively. The change in cell potential is therefore attributed to the change in potential drop in the two regions:

\[
\Delta U = \Delta \psi = \Delta \psi_{sc} + \Delta \psi_h
\]  

[9]

with
\[ \psi_{sc} = (E_c - E_c^S)/q \]  \[\text{[10]}\]

where \( q \) is the charge on an electron.

The distribution of charge in the semiconductor can be calculated from Poisson's equation (48)

\[ \frac{d^2 \psi(x)}{dx^2} = \frac{-4\pi \rho(x)}{\varepsilon} \]  \[\text{[11]}\]

where \( \psi(x) \) is the potential at point \( x \), \( \rho(x) \) is the charge density and \( \varepsilon \) is the direct constant. In the semiconductor the charge density is given by

\[ \rho(x) = q[-n(x) = p(x) + N_d + N_a] \]  \[\text{[12]}\]

where \( n, p, N_d \) and \( N_a \) are the concentrations of electrons, holes, donors and acceptors.

From the charge in the space charge region given by

\[ Q_{sc} = \varepsilon \varepsilon_0 \frac{d\psi_{sc}}{dx} \bigg|_{x=0} \]  \[\text{[13]}\]

and Eqs. [11] and [12], it is possible to calculate the space charge capacitance

\[ C_{sc} = -d \frac{Q_{sc}}{d \psi_{sc}} \]  \[\text{[14]}\]

The solution (48) of the differential equation yields for an \( n \)-type semiconductor the well known Mott-Schottky relationship (51)

\[ C_{sc}^{-2} = \frac{2 kT}{q \varepsilon \varepsilon_0 N_d} (y - f + \ln f) \]  \[\text{[15]}\]
where $y = q \psi_{sc}$, $N_d$ is the donor concentration and $f$ is the dissociation ratio, $f = N_d^+/N_d$. An analogous expression is obtained for p-type semiconductors with the exception that the acceptor density $N_a$ is substituted for $N_d$.

When the donor dissociation is essentially 100% (i.e., $f=1$) and $\psi_{sc} \gg \psi_h$, Eq. [15] can be expressed as

$$C_{sc}^{-2} = \frac{2}{\varepsilon \varepsilon_0 q N_d} (U-U_{fb}-kT/q)$$

[16]

where $U_{fb}$ is the potential where the bands are flat ($E_c = E_c^s$). Anodic oxides have donor densities which are unusually high. This high doping level causes a significant portion of the potential drop to be in the Helmholtz layer (52);

$$U-U_{fb} = \Delta \psi_{sc} + \Delta \psi_h$$

[17]

Only when $\Delta \psi_h = 0$ or $\Delta \psi_h = K \Delta \psi_{sc}$ where $K$ is a constant does there exist a linear relationship between $U$ and $C_{sc}^{-2}$.

The measured differential capacitance ($C_m$) in an electrochemical cell reflects a series array of capacitive components:

$$C_m^{-1} = C_{sc}^{-1} + C_h^{-1} + C_c^{-1}$$

[18]

By using a counter electrode of large area, the capacitance of the counter electrode ($C_c$) can be eliminated. The Helmholtz capacitance ($C_h$) is essentially constant (30 uf) over the passive regions of iron and nickel (53,54). Therefore, the space charge capacitance is derived from the measured capacitance by (55)
Results and Discussion--Figure 10 illustrates the electrochemical passivity of iron and nickel at pH 8.4. Prior to measurement, the electrodes were polarized at a highly negative potential (-1.1V for Ni, -0.85V for Fe) for 1 hour to reduce any air formed surface oxides. The potential was then scanned in the anodic (positive) direction at +1.0 mV/sec. The cathodic current at U < -0.65V corresponds to reduction of water to form hydrogen:

\[
2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 20\text{H}^-
\]  \[20\]

The subsequent increase in anodic current (-0.6V for Fe, -0.4V for Ni) results from metal dissolution by Eq. [1] for Fe and for Ni by

\[
\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^- \]  \[21\]

The initial potential for dissolution is characteristic of the particular metal. The competing oxidation reactions for oxide formation

\[
\text{Ni} + 20\text{H}^- \rightarrow \text{NiO} + \text{H}_2\text{O} + 2e^- \]  \[22\]

\[
2\text{Fe} + 60\text{H}^- \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + 6e^- \]  \[23\]

proceed simultaneously with metal dissolution until the surface is completely covered with a barrier film. Eqs. [22] and [23] serve only as examples. Several other reaction schemes have been postulated which account for the observed behavior through formation of oxide or hydroxide films (56).

The small residual currents \(I_p\) in the passive region reflect a
Figure 10
Current versus Potential Curves for Iron and Nickel

pH 8.4
Scan rate +1mV/sec
kinetic equilibrium between oxide formation and oxide dissolution. Overall reaction equations for the dissolution process in basic media are

\[ \text{NiO} + \text{H}_2\text{O} \rightarrow \text{Ni}^{2+} + 2\text{OH}^- \]  \[24\]

and

\[ \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + 6\text{OH}^- \]  \[25\]

The increase in anodic current observed at +0.75 V for Ni is associated with the conversion of the passive film to a higher oxidation state or to a different oxide or hydroxide. The anodic reaction at +1.0 V for both Fe and Ni is oxidation of water to yield \( \text{O}_2 \):

\[ 4\text{OH}^- \rightarrow \text{O}_2 \uparrow + 2\text{H}_2\text{O} + 4\text{e}^- \]  \[26\]

Eqs. [20] through [26] are only possible overall reaction equations. The mechanism of each involves several steps.

The measured differential capacitance, \( C_m \) (Fig. 11) is sensitive to the oxide thickness. In order to maintain a uniform oxide thickness during capacitance measurements, the following procedure was employed. The potential was held constant at +0.6 V for Ni and +0.7 V for Fe prior to application of a potential pulse which instantaneously changed the potential to its measurement value. The capacitance bridge was then quickly balanced after which the potential was quickly returned to its initial value and the procedure repeated. The time to balance the bridge was less than 10 sec.

The thicknesses of the passive films at various growing potentials was calculated from anodic charging curves (Chapter VI). At pH 8.4 the passive film on iron is approximately 30 Å thick at \( U = +0.70 \text{V} \). The
Figure 11
Total Measured Capacitance versus Potential

pH 8.4

Frequency = 1000 Hz

Amplitude = 5 mV
thickness of the nickel film is approximately \(10^\Omega\) at \(U = +0.60V\).

The shape of the capacitance curve (Fig. 11) depends on several factors including oxide conductivity, dielectric constant, Faradaic processes occurring at the electrode and the relative partitioning of the potential drop in the oxide and Helmholtz layers. The marked increase in \(C_m\) at +0.90V for Fe is due to the disruption of the double layer by the oxygen evolution reaction. The sudden increase in \(C_m\) at +0.70V for Ni corresponds to the anodic reaction accompanying the formation of a new oxide structure as indicated in Fig. 10.

Using Eq. [19] to correct for the constant Helmholtz capacitance, it is possible to calculate the space charge capacitance, \(C_{sc}\), of the oxide layer. The results are shown in Fig. 12. The transition from a region of essentially constant capacitance \((U > -0.10V \text{ for Fe, } U < -0.30V \text{ for Ni})\) to a parabolic dependence substantiates the existence of a space charge region.

The linear relationship between \(C_{sc}^{-2}\) and \(U\) (Figs. 13 and 14) is predicted by Eq. [16]. The linear dependence indicates that the potential drop in the Helmholtz layer, \(\psi_h\), is constant over the range of electrode potential where the graph is linear. The Mott-Schottky plots provide several important semiconductor quantities. The slope of each linear plot allows calculation of the donor or acceptor density (see Eq. [16]), and the sign of the slope indicates n- or p-type conductivity. The intercept \((C_{sc}^{-2} \rightarrow 0)\) provides a value for the flat band potential \((U_{fb})\). The results of these calculations are reported in Table 1.

The negative slope in Fig. 13 identifies the anodic oxide on Ni as a p-type semiconductor. This result would be expected if the oxide is NiO which is inherently p-type (57). The acceptor concentration of
Figure 12
Space Charge Capacitance versus Potential

pH 8.4
Figure 13
Mott-Schottky Plot for Nickel
$10^{20}/cm^3$ was calculated from the slope using Eq. [16] by assuming a

dielectric constant of 12 (58). If we assume the anodic oxide to be NiO,
then the acceptors can be identified as $Ni^{3+}$ ions energetically situated
less than 0.1eV from the valence band (57,59). Thermal excitation of an

electron from the valence band to the $Ni^{3+}$ acceptor level accounts for
the p-type conductivity.

The positive slope in Fig. 14 identifies the anodic oxide on Fe

as an n-type semiconductor. The Mott-Schottky plot shows two distinct
regions of linearity. An analogous behavior has been observed by Kennedy

and Frese (40) for bulk $αFe_2O_3$ electrodes. They suggest that the two
linear portions are due to contributions from two donor levels and a
critical voltage ($U_c$) for ionization of the deep donor. The linear re-

gion with the greater slope is associated with shallow donor of concent-

ration $N_{D1}$. The linear region at more anodic potentials is the result

of contributions from both the shallow donor and a deep donor of concen-

tration $N_{D2}$. According to Kennedy (40), the two slopes may be expressed as:

$$S(1) = \frac{2}{\varepsilon\varepsilon_0 qN_{D1}}, \quad U < U_c$$  \hspace{1cm} [27]

and

$$S(2) = \frac{2}{\varepsilon\varepsilon_0 q(N_{D1} + N_{D2})}, \quad U > U_c$$  \hspace{1cm} [28]

where $U_c$ is the critical voltage for ionization of the deep donor.

Donor concentrations in the passive film on iron using Eqs. [27]

and [28] are reported in Table 1. The reported dielectric constant of
$γFe_2O_3$ ($\varepsilon=10$) was used in the calculation (60). The results are in gen-

eral agreement with the capacitance measurements of Stimming and Schulze
Figure 14
Mott-Schottky Plot for Iron
(61). If the electronic structure of $\gamma Fe_2O_3$ is similar to that of $\alpha Fe_2O_3$, then the shallow donor can be identified as Fe$^{2+}$ ions (59,62). The identity and position of the deep donors are not known conclusively. There is some evidence (40) to suggest that the shallow and deep donors are both Fe$^{2+}$ ions in octahedral and tetrahedral lattice sites respectively. The essentially equal magnitudes of $N_{D1}$ and $N_{D2}$ and the fact that the iron used in this investigation is pure (99.99% Fe) supports this contention. A donor density of $10^{20}$/cm$^3$ corresponds to a ferrous ion concentration of approximately 1% of the total cations ($10^{22}$/cm$^3$) in the lattice.

In broad band single crystal semiconductors, the common use of the terms donors and acceptors is associated with impurity additions. For anodic oxides, however, the n- or p- type conductivity occurs naturally through non-stoichiometry. Bulk samples of iron oxides tend to be oxygen deficient. The absence of oxygen anions produces a relatively large (1%) concentration of ferrous ions in the lattice of the anodic oxide. Similarly NiO tends to be cation deficient which leads to a significant concentration of Ni$^{3+}$ acceptors. The relative deficiency of cations or anions is related to their mobility during oxide growth.

A fundamental parameter in characterizing the semiconductor electrochemical properties of anodic oxides is the flat band potential $U_{fb}$. $U_{fb}$ can be calculated from the intercept of the Mott-Schottky plot.

From Eq. [16]

$$U_{\text{sc}} (\text{c}^{-2} \rightarrow 0) = U_{fb} - kT/q$$

$U_{fb}$ is that potential where the band energy in the bulk is equal to its surface band energy. This is illustrated in Fig. 15. Knowledge of
Table 1: Semiconductor Parameters from Mott-Schottky Plots

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>pH</th>
<th>$N_{D1}$ (cm$^{-3}$)</th>
<th>$N_{D2}$ (cm$^{-3}$)</th>
<th>$N_a$ (cm$^{-3}$)</th>
<th>$U_{fb}$ (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$Fe$_2$O$_3$</td>
<td>n</td>
<td>6.9</td>
<td>2.0x10$^{20}$</td>
<td>3.9x10$^{20}$</td>
<td>---</td>
<td>-0.173</td>
</tr>
<tr>
<td>$\gamma$Fe$_2$O$_3$</td>
<td>n</td>
<td>7.8</td>
<td>1.9x10$^{20}$</td>
<td>4.9x10$^{20}$</td>
<td>---</td>
<td>-0.225</td>
</tr>
<tr>
<td>$\gamma$Fe$_2$O$_3$</td>
<td>n</td>
<td>8.4</td>
<td>2.1x10$^{20}$</td>
<td>1.9x10$^{20}$</td>
<td>---</td>
<td>-0.268</td>
</tr>
<tr>
<td>$\gamma$Fe$_2$O$_3$</td>
<td>n</td>
<td>9.0</td>
<td>1.9x10$^{20}$</td>
<td>1.7x10$^{20}$</td>
<td>---</td>
<td>-0.317</td>
</tr>
<tr>
<td>NiO</td>
<td>p</td>
<td>7.8</td>
<td>---</td>
<td>---</td>
<td>1.9x10$^{20}$</td>
<td>+0.070</td>
</tr>
<tr>
<td>NiO</td>
<td>p</td>
<td>8.4</td>
<td>---</td>
<td>---</td>
<td>2.1x10$^{20}$</td>
<td>+0.037</td>
</tr>
<tr>
<td>NiO</td>
<td>p</td>
<td>9.0</td>
<td>---</td>
<td>---</td>
<td>1.8x10$^{20}$</td>
<td>+0.016</td>
</tr>
</tbody>
</table>
Figure 15
Energy Level Diagrams for the Anodic Oxides on Iron and Nickel at the Flat Band Potential
$U_{fb}$ allows calculation of the position of $E^S_C$ and $E^S_V$ relative to the energy levels in the electrolyte. Applying Eq. [4] to the iron oxide, the conduction band is less than 2 kT (0.05 eV) above the Fermi energy level. If we assume 100% donor ionization and that the density of states in the conduction band is equal to the number of cations in the lattice ($10^{22}$/cm$^3$). The same calculation for Ni places the valence band within 0.05 eV of $E_F$. Since $U_{fb}$ defines the position of the Fermi energy, a value for $E^S_C$ or $E^S_V$ on the electrode voltage scale can be obtained ($E^S_C = U_{fb} + 50$ mV for Fe, $E^S_V = U_{fb} - 50$ mV for Ni). There is undoubtedly considerable error in the above calculation due to the uncertainty in the position of the donor and acceptor energy levels, especially for Fe where there is evidence for a deep donor. A more accurate method for determining $U_{fb}$ is discussed in the next chapter.

It has been empirically observed at single crystal semiconductors (Ge, GaAs, ZnO) that $U_{fb}$ changes in a regular way with pH (63-65). A slope of 59 mV/pH is generally observed. The reason for this dependence has not been quantitatively established but is believed to be associated with $OH^-$ adsorption or chemisorption on the semiconductor surface. The pH dependence of $U_{fb}$ at the anodic oxides on iron and nickel (Fig. 16) serves to reinforce the contention that the passive films are semiconductors.
Figure 16
Flat Band Potential versus pH
Chapter IV

Photocurrent Measurements

Theory—When a semiconductor electrode is illuminated with light of energy greater than $E_g$, electrons and holes are generated in the conduction and valence bands respectively. The disruption of the equilibrium concentrations of charge carriers gives rise to a measurable photovoltage:

$$U^* = U_{\text{light}} - U_{\text{dark}} \quad [30]$$

and to a photocurrent:

$$i^* = i_{\text{light}} - i_{\text{dark}} \quad [31]$$

if energetically suitable donors or acceptors exist in solution. The theoretical prediction is complex and depends on several criteria which are not necessarily fulfilled for oxide covered metals. The outline given here, taken in part from derivations for thick single crystal semiconductors (66-68), is modified for the case of thin oxide films.

If monochromatic light of energy $h\nu > E_g$ and photon flux $\phi$ is incident on a semiconductor, electron-hole pairs are created at a rate (66)

$$R_g = \alpha \Phi \quad [32]$$

where $\alpha$ is the absorption coefficient. Recombination occurs at a rate

$$R_1 = r n^* p^* \quad [33]$$

where $r$ is the rate constant and $n^*$ and $p^*$ are the electron and hole concentrations under illumination. In the dark, recombination depends on the equilibrium concentrations of electrons and holes.
\[ R_d = r n_o p_o \]  \[ 34 \]

Electroneutrality requires that
\[ \Delta n^* = n^* - n_o = \Delta p^* = p^* - p_o \]  \[ 35 \]

Under illumination if there is no surface recombination, the rate of generation is equal to the rate of recombination
\[ \alpha \Phi = r (n^* p^* - n_o p_o) \]  \[ 36 \]

The change in the effective free energy of holes (\( \Delta \mu_p \)) or electrons (\( \Delta \mu_e \)) when a semiconductor electrode is illuminated is determined by the change in concentration of the charge carriers and is given by
\[ \Delta \mu_e = RT \ln \left( 1 + \frac{\Delta n^*}{n_o} \right) \]  \[ 37 \]

and
\[ \Delta \mu_p = RT \ln \left( 1 + \frac{\Delta p^*}{p_o} \right) \]  \[ 38 \]

For an n-type semiconductor \( n^* \approx n_o \) and hence the change in concentration of minority carriers predominantly determines the photovoltage \( U^* \) of the electrochemical cell. If electrode reactions are controlled by the concentration of minority carriers, the photovoltage at constant current is
\[ \Delta \psi_{sc} = U^* = \frac{\Delta \mu_p}{F} = RT \ln \left( 1 + \frac{\Delta p^*}{p_o} \right) \]  \[ 39 \]

where \( F \) is the Faraday constant.

A quantitative prediction of the photovoltage is made difficult by an inability to determine the rates of bulk and surface recombination.
For a biased semiconductor electrode, Eq. [36] may be written

\[ \alpha \phi = r \left( n^* p^* - n_o p_o \right) + R_s \]  \[40\]

where \( R_s \) is the surface recombination rate which includes recombination through surface states and charge transfer to solution energy states.

Under conditions of constant voltage, the effect of light is to increase the rate of charge transfer across the oxide/electrolyte interface. According to Gärtnner (69), the photocurrent \( i^* \) consists of two components, one from carriers generated in the space charge region and one from carriers generated in the bulk which diffuse to the space charge region. The current generated in the space charge region is given by

\[ i_{sc}^* = q \phi \left[ \exp (-\alpha L) - 1 \right] \]  \[41\]

where \( L \) is the space charge width or Debye length given by

\[ L = L_o \left( U - U_{fb} \right)^{1/2} \]  \[42\]

\( L_o \) is the Debye length corresponding to a 1 volt potential difference:

\[ L_o = \left( 2 \varepsilon \varepsilon_o / q N_o \right)^{1/2} \]  \[43\]

The current due to diffusion from the bulk for an n-type semiconductor is

\[ i_d^* = q \phi \alpha \frac{\exp (-\alpha L) + \alpha p_o D_p}{1 + \alpha l_p} \]  \[44\]

The diffusion length is given by

\[ l_p = \frac{d_p}{d_p + d_e} \left( \frac{k T}{4 \pi \varepsilon q^2 N_D} \right)^{1/2} \]  \[45\]
where \( d_p \) and \( d_e \) are the hole and electron mobilities. The absorption coefficient for absorption close to the band edge has been evaluated by Johnson (70) and has the form

\[
\alpha = A \frac{(\hbar \nu - E_g)^{k/2}}{\hbar \nu}
\]  

[46]

where \( A \) is a constant and \( k \) depends on whether the transition is direct \((k=1)\) or indirect \((k=4)\).

**Results and Discussion**—When illuminated with light of energy greater than \( E_g \), the passive films on iron and nickel generate photocurrents which have a sizable magnitude considering their thickness. This observation is of fundamental importance in substantiating the semiconducting properties of these films. The appearance of a sizable photoresponse clearly demonstrates not only a degree of conductivity but also implies a considerable amount of crystallinity. Although an amorphous or loosely coordinated oxide lattice can absorb light energy, it is doubtful that this would result in measurable photoconductivity unless there exists at least short range crystalline order.

At constant electrode potential, a linear relationship exists between the incident light intensity and the resultant photocurrent (Fig. 17). This dependence is predicted by Eq. [41].

From the dependence of photocurrents on light energy, the band gap \((E_g)\) of the anodic oxides can be obtained. For iron passive films, the photocurrent response was investigated as a function of pH, electrode potential, and solution composition. In general, the spectral response curves for all solutions and electrode potentials were identical except for magnitude. This infers that the chemical environment of iron ions
Figure 17
Photocurrent versus Light Intensity

Polychromatic Light $200 < \lambda < 800\text{nm}$
$U = +0.80\text{v}$
In $\text{Na}_2\text{SO}_4$
pH 8.4
In passive films is essentially identical regardless of hydrogen ion concentration or polarization.

The dependence of the photocurrents on light energy in the visible region can be seen in Fig. 18. The curves are not corrected for light attenuation by the monochrometer system, source intensity or solution absorbance. The measurements were taken in solutions which were IN in NaNO₃. The nitrate ion absorbs strongly in the UV which serves to eliminate second order diffraction from the monochrometer grating. The increase in photoresponse at 340nm is therefore associated with the decreasing absorbance of NO₃⁻ ion in solution. The shape of the remainder of the curve is jointly determined by the efficiency of the monochrometer grating and the absorbance of the oxide film. The spectral response in IN Na₂SO₄ solutions (not shown) is equivalent in all respects to that in nitrate solutions in the portion of the visible region where anion absorbance does not occur.

The UV spectral response of the iron passive film is shown in Fig. 19. The electrolyte was IN in Na₂SO₄ which is transparent in the UV. The shape of the curve generally reflects the efficiency of the UV grating used in the monochrometer (see Fig. 5).

Curves A and B in Figs. 18 and 19 demonstrate the pH dependence of the spectral response. At equivalent voltages relative to Ufb, the magnitude of the photocurrent at any wavelength is proportional to the oxide thickness. In acidic solutions, the oxide thickness is less due to a higher dissolution rate. It can be inferred from the equal wavelength dependence of the photoresponse curves that the oxide environment of iron ions is the same in acidic and basic media.

A completely normalized photocurrent vs wavelength curve (Fig. 20)
Figure 18
Photocurrent versus Wavelength in the Visible Region (Iron)

Curve A
pH 8.4
U = 0.80V
IN NaNO₃

Curve B
pH 3.0
U = 1.10V
IN NaNO₃

I₅₀₀nm = I₀
Figure 19
Photocurrent versus Wavelength in the UV Region (Iron)

**Curve A**
- pH 8.4
- $U = +0.80V$
- IN $Na_2SO_4$

**Curve B**
- pH = 3.0
- $U = +1.1V$
- IN $Na_2SO_4$
was constructed from the spectral response curves if Figs. 17 and 18. The data was normalized by correcting for the monochrometer efficiency, the absorbance of the quartz window and the light source intensity. It is possible to correlate the photoconductivity curve with the optical absorption of iron oxides.

Ferric oxide has two stable crystalline phases at room temperature. The α phase has a corundum structure and the γ phase a spinel-like cubic structure. The anodic oxide on iron has been postulated to be γFe$_2$O$_3$ based on x-ray (8), electron diffraction (17) and Auger analysis (18). The optical absorption spectra of α and γ Fe$_2$O$_3$ are similar, differing only slightly in d-level transitions (71). The principal feature of the absorption spectra which is characteristic of iron in an octahedral oxygen lattice is a strong absorption edge around 2.2 eV (72,73). The absorption band reaches a maximum around 3 eV (410nm) and is several orders of magnitude more intense than the crystal field transitions. The absorption has been identified as a charge transfer band (72) in which an electron is transferred from a ligand orbital to a Fe$^{+3}$ ion.

The optical absorption data is in agreement with the normalized photoconductivity data of Fig. 20. A d-level transition would not be expected to show continuous absorption in the UV. Furthermore a charge transfer absorption is likely to give photoconductivity of the Verway type (74). The "tail" in the photocurrent spectra which extends into the visible region is also observed in the optical absorption spectra.

In Fig. 20, $E_g$ is shown as the minimum energy required to observe a photocurrent response (2.0 eV). By defining $E_g$ in this way, the band gaps depicted in energy level diagrams (Fig. 15) are actually "forbidden" energy regions. This facilitates qualitative correlation of the band
Figure 20
Normalized Photoresponse Curve for Iron

\[ I = I_o \]

pH 8.4

\[ U = +0.80V \]
structure with electrochemical phenomena. It should be stressed, however, that regions labeled as bands are actually distributions of energy levels which are not necessarily homogeneous.

The unnormalized photocurrent spectra for nickel (Fig. 21) show the photoresponse to be primarily in the UV. Curves A and B were taken with electrodes biased at +0.90V and -0.50V respectively at pH 8.4. Curve C was taken in a 0.01N H₂SO₄ solution (pH 3.1). All three curves show the same wavelength dependence suggesting that the optical absorption which results in photocurrents does not depend on pH or electrode bias.

The normalized photoresponse spectra (Fig. 22) is clearly analogous to that of iron. The wavelength dependence of the photoresponse is consistent with the optical spectral of NiO (75), except that no d-level absorption peaks are superimposed on the long wavelength tail. The steep rise in photocurrent into the UV can be correlated with a charge transfer absorption which is characteristic of NiO (75):

\[ \text{Ni}^{2+} + 0^{2-} + h\nu \rightarrow \text{Ni}^{4+} + 0^- \]  

[48]

The value of \( E_g \) (3.3eV) was chosen to reflect a minimum energy for photoconduction. This value is in general agreement with an observed photoconductivity edge in NiO of 3.7eV (76).

There is considerable speculation as to the chemical composition of passive films. It would be advantageous to differentiate between the oxides and hydroxides based on our photocurrent spectra. This is not entirely possible for the following reason. The existence of a strong absorption edge which reaches a maximum in the UV is a general feature of iron and nickel ions coordinated to oxygen. If the photocurrents depend on a d-level excitation, the absorption maxima of which vary
Figure 21
Photocurrent versus Wavelength for Nickel

Curve A
pH 8.4
U = +0.90V

Curve B
pH 8.4
U = -0.50V

IN Na₂SO₄
1500nm = I₀

Curve C
pH 3.1
U = +1.1V
Figure 22
Normalized Photoresponse Curve for Ni
considerably between oxides and hydroxides, such differentiation might be possible.

Partial resolution of this problem is based on the fact that an increase in electrode current is observed when the passive films are illuminated. A certain degree of conductivity is implied. Transition metal hydroxides tend to be amorphous and in general do not exhibit semiconductor behavior. This is due in part to larger metal-metal distances in hydroxides as opposed to oxides. From capacitance measurements the passive films on iron and nickel have been shown to be n- and p-type semiconductors respectively which is consistent with the conductivity of Fe$_2$O$_3$ and NiO. There is also considerable direct analytical evidence to support the contention of oxide rather than hydroxide films. This has been discussed previously.

To obtain the photocurrent vs potential curves (Figs. 23-25) the same procedure used to obtain capacitance measurements was followed. The electrodes were polarized at +0.70V and +0.60V for iron and nickel respectively prior to application of a voltage pulse to the potential of measurement. The photocurrent was quickly determined (less than 5 sec) and the potential was then instantaneously returned to the initial condition. The purpose of this procedure was to maintain a constant oxide thickness during the measurements.

From the dependence of photocurrents on electrode potential, an accurate measure of $U_{fb}$ can be obtained for iron (Fig. 24). The magnitude of the photoresponse shows a clear minimum which can be correlated with band bending. Anodic of the minimum the bands are bent "down" i.e. $E_c < E_c^s$ (for example see Fig. 9B). Holes generated in the valence band by illumination are forced to the surface by the electric field across
Figure 23
Photocurrent versus Electrode Potential for Iron

IN NaNO$_3$

pH 8.4

$I = 5 I_0$
Figure 24
Photocurrent versus Electrode Potential for Iron

IN NaNO$_3$

pH 8.4

$I = 5 I_0$
Figure 25
Photocurrent versus Electrode Potential for Nickel

IN Na₂SO₄
pH 8.4
the oxide. The disruption of the equilibrium concentration of charge carriers by illumination causes a shift in the Fermi energy and an increase in anodic (oxidation) current is observed. The magnitude of the current is proportional to the band bending. At the minimum the bands are flat (see Fig. 15). Cathodic of the minimum the bands are bent "up". The opposite effect is observed. Photogenerated electrons are forced to the surface where reduction takes place giving rise to cathodic currents. The change in sign of the photocurrents is detected with the lock-in amplifier as a shift in phase of the photocurrent signal. The same behavior is also observed for the nickel passive film (Fig. 25). The flat band potentials from photocurrent measurements ($U_{fb}^*$) at different pH values are reported in Table II.

The sharp increase in the photoresponse at anodic potentials for iron (Fig. 23) and for nickel (Fig. 25) indicate that the observed photocurrents in the passive region are limited by the availability of suitable donors or acceptors in solution. Only at those potentials where a reaction is taking place does the effect of illumination become pronounced.
<table>
<thead>
<tr>
<th>pH</th>
<th>$U_{fb}^*$</th>
<th>Fe $U_{fb}^*$</th>
<th>Ni $U_{fb}^*$</th>
<th>U_{fb}^*</th>
</tr>
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<tbody>
<tr>
<td>6.9</td>
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<td>-0.030</td>
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<td>9.0</td>
<td>-0.317</td>
<td>-0.180</td>
<td>+0.016</td>
<td>+0.120</td>
</tr>
</tbody>
</table>

$U_{fb}^*$ -- Flat band potential from capacitance measurements

$U_{fb}^*$ -- Flat band potential from photocurrent measurements
Chapter V

Kinetics of Redox Reactions

Theory--Simple one electron exchange reactions of the type

\[ \text{O} + e^+ \rightarrow \text{R} \] \[49\]

can be either mass transport or activation controlled. This statement
is predicated on the assumption that no chemical reactions or structural
rearrangements involving reactants or products occur and that the elec-
trode does not participate directly as a reactant. For mass transport
controlled reactions if the solution is not agitated, the rate is de-
termined by the concentration of reactants at the surface (77).

\[ i = i_1 \left[ 1 - \frac{c^s_R}{c^0_R} \right] \] \[50\]

or

\[ i = i_1 \left[ 1 - \frac{c^s_0}{c^0_0} \right] \] \[51\]

where \( i_1 \) is a limiting current density which is a function of the dif-
fusion coefficients of the reactants. \( c^s_R \) and \( c^0_R \) are the concentrations
of reduced species at the surface and in the bulk respectively and \( c^s_0 \)
and \( c^0_0 \) are the concentrations of oxidized species at the surface and
in the bulk. The surface concentrations as a function of electrode
potential can be obtained from Nernst's equations for a simple concen-
tration galvanic cell

\[ c_{R,0} = c_{R,0}^0 \exp [\pm n_c F/RT] \] \[52\]

where the negative sign is for reduction and the positive sign for the
oxidation. \( n_c \) is the concentration overpotential
\[ n_c = U - U_R \]  \hspace{1cm} \text{[53]}  

where \( U_R \) is the equilibrium redox potential of Eq. [49]. Substituting [52] into Eqs. [50] and [51], we obtain a general expression for the rate of mass transport controlled reactions

\[ i = i_1 [1 - \exp(\pm n_c F/RT)] \]  \hspace{1cm} \text{[54]}  

If the rate of the reaction is partially a function of diffusion and partially dependent on the rate of charge transport, the cell current can be expressed as

\[ i = F \left( k_f c_0^s - k_b c_R^s \right) \]  \hspace{1cm} \text{[55]}  

where \( k_f \) and \( k_b \) are the rate constants for reduction and oxidation respectively. The dependence of the rate constants on electrode potential is given by

\[ k_f = k_o \exp \left[ -\beta Fn/RT \right] \]  \hspace{1cm} \text{[56]}  

and

\[ k_b = k_o \exp \left[ (1-\beta)Fn/RT \right] \]  \hspace{1cm} \text{[57]}  

where \( \beta \) is the transfer coefficient. Substituting Eqs. [56] and [57] into Eq. [55] we obtain a general equation for the \( i/U \) dependence of a reaction under intermediate control

\[ i = F k_o c_R^s \exp \left( \frac{(1-\beta)Fn}{RT} \right) - c_0^s \exp \left( \frac{\beta Fn}{RT} \right) \]  \hspace{1cm} \text{[58]}  

If the reaction is completely activation controlled, \( c_0^o = c_0^s \) and \( c_R^o = c_R^s \). Eq. [58] becomes the well known Butler-Volmer equation (77,
\[ i = i_o \exp \left( \frac{(1-\beta)F_n}{RT} \right) - \exp \left( -\frac{\beta F_n}{RT} \right) \]  \[ 59 \]

where \( i_o \) is the exchange current density.

**Results and Discussion**—Tafel plots (log \( i \) vs \( U \)) for the reaction

\[ [\text{Fe(CN)}_6]^{3-} + e^- + [\text{Fe(CN)}_6]^{-4} \]  \[ 60 \]

are shown in Fig. 26. The distinguishing feature of the curves is the much lower current densities for iron. The kinetics of the reaction for iron are activation controlled and follow an exponential \( i/U \) dependence according to Eq. [59]. The kinetics at nickel and platinum electrodes have a \( i/U \) dependence which is described by Eq. [54]. With time the passive film on iron thickens resulting in a shift in the Tafel plot to generally lower current densities.

The obvious question is why are the rates of oxidation and reduction so different for iron and nickel electrodes. There is approximately two metals around the redox potential (\( U_R = +0.22V \)). Secondly, why are the redox kinetics at nickel and platinum essentially identical. It might be assumed that the thicknesses of the metal oxides would be responsible. Although oxide thickness does influence the kinetic behavior (45), it does not explain the vastly different rates. Platinum, an inert noble metal, has a surface oxide thickness of between \( 1-3\text{Å} \) (79). The passive film on Ni is \( 10-20\text{Å} \) thick. Hence on the basis of thickness alone, we would not expect nickel and platinum electrodes to show identical kinetic behavior. Also the thickness of the passive film on iron (20-40Å) does not seem sufficiently large enough to reduce the rate
Figure 26
Kinetics of the Hexacyanoferrate Redox Couple

- Iron initial measurement
- Iron after 7 days
- Nickel
- Platinum

pH 8.4
0.5 mV/sec potential scan rate
of charge transfer 1000-fold.

To explain the relative rates of electrochemical reactions at passive metal electrodes the way in which charge is transferred across or through the oxide layers must be examined. An in depth discussion of the quantum mechanical aspects of activation rate control processes is beyond the scope of this thesis. It is known, however, that the rate determining step is the transfer of an electron from the solid phase to the aqueous phase or vice versa (45, 80-83). It is important to ascertain the energetic location of the electron prior to transfer. Several postulated mechanisms are illustrated in Fig. 27 by arrows A, B and C. A represents the tunneling of an electron from the conduction band of the oxide to a molecule in solution (81). The density of electronic states for the ferro/ferri cyanide redox couple is represented as the log of a Gaussian distribution in Fig. 27. Arrow B denotes direct elastic tunneling (82) and C represents resonance tunneling (80) between the metal and electrolyte.

One reason that tunneling mechanisms are postulated to explain the activation controlled kinetics at iron electrodes is the assumption that there is insufficient charge density at the oxide surface to support large electron transfer rates. Some theories (35) explain the difference in kinetic rates for iron and nickel by assuming that the film on iron is an insulator while that of nickel is a conductor. A surface oxide which has intrinsic conduction would be expected to have a large surface charge density. This does not seem likely based on the photoconductivity and capacitance measurements presented. The conductivity in the iron and nickel oxides is extrinsic (n- and p-type) in nature and significant surface charge concentrations should depend on electrode
bias. The difference in surface charge density on iron and nickel films can be accounted for by consideration of their electronic structure and semiconducting characteristics.

From the values of $U_{fb}$ calculated from capacitance and photocurrent measurements (Table II), the position of the conduction and valence bands at the equilibrium redox potential can be determined. This situation is illustrated in Figs. 27 and 28. For iron at pH 8.4, $U_{fb} = -0.15 \pm 0.05V$. At the equilibrium redox potential ($U_R = +0.22V$) the bands are bent up ($E_c - E_c^S = U_R - U_{fb} = +0.37V$). Since the passive film is an n-type semiconductor, this results in a depletion layer in the oxide. The majority carriers (electrons) are forced to the interior of the oxide. In the potential range where the kinetics of the ferro/ferricyanide redox couple are investigated (Fig. 26, +0.9 to -3.0V) a depletion layer is always present in the iron film. An alternative mechanism ie. electron tunneling to or from a region of high charge density is required for oxidation or reduction. The rate of transfer process is proportional to the distance an electron must traverse. The low rate of electron exchange is therefore indicative of the absence of surface charge carriers which would be present on a purely metallic (Hg) or on a metal with a thin intrinsically conducting film (Pt).

At nickel electrodes the situation is reversed (Fig. 28). The position of $U_R$ relative to $U_{fb} (+0.15 \pm 0.05V)$ also causes the bands to bend up, but because the passive film on Ni is p-type this results in an accumulation layer. The majority carriers (holes) are forced to the surface. In this condition there exists a surplus charge concentration at the surface of the oxide. The distance required to transfer electrons across the interface is substantially reduced and the electrode behaves
Figure 27

Energy Diagram for the Iron/Oxide/Electrolyte Interface at the Equilibrium Redox Potential of the Hexacyanoferrate Redox Couple
Figure 28
Energy Diagram for the Nickel/Oxide/Electrolyte Interface at the Equilibrium Redox Potential of the Hexacyanoferrate Redox Couple
like a metal. The rate of transfer is faster than the supply of react-
ants in solution to the electrode surface and diffusion controlled kine-
tics are observed.
Chapter VI
Passivation

In this chapter we will be concerned with the process which gives rise to semiconducting surface oxides. To this point, only films formed by prolonged (1 hour) anodic polarization have been dealt with. A question of obvious concern is when do the films assume semiconducting characteristics. If the conductive properties stem from nonstoichiometry, the mechanism may be a slow process which developed only through inhibited cation migration. An amorphous or sorbed oxygen layer could induce passivity and with time (minutes or hours) the semiconductive behavior would become pronounced as the adsorbed layer slowly crystalized. Alternatively, the composition and conductivity of the surface oxide may be inherent and passivation would then be a function of surface coverage only.

In Figs. 29 and 30, total electrode current (\(i\)) and photocurrent (\(i^*\)) were measured when an electrode was suddenly (<0.01 sec) polarized to a potential in the passive region (+0.70V for Fe, +0.60V for Ni). Prior to each measurement, the electrodes were held at a highly cathodic potential (-1.0V) to reduce any oxide films initially present. Although it is impossible to determine conclusively if the surface is oxide-free, it will be assumed that this is so. Elipsometric data for iron and nickel support this contention (21,28). Measurements of the charge associated with reduction of the films (8,23) are also in agreement with this assumption.

Iron and nickel electrodes show essentially identical behavior. The current decreases from a large initial value in a manner which is consistent with the kinetic behavior of oxide film growth (14-16, 29). The increase in the photoresponse corresponds to the increasing thickness
Figure 29
Current and Photocurrent versus Time for Sudden Anodic Polarization (Iron)

$U = +0.70V$
P$H = 8.4$
$I = 5 \times 10$

Figure 30
Current and Photocurrent versus Time for Sudden Anodic Polarization (Nickel)

$U = +0.60V$

$\text{pH} 8.4$

$I = 5 \times 10^{-3}$
of the films. At \( t = 60 \) seconds, the magnitude of \( i^* \) for Fe is 90% for the value it assumes after 1 hour of polarization. For Ni the 90% point is reached in approximately 30 seconds. The magnitude of the photo-response appears only to be a function of the amount of oxide present. This behavior suggests that the semiconducting nature of the film is not a slowly developing process and that the passive films are inherently photoconductive. It can be inferred that passivation occurs through the growth of a crystalline oxide which is completely formed within several seconds of the initial polarization.

The thicknesses of the passive films can be calculated from the anodic charging curves of Figs. 29 and 30 with the aid of a current integrator. After reducing each electrode at -1.0 V for 1 hour and charging the electrolyte under nitrogen, the total charge \( (Q_t) \) during a 1 hour growth period was measured. The solution was then analysed by atomic absorption spectroscopy for dissolved iron or nickel. The charge in the film \( (Q_f) \) was then determined by subtracting the charge of dissolved cations \( (Q_d) \) from the total charge passed:

\[
Q_t - Q_d = Q_f
\]

[61]

For iron the amount of dissolution was negligible and for Ni it amounted to approximately 60% of the total charge passed.

Oxidation was assumed to take place by Eqs. [22] and [23] and dissolution by Eqs. [24] and [25]. From the oxide density* and \( Q_f \) the thickness of the oxide film was calculated. At pH 8.4 the oxide thickness on

\* Density of \( \gamma Fe_2O_3 = 5.1 \text{ g/cm}^3 \) (8)

Density of NiO = 6.8 g/cm\(^3\) (21)
an Fe electrode is $30 \pm 3\AA$. This amounts to about 4 unit cells of $\gamma$Fe$_2$O$_3$. The anodic oxide on nickel after 1 hour polarization is $11 \pm 2\AA$ thick which corresponds to 2 unit cells of NiO. The change in thickness with time after 1 hour of polarization is less than $0.2\AA$/hr.

When the electrode potential is slowly scanned in the anodic direction, from the region of $H_2$ evolution, the increase and subsequent decrease of anodic current is indicative of the active to passive transition. This is illustrated in Fig. 31 for Fe and Ni at pH 8.4 and 3.1 respectively. The region of interest is that portion of the curve where metal dissolution and oxide formation are in competition (A to B for Fe, C to D for Ni, Fig. 31). The electrodes were held at $-1.0\text{V}$ for 1 hour prior to scanning the potential in the anodic direction at $+1.0\text{mV/sec}$. The photoresponse of each electrode was measured simultaneously as is shown in Fig. 32.

At points A and C the electrode is usually considered by most researchers to be film free (6). The photocurrent measurements do not, however, support this assumption. Cathodic of points A and C for Fe and Ni respectively, a residual photoresponse is observed which is not negligible. If the photoresponse is derived from oxide absorbance, the condition of an electrode after prolonged cathodic polarization cannot be described as a clean metal surface. There may be additional explanations of the origin of small residual photocurrents such as an electrode heating effect on absorbance by adsorbed or chemisorbed molecules.

In the regions AB and CD (Fig. 31) there are two competing reactions, metal dissolution and film formation. The increase in photocurrents (Fig. 32) for both Fe and Ni is indicative of the increasing amount of
surface oxide present. The existence of a photoresponse in this region reinforces the postulate that the passive film is semiconducting when initially present.

The usual interpretation of the curves in Fig. 31 is that passivation is not complete i.e. the surface is not completely covered until the current drops to a low level (points E and F). The photoresponse, however, reaches a maximum at potentials corresponding to the current maximum. This suggests that the surface is substantially covered with an oxide film in the region of highest metal dissolution rates. It may be the case that metal dissolution only occurs through active sites (localized dissolution) on a surface which is predominantly passivated, even at potentials previously thought to be oxide free. Although the above observations are qualitative, they may have far reaching effects on passivation theory.
Figure 31
Current versus Potential in the Active to Passive Transition Region

Fe
pH 8.4

Ni
pH 3.1

Scan Rate 1 mV/sec
Figure 32
Photocurrent versus Potential in the Active to Passive Transition Region

Fe
pH 8.4
In Na$_2$SO$_4$

Ni
pH 3.1
IN Na$_2$SO$_4$

I = 5 I$_0$
200 < $\lambda$ < 900 nm
Chapter VII
Conclusions

The passive film on iron is an n-type semiconductor. The conduction band consists of Fe$^{3+}$ ions energetically situated approximately 2.0eV from an O$^{2-}$:2p valence band. The n-type conductivity arises by thermal excitation of electrons from two donor levels. The donors are probably ferrous ions in octahedral and tetrahedral sites.

The passive film on nickel is a p-type semiconductor. The valence band comprises ground state Ni$^{+2}$ ions energetically situated approximately 3.3eV from the conduction band (Ni$^+\cdot$d$^8$). Thermal excitation of electrons from the valence band to Ni$^{+3}$ acceptor ions accounts for the p-type conductivity.

The energy band models for iron and nickel films generally correspond to those expected for Fe$^{+3}$ and Ni$^{+2}$ ions in a nonstoichiometric oxide lattice.

The passive films on iron and nickel are photoconductive. The energy dependence of the photoresponse can be correlated with the optical absorption spectra and photoconductivity data of Fe$_2$O$_3$ and NiO. The dependence of the photoresponse on light energy is unchanged by variations in electrolyte composition (pH, anions, etc.). This strongly suggests that the chemical environment of cations in the passive films is identical for films grown in acidic or basic media. This observation tends to support the oxide film theory rather than the adsorption theory of passivity.

The rate of charge transfer through the oxide depends on electrode bias in a manner which is consistent with a band conduction model. At potentials close to the redox potential of the hexacyanoferrate couple, the passive film on iron forms a depletion layer and hence exhibits acti-
vation controlled electrode kinetics. The passive film on nickel forms an accumulation layer in this potential region and therefore exhibits metal-like behavior i.e., diffusion controlled kinetics.

The process of passivation occurs by the formation of a barrier oxide film. Active metal dissolution takes place through active sites on a surface which is substantially covered with oxide prior to complete passivation. Passivation is therefore associated with complete coverage of the metal rather than initial formation of an oxide layer.
Appendix I

Computer Program for Calculation of Capacitance Data

1 DIMENSION GP(50), BP(50), RS(50), XS(50), RP(50), XP(50)
2 DIMENSION CS(50), CP(50), CSS(50), CPS(50)
3 DIMENSION CSC(50), CSCS(50), CPC(50), CPCS(50)
4 DIMENSION TX(50), TB(50), V(50)
5 DIMENSION P(50), PH(50), PS(50), R(50)
6 1 FORMAT (5X, F10.5, 2E10.3, 110, F10.5)
7 2 FORMAT (5X, 3E10.3)
8 3 FORMAT (1H1, 4X, 'AREA', 5X, F10.5, 'SQ CM')
9 4 FORMAT (1HO, 4X, 25HFREQ.SETTING, ACTUAL FREQ., F10.1, 5X, F10.1)
10 5 FORMAT (1HO, 4X, 'V, XS, XP, RS, RP, GP, BP,')
11 6 FORMAT (1HO, 4X, 7(1PE10.3, 3X))
12 7 FORMAT (1H1, 4X, 'V, CS, CSS, CP, CPS')
13 8 FORMAT (1H1, 4X, 'V, CSC, CSCS, CPC, CPCS, TX, TB')
14 9 FORMAT (1H1)
15 10 FORMAT (1HO, 4X, 5(1PE.0.3, 3X))
16 11 FORMAT (1H1, 4X, 'V, R, P, PS, PH')
17    READ (5, 1) A, FO, F, M, EFB
18    IF (A.EQ.0.0) GO TO 100
19    DO 20 N=1, M
20   20 READ (5, 2) V(N), XS(N), RS(N)
21    CALL SORT (M, RS, XS, V)
22    DO 30 N=1, M
23    GP(N) = RS(N)/(RS(N)**2 + (XS(N)**2))
24    BP(N) = (-XS(N))/((RS(N)**2) + (XS(N)**2))
\[ \text{RP}(N) = RS(N) \times (1.0 + ((XS(N)/RS(N))^{2})) \]
\[ \text{XP}(N) = XS(N) \times (1.0((RS(N)/XS(N))^{2})) \]
\[ \text{CS}(N) = (-1.0)/(2.0\times3.1416\times F0\times XS(N) \times A) \]
\[ \text{CP}(N) + BP(N)/(2.0\times c.1416\times F \times A) \]
\[ \text{CSS}(N) = 1.0/(CS(N)^{2.0}) \]
\[ \text{CPS}(N) = 1.0/(CP(N)^{2.0}) \]
\[ CH = (+30.0E-06) \]
\[ \text{CSC}(N) = (CH \times CS(N))/(CH-CS(N)) \]
\[ \text{CSCS}(N) = 1.0/(CSC(N)^{2}) \]
\[ \text{CPC}(N) = (CH \times CP(N))/(CH-CP(N)) \]
\[ \text{CPCS}(N) = 1.0/(CPC(N)^{2}) \]
\[ TX(N) = 0.0 \]
\[ RR = RS(N)/(-XS(N)) \]
\[ \text{IF} (\text{ABS}(RR) \gt 1.0) \text{ GO TO 30} \]
\[ TX(N) = (\text{ARCCOS}(RS(N)/(-XS(N)) \times 360.0)/(2.0\times3.1416) \]
\[ \text{TB}(N) = (\text{ATAN}(BP(N)/GP(N)) \times 360.0)/(2.0\times3.1416) \]
\[ \text{DO 35 N=1, M} \]
\[ P(N) = 0.0 \]
\[ PH(N) = 0.0 \]
\[ PS(N) = 0.0 \]
\[ P(N) = \text{ABS}(V(N)-EFB) \]
\[ R(N) = CSC(N)/CH \]
\[ PS(N) = P(N)/(1.0+R(N)) \]
\[ PH(N) = P(N)-PS(N) \]
\[ \text{35 CONTINUE} \]
\[ \text{WRITE (6,3) A} \]
\[ \text{WRITE (6,4) F0, F} \]
52 WRITE (6,5)
53 DO 40 N=1, M
54 40 WRITE (6,6) V(N), XS(N), XP(N), RS(N), RP(N), GP(N), BP(N)
55 WRITE (6,7)
56 DO 50 N=1, M
57 50 WRITE (6,10) V(N), CS(N), CSS(N), CSS(N), CP(N), CPS(N)
58 WRITE (6,8)
59 DO 60 N=1, M
60 60 WRITE (6,6) V(N), CSC(N), CSCS(N), CPC(N), CPCS(N), TX(N), TB(N)
61 WRITE (6,11)
62 DO 70 N=1, M
63 70 WRITE (6,10) V(N), R(N), P(N), PS(N), PH(N)
64 WRITE (6,9)
65 100 CONTINUE
66 STOP
67 END
68 SUBROUTINE SORT (N,R,X,P)
69 DIMENSION (R(50), X(50), P(50))
70 I = N
71 1 J=1
72 1 L=I-1
73 IF (I) 6,6,2
74 2 DO 4 K=1, I
75 L=K+1
76 IF(P(K) - P(L)) 4,4,3
77 3 PP=P(K)
78 RR=R(K)
79    \( XX = X(K) \)
80    \( P(K) = P(L) \)
81    \( R(K) = R(L) \)
82    \( X(K) = X(L) \)
83    \( P(L) = PP \)
84    \( R(L) = RR \)
85    \( X(L) = XX \)
86    4 CONTINUE
87    J = 2
88    5 GO TO (6, 1), J
89    6 RETURN
90    END
# Appendix 2
## Definition of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_0^s$</td>
<td>Concentration of oxidized species at the surface</td>
</tr>
<tr>
<td>$c_0^o$</td>
<td>Concentration of oxidized species in the bulk of the solution</td>
</tr>
<tr>
<td>$c_R^s$</td>
<td>Concentration of reduced species at the surface</td>
</tr>
<tr>
<td>$c_R^o$</td>
<td>Concentration of reduced species in the bulk of the solution</td>
</tr>
<tr>
<td>$C_c$</td>
<td>Capacitance of the counter electrode</td>
</tr>
<tr>
<td>$C_g$</td>
<td>Capacitance of the Helmholtz layer</td>
</tr>
<tr>
<td>$C_m$</td>
<td>Total measured capacitance</td>
</tr>
<tr>
<td>$C_{sc}$</td>
<td>Capacitance of the space charge region</td>
</tr>
<tr>
<td>$d_e$</td>
<td>Electron mobility</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Hole mobility</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Acceptor level energy</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Energy of the bottom edge of the conduction band in the bulk</td>
</tr>
<tr>
<td>$E_{c}^s$</td>
<td>Energy of the bottom edge of the conduction band at the surface</td>
</tr>
<tr>
<td>$E_d$</td>
<td>Energy of the donor level</td>
</tr>
<tr>
<td>$E_f$</td>
<td>Fermi energy</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap</td>
</tr>
</tbody>
</table>
\( f \)  
Dissociation ratio

\( F \)  
Faraday constant \( \text{Mole}^{-1} \)

\( h \)  
Plank's constant \( \text{erg s} \)

\( i \)  
Current density \( \text{A cm}^{-2} \)

\( i_p \)  
Residual current in the passive region \( \text{A cm}^{-2} \)

\( i_l \)  
Limiting current for diffusion controlled kinetics \( \text{A cm}^{-2} \)

\( i_o \)  
Exchange current density \( \text{A cm}^{-2} \)

\( i^* \)  
Photocurrent \( \text{A cm}^{-2} \)

\( i_{sc}^* \)  
Photocurrent from the space charge region \( \text{A cm}^{-2} \)

\( i_d^* \)  
Photocurrent from diffusion \( \text{A cm}^{-2} \)

\( l \)  
Light intensity \( \text{A cm}^{-2} \)

\( k \)  
Boltzman's constant \( \text{erg deg}^{-1} \)

\( k_f \)  
Cathodic rate constant \( \text{cm s}^{-1} \)

\( k_b \)  
Anodic rate constant \( \text{cm s}^{-1} \)

\( k_o \)  
Formal rate constant \( \text{cm s}^{-1} \)

\( l_p \)  
Diffusion length for holes \( \text{cm} \)

\( L \)  
Debye length \( \text{cm} \)

\( L_o \)  
Debye length for a 1 volt potential difference \( \text{cm} \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_o$</td>
<td>Equilibrium concentration of electrons in the conduction band</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$n_s$</td>
<td>Concentration of electrons in the conduction band at the surface</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$n^*$</td>
<td>Concentration of electrons under illumination</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$N_a$</td>
<td>Concentration of acceptors</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$N_c$</td>
<td>Density of states in the conduction band</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$N_d$</td>
<td>Concentration of donors</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$N_d^+$</td>
<td>Concentration of ionized donors</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$P_o$</td>
<td>Equilibrium concentration of holes in the valence band</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$P_s$</td>
<td>Concentration of holes in the valence band at the surface</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$p^*$</td>
<td>Concentration of holes under illumination</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$q$</td>
<td>Electron charge</td>
<td>Coulomb</td>
</tr>
<tr>
<td>$Q_t$</td>
<td>Total accumulated charge</td>
<td>Coulomb</td>
</tr>
<tr>
<td>$Q_f$</td>
<td>Charge in the film</td>
<td>Coulomb</td>
</tr>
<tr>
<td>$Q_d$</td>
<td>Charge due to dissolution</td>
<td>Coulomb</td>
</tr>
<tr>
<td>$r$</td>
<td>Recombination rate constant</td>
<td>cm$^6$ s$^{-1}$</td>
</tr>
<tr>
<td>$R_{g}$</td>
<td>Rate of generation of electron-hole pairs under illumination</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$R_l$</td>
<td>Rate of recombination under illumination</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$R_d$</td>
<td>Rate of recombination in the dark</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>deg K</td>
</tr>
<tr>
<td>U</td>
<td>Electrode potential</td>
<td>V</td>
</tr>
<tr>
<td>$U_{fb}$</td>
<td>Flat band potential</td>
<td>V</td>
</tr>
<tr>
<td>$U_R$</td>
<td>Equilibrium redox potential</td>
<td>V</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient</td>
<td>eV</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Transfer coefficient</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Dielectric constant</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Capacity of vacuum</td>
<td>farad cm$^{-1}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
<td>cm</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>Free energy of electron</td>
<td>erg</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>Free energy of holes</td>
<td>erg</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Charge density</td>
<td>Coulomb cm$^{-3}$</td>
</tr>
<tr>
<td>$\psi_{m/sc}$</td>
<td>Potential drop across the metal/semiconductor interface</td>
<td>V</td>
</tr>
<tr>
<td>$\psi_{sc/el}$</td>
<td>Potential drop across the semiconductor/electrolyte interface</td>
<td>V</td>
</tr>
<tr>
<td>$\psi_h$</td>
<td>Potential drop in the Helmholtz layer</td>
<td>V</td>
</tr>
<tr>
<td>$\psi_{sc}$</td>
<td>Potential drop in the semiconductor</td>
<td>V</td>
</tr>
</tbody>
</table>
\( \phi \)  
Photon flux  
\( \text{s}^{-1} \)

\( \Psi \)  
Galvani Potential  
\( V \)

\( \eta \)  
Overpotential  
\( V \)

\( \eta_c \)  
Concentration overpotential  
\( V \)
Appendix 3
List of Equipment

1. Amel Model 551 Potentiostat
2. Amel Model 566 Analog Function Generator
3. Exact Model 500B Waveform Generator
4. General Radio Model 1603-A Z-Y Bridge
5. Hewlett Packard Model 7044-A X-Y Recorder
6. Jarrell Ash Model 82-410 Monochrometer
7. Oriel Model 7292 Universal Illuminator
8. Oriel Model 7072 Photodiode Detector
11. Tektronix Model 7603 Oscilloscope
12. Tektronix Model 5115 Storage Oscilloscope
13. Tektronix Model DM 503 Digital Multimeter
14. Tektronix Model DC 504 Counter/Timer
References

3. J. Keir, Phil Trans., 80, 359 (1790).
10. V. Markovac and M. Cohen, ibid., 114, 674 (1967).