ELECTROCHEMISTRY OF IRON-CHROMIUM ALLOYS

by

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B.Eng. Chemical Engineering
University of Pretoria
(1986)

Submitted to the Department of Materials Science and Engineering in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

IN

MATERIALS SCIENCE AND ENGINEERING

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

February 1991

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

ARCHIVES
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Submitted to the Department of Materials Science and Engineering on January 11, 1991 in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Materials Science and Engineering

ABSTRACT

An experimental study was conducted to determine the influence of chromium on the electronic and structural characteristics of protective passive films formed on iron-chromium alloys. The primary technique for investigating these materials was photoelectrochemical spectroscopy. Secondary techniques included DC voltammetry and AC impedance spectroscopy. Alloys with 0-30 wt % Cr were examined.

The results of the investigation demonstrate that the discontinuity in corrosion behaviour at 12.5 wt% Cr reported in the literature, above which Fe-Cr alloys exhibit greatly increased corrosion resistance, is a special case at near neutral pH under aerated conditions. The discontinuity occurs when, by the addition of Cr, the critical current density of the alloy is decreased to below the diffusion limited oxygen reduction current density. Alloys containing less than this Cr concentration corrode actively at high corrosion rates, while at Cr concentrations exceeding this amount, the materials are spontaneously passive. It was demonstrated that a different 'critical Chromium concentration' results if a system parameter such as the electrolyte aggressiveness is changed.

It was established that the passive film on Fe-Cr alloys consist of a bi-layer structure. The outer layer is enriched in Fe and corresponds most closely to \(\alpha\)-Fe\(_2\)O\(_3\), while the inner layer is Cr enriched. The passive film on all the alloys examined was found to behave like a highly doped n-type semiconductor. It was found that the outer layer of the passive film is doped increasingly n-type as the Cr concentration of the base alloy is increased. It was demonstrated that n-type doping decreases the equilibrium number of oxygen vacancies in the passive film. A decrease in the number of oxygen vacancies was shown to be beneficial to corrosion resistance. The rate limiting step for metal loss was determined to be oxide dissolution kinetics and not metal cation transmission through the passive film.

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EXECUTIVE SUMMARY

Objectives

The electrochemical behaviour of a series of Fe, Cr and a series of Fe-Cr alloys containing 5 wt% to 30 wt% Cr was examined using conventional DC electrochemical techniques, as well as novel techniques such as AC impedance spectroscopy and photoelectrochemistry. The goal of the research was to examine specific corrosion characteristics of the Fe-Cr alloy system, such as the observed behaviour that alloys in this system containing more than 12% Cr show greatly improved corrosion characteristics, and in many applications maintain a rust free or ‘stainless’ surface appearance. The ultimate objective was to construct a model for passivity in this alloy system that would account for the observed phenomenon, while providing a fundamental picture of the underlying electrochemical processes that contribute to passivity in this commercially very important alloy system. In this model the primary focus was the role of chromium on the enhancement of passivity in the Fe-Cr alloy system and related commercial alloys.

Results

DC and open circuit measurements

Spontaneous passivity in the Fe-Cr system in acidified electrolytes was shown to be controlled by the oxygen diffusion limited reduction reaction current density which is approximately equal to $2.5 \times 10^{-4} \text{ A/cm}^2$ under natural convection. It was shown that the presence of the oxygen diffusion reaction is required in order to ensure stable spontaneous passivity in these electrolytes.

The results of the investigation indicate that the discontinuity in corrosion behaviour at 12.5 wt% Cr reported in the literature, above which Fe-Cr alloys exhibit greatly increased corrosion resistance, is a special case at near neutral pH under aerated conditions. The observed appearance of ‘stainless’ behaviour at ~ 12 wt% Cr, was shown to be an isolated case for near neutral electrolytes. This transition coincides with the point at which the
oxygen diffusion limited reduction current density under conditions of natural convection, exceeds the critical anodic current density of the 12 wt% alloy. It was demonstrated that a different 'critical Chromium concentration' results if a system parameter such as the electrolyte aggressiveness or convection state of the electrode is changed.

**Impedance measurements**

The impedance measurements indicated that the passive film formed on Fe and Fe-Cr alloys behaves like a highly doped n-type semiconductor. Capacitance measurements showed that the capacity of the electrodes was controlled by space charge layer formation, ruling out a dielectric passive film. The electric field strength of the passive film was estimated to be between 1.48 and 5.19x10^8 V/m.

**Photoelectrochemistry**

Similar characteristic photoresponse for all the alloys investigated was obtained, except for the pure Cr on which no photocurrent could be measured. The photocurrent characteristics correspond most closely to α-Fe₂O₃. This similar characteristic, indicates an Fe oxide over layer. This over layer is present even in acidic solutions. The amount of Fe in the passive film is directly proportional to the amount of Fe in the base alloy, and no discontinuity in behaviour was observed at 12 wt% Cr. The absence of such a discontinuity complements the results of the DC polarisation experiments from which was concluded that no single discontinuity in the corrosion behaviour of the alloys in the Fe-Cr alloy system exists.

The photoelectrochemical response of the passive film showed Poole-Frenkel behaviour at low overpotentials. At higher potentials, deviation from Poole-Frenkel behaviour occurred. The deviation from Poole-Frenkel behaviour was attributed to tunneling phenomena. The tunneling was shown to commence at constant band bending for all the alloys investigated, confirming that the photoelectrochemical response measured is characteristic of only the Fe oxide over layer, which remains the same for all the alloys investigated.
The flat band potentials, $E_{fb}$, as obtained by photoelectrochemical measurements, showed a monotononic decrease as a function of the wt% Cr in the alloy. The change in flat band potential of the over layer indicates that the over film part of the passive film is doped by higher valence state Cr species. It was shown that the measured flat band characteristics and the invariant photocurrent could be explained by a bi-layer passive film, in which an outer Fe enriched oxide layer is overlaid on an inner Cr enriched oxide layer.

**Conclusion - a model for passivity in the Fe-Cr system**

Passivity in the Fe-Cr alloy system is due to a compact passive film. The passive film behaves like an n-type semiconductor, which, depending on the potential regime and the Cr concentration in the alloy, may behave either as a classical doped semiconductor, or as an exhausted dielectric. The passive film consists of an inner Cr oxide rich layer, and an outer Fe oxide rich layer. The outer Fe oxide layer is present even in very acidic solutions. The outer part of the passive film was shown to be doped more n-type by Cr species. The n-type doping has the effect of decreasing the number of oxygen vacancies in the passive film. Growth of the passive film is controlled by the diffusion of oxygen vacancies, so that a decrease in this species slows down the growth of the passive film, resulting in a thinner passive film.
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ACKNOWLEDGEMENT

I am grateful to God who has given me the abilities and opportunities to pursue the research and study that has made possible the realisation of this thesis. Without the knowledge that our actions and deeds fit into a greater plan of things under His supreme guidance this thesis would never have been completed.

On a personal level I am internally grateful to Professor Ronald M. Latanson under whose supervision the work documented in this thesis was carried out. His constant support, enthusiasm and council changed the time in the H. H. Uhlig corrosion Laboratory from more than just time spent towards earning a degree, into a true educational experience. To the other members of my thesis committee Professor Donald R. Sadoway and Professor Harry L. Tuller I wish to express my deepest appreciation for going far beyond doing simply what is expected from a thesis committee, in always showing a deep interest in the research work. Without the fresh perspective that both of these members provided, this would have been a far lesser work.

I also wish to thank all the members of the H. H. Uhlig Laboratory, both past and present for each contributing a piece towards the happy experience that my time at MIT has been.

To my wife Carin, who has had to deal with the ups and downs that accompany every major undertaking like this, and who through all was nothing but loyal, supportive, self sacrificing and understanding, I would like to express more than just gratitude, but wish to express the hope that the happiness that is our relationship may keep on growing in the fashion that it has been for the past ten years.

My eternal indebtedness also to my mother, who more than anybody else contributed to forming me into the person I am, and whose endless love and support shows in every step that I take along life’s path, and to the rest of my family who complete the circle of people that I am closest to.
1. INTRODUCTION

One of the most useful corrosion properties of many structural materials such as iron, cobalt, nickel, titanium, chromium and their alloys is the phenomenon of passivity [Sato 1981]. Passivity was first observed in the early eighteenth century, and the first report that passivity can be achieved by anodic polarisation is ascribed by Gmelin to Hisinger and Berzelius [Gmelin 1929]. Upon anodic polarisation of a metal electrode, the current density, corresponding to metal ions going into solution increases. This increase in the current density, is in accordance with the increased thermodynamic driving force for the dissolution reaction. With certain material/electrolyte combinations, and with further anodic polarisation the corrosion current decreases by as much as six orders of magnitude upon reaching a certain critical potential $E_{\text{crit}}$. This is considered as the onset of a so called 'passive state' in which the dissolution rate of the material is very low. It is immediately obvious that such a state is highly desirable when designing for resistance against corrosion.

One of the most widely used classes of engineering materials for corrosion resistance are the so called 'stainless steels'. These alloys are based primarily on the Fe-Cr and Fe-Cr-Ni alloy systems. Conventionally, it is believed that in the Fe-Cr alloy system, a discontinuity in corrosion behaviour takes place at ~12 wt% Cr, such that alloys with more than this 'critical' amount of Cr show corrosion behaviour that is closer to that of Cr, than that of Fe. As chromium shows both a very low passive current density and passivation at relatively cathodic potentials, this effect is extremely beneficial in alloying metals for corrosion resistance. Despite the technological importance of these alloys, and a multitude of investigations of the corrosion resistance of chromium containing alloys, relatively little is known about passive film formation on Cr, and alloys that form Cr based passive films. Studies of the passive films formed on binary Fe-Cr alloys provide a useful fundamental starting point for proceeding to the passive films on the more complex engineering alloys available commercially. This thesis is concerned with the study of the passive films that form on alloys in the Fe-Cr alloy system, and that prevents the metal from reverting to the thermodynamically stable oxide.
In order to decide which variables must be studied, it is necessary to consider the elemental processes that take place during corrosion. In the electrochemical degradation process the species that are transported are electrons and ions. As a result, knowledge of the transport properties of the film on the surface of a metal in the passive regime is of utmost importance. These properties include ionic and electronic conduction mechanisms, as well as thickness of the passive film. This thesis focussed on the investigation of the electronic properties of passive films on Fe-Cr alloys by means of novel techniques such as photoelectrochemical spectroscopy. Electronic properties of the passive film are important not only because of the influence that they have on the transport properties, but also because electronic effects determine the chemistry that this phase will exhibit.

A series of Fe-Cr alloys with Cr contents between 5 and 30 at% as well as the pure elements were investigated. The experimental investigation can be divided into three parts: (i) DC electrochemical techniques. (ii) AC impedance spectroscopy. (iii) Photoelectrochemical spectroscopy. After presenting an introduction in chapter 2, relevant literature in chapter 3, and a summary of research objectives in chapter 4, the results of each type of experiment (as per the classification above) are presented as separate chapters. Each of these chapters (5-7) can be read independently. Chapter 8 proposes a model for passivity in the Fe-Cr alloy system based on a synthesis of the experimental results. Chapter 9 summarises the conclusions from chapters 5-8. Recommendations for future work are given in chapter 10.
2. PASSIVITY - AN INTRODUCTION

2.1. Definition of passivity

According to Uhlig [Uhlig 1985] passivity can be defined in two ways. The first of these defines a metal as passive if it substantially resists corrosion in a given environment as the result of marked anodic polarisation. This definition is most generally used, and it will be utilised for the purposes of this document. Passivity according to this definition is therefore a state in which the rate of anodic dissolution is less than the rate of dissolution at a less noble potential. The second definition of passivity states that a metal is passive if it substantially resists corrosion in a given environment, despite a marked thermodynamic tendency to react.

On moving from the active to the passive state, the current density may decrease by as much as six orders of magnitude. Passivity is therefore a potential driven phase transformation that is associated with the formation of a two dimensional or three dimensional passive film that prevents the metal from reverting back to its thermodynamically most stable state, the metal oxide.

2.2. Mixed potential theory

For the electrochemical corrosion reaction to proceed, the presence of a cathodic and an anodic half reaction is necessary. In corrosion reactions the anodic reaction is usually that of the metal going into solution e.g.:

\[ \text{M} \rightarrow \text{M}^{x+} + x\text{e}^{-} \]  \hspace{1cm} [2.1.]

In the absence of chemical species other than water, the balancing cathodic half reaction is supplied by the cathodic hydrogen reaction:

\[ 2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2 \hspace{1cm} E^0 = -0.241 \text{ V} \]  \hspace{1cm} [2.2.]
In aerated media, the cathodic oxygen reduction reaction, which may be written as:

\[ \text{O}_2 + 4 \text{H}^+ + 4 \epsilon \rightarrow 2\text{H}_2\text{O} \quad \text{E}^o = 0.988 \text{ V} \]  \[2.3.\]

in acidic media, or as:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4 \epsilon \rightarrow 4 \text{OH}^- \quad \text{E}^o = 0.160 \text{ V} \]  \[2.4.\]

in basic media, may occur simultaneously with the cathodic hydrogen reaction.

In order to be passive, the potential of the material must be in the passive potential regime. In the case where there are no other oxidants present, one or both of the above reactions must therefore raise the open circuit potential of the material into the passive potential regime. The afore-mentioned situation is illustrated in figure [2.4.1.] for the case where the cathodic oxygen reduction reaction is responsible for raising the potential into the passive regime. In order to raise the potential of the material into the passive potential regime, it is clear that the cathodic reaction under interest must be able to sustain a current density greater than the current density of the anodic characteristic along every point of the anodic polarisation curve, from the corrosion potential up to the potential at the onset of passivity. In practice the point that is the ‘hardest’ to overcome is the critical potential/current density, which is indicated in figure [2.4.1.] by the point \( E_{\text{crit}}, i_{\text{crit}} \).

In aerated aqueous media, where both cathodic reactions mentioned above are present, the critical potential, \( E_{\text{crit}} \) may be situated in a regime where: (i) the cathodic hydrogen reaction (ii) the cathodic oxygen reduction reaction in the non-diffusion limited regime or (iii) the cathodic oxygen reduction reaction in the diffusion limited regime is the reaction supplying the majority of the cathodic component. These three situations are schematically shown in figure [2.4.2.]. The acidity of the solution and the material under investigation determine which situation will be controlling the corrosion potential.

With materials that passivate at very cathodic potentials (e.g. Cr) and in very acidic media, the hydrogen reaction may be responsible for passivity, while in higher pH solutions and
with materials that passivate at more anodic potentials (e.g. Fe), the oxygen reaction is usually responsible for passivity.

2.3. Alloing effects

Alloing with transition metals is widely used in order to confer enhanced corrosion resistance on alloys. The mechanism by which such alloing elements bestow beneficial corrosion resistance to an alloy varies from one alloy system to another. For instance in the Fe-Cr system studied in the research presented in this thesis, the effect of Cr addition to Fe is mostly concerned with modifying (i) The value of the critical current density $i_{\text{crit}}$, to a lower value. (ii) Lowering the critical potential, $E_{\text{crit}}$, to a more cathodic potential. (iii) Lowering the passive current density $i_{\text{pass}}$ to a lower value. This alloing is therefore concerned mainly with the modification of the anodic dissolution characteristics of the alloy. Modification of the anodic dissolution characteristics is commonly used when engineering corrosion resistant alloys.

As an example of a totally different mechanism for increasing the corrosion resistance, consider alloing of an Fe-Cr alloy with a noble metal. First studied by Tomashov [Tomashov 1958], later by Stern and Greene [Greene 1961], and more recently by Higgenson [Higgenson 1989], addition of platinum group metals to Fe-Cr alloys was found to greatly increase the corrosion resistance in deaerated acidic solutions. In this case the mechanism for protection is the increased exchange current density for the cathodic hydrogen reduction reaction, which changes the corrosion potential from the active corrosion regime to the passive regime, as well as modification of the anodic dissolution characteristics. Modification of the anodic characteristic takes place by either: (i) A blocking mechanism of the noble metal on the active dissolutions sites or (ii) by a screening effect of the cathodic component that crystallizes on the surface and screens the active or anodic portion of the surface [Tomashov 1984]. This process is schematically illustrated in figure [2.4.3.], where the addition of Pt to Cr is considered. As can be seen from this figure, both the critical current density, and the passive current density are lowered by the anodic modification of the alloy by the Pt, while the hydrogen kinetics are greatly boosted by the greater exchange current density for the cathodic hydrogen reaction on the Cr-Pt
alloy, as compared to the pure Cr. The result of these modifications is that the unalloyed Cr shows two open circuit potentials (one in the active and one in the passive regime) [Moffat 1989], indicating unstable behaviour, while the alloyed Pt-Cr alloy shows a corrosion potential in the passive regime.

As a last example, consider the addition of small amounts of Mo to austenitic stainless steels. This addition greatly enhances the resistance of the material to localised corrosion. The Mo inhibits dissolution during active corrosion by enriching on the surface, consequently lowering the critical current density, and thus facilitating passivation [Klimmeck 1980, Goetz 1982].

From these few examples alloying effects are seen to be varied in nature, so that each alloying addition must be studied on a case by case basis. Because alloying can have such a pronounced influence on the corrosion properties, and because materials engineers are always striving to reduce, replace or eliminate expensive alloying additions, alloying effects are extremely important when studying corrosion.
2.4. Figures - Introduction
Figure [2.4.1.] Schematic diagram of an anodic polarization curve of a material that shows an active-passive transition.
Figure [2.4.2.] Diagram to show how the (i) hydrogen (ii) non-diffusion limited or (iii) diffusion limited oxygen, cathodic reactions may take the specimen past $E_{\text{corr}}$. 
Figure [2.4.3.] Schematic diagram to show how an increase in \( i_{o_{H^2/H^+}} \), coupled with anodic modification, is responsible for establishing passivity when Pt is added to Cr.
3. LITERATURE REVIEW OF PASSIVITY OF Fe-CR ALLOYS

3.1. Thermodynamics of iron and chromium in aqueous solutions

The stability diagrams for iron at 25 °C in aqueous media were calculated by Pourbaix and De Zoubov [Pourbaix 1974]. Two stability diagrams are given as figures [3.6.1.] and [3.6.2.]. Figure [3.6.1.] was calculated considering the unhydrated oxides as the stable phase, while figure [3.6.2.] was calculated using the hydroxides as the stable phases.

The thermodynamic equilibrium diagrams for chromium at 25 °C in aqueous media were calculated by Deltombe, De Zoubov and Pourbaix [Pourbaix 1974]. The stability diagram considering the unhydrated oxide CrO_3 is shown in figure [3.6.3.]. A diagram considering the hydrated Cr oxide, Cr(OH)_3 was also calculated and is shown in figure [3.6.4.]. An approximate solution considering Cr(OH)_3·nH_2O is shown in figure [3.6.5.].

The potential of formation of a protective Fe_2O_3 film is more anodic than the equilibrium potential of the cathodic hydrogen reaction, therefore, it is clear that iron will be unstable in the absence of an oxidizer other than hydrogen. The presence of oxygen, and/or other oxidizer(s), is therefore required to raise the potential of an iron electrode into the regime where a protective oxide film can form. From the stability diagram of Fe it is clear that ease of passivation is facilitated by an increase in the pH. The protective Fe oxide exhibits a region of stability even at the highest pH values possible in an aqueous solution at 25 °C.

Cr is a very base metal, and its domain of stability lies considerably below that of water. The potential of stability of Cr oxides is such that, if the kinetics permit, it is possible to form a stable oxide by the hydrogen reaction alone. This ability is due to the potential of formation of a protective Cr oxide film being more cathodic than the equilibrium potential of the cathodic hydrogen reaction. Passivity of chromium is therefore thermodynamically possible in deaerated aqueous solutions, although kinetics may prevent it from occurring.

Another very important aspect which is evident when comparing the stability diagrams of the two elements is that the iron oxide is stable at higher potentials, where the Cr dissolves
as the \( \text{CrO}_4^{2-} \) ion. It is also apparent from the stability diagram that the Cr oxide is stable over a wide range of pH, but that at very high pH the Cr goes into solution as \( \text{CrO}_3^{3-} \). This behaviour contrasts with that of Fe oxides, which remain stable even at the highest pH values possible in water.

If some of the thermodynamic characteristics of the component elements are preserved in the alloy, the allying of chromium with iron would result in an alloy that is expected to exhibit: (i) Improved corrosion resistance in the acidic pH regime as compared to the resistance of the pure iron. (ii) Possible formation of a Cr oxide based passive film at potentials lower than the potential at which an Fe oxide based passive film can be expected to be stable. (iii) Passive behaviour at potentials higher than the potential at which Cr dissolves transpassively via formation of an Fe oxide based passive film. (iv) Improved corrosion resistance in very basic electrolytes when compared to pure chromium.

3.2. Composition of passive films formed on Fe, Cr and their alloys

3.2.1. Adsorbed oxygen film or bulk oxide?

Some researchers argue that the passive film is essentially a chemisorbed oxygen film [King 1959]. This argument is based on the comparison of the free energy value for the adsorption reaction, with the free energy as calculated from the Flade potential via the equation \( \Delta G = -nF \Delta E_f \). Additional supporting evidence comes from coulometry which shows that less than a monolayer is necessary to passivate Cr [King 1959]. Film thickening at higher potentials was postulated to be an adsorbed oxygen complex, consisting of O, OH, H\(_2\)O or various solute ions.

Frankenthal maintains that a sequence of oxygen adsorption and oxide formation takes place [Frankenthal 1967, 1969 a, 1969 b]. His data indicates formation of an adsorbed oxygen film, which he called the primary passive film, within 5 mV of the activation potential. A regime where cathodic currents flowed was observed during anodic polarisation of a 24 wt% Cr Fe-Cr alloy. This regime is shown in figure [3.6.6.]. The observed cathodic loops are similar to the behaviour of pure Cr. Frankenthal defined the
activation potential as the potential at the point where the maximum cathodic current flows during anodic polarisation. This point is indicated in figure [3.6.6]. Formation of the passive film at potentials just anodic to this potential is reversible initially but becomes irreversible upon ageing. A secondary irreversible film forms at more anodic potentials. Frankenthal’s observations agree with that of Aronowitz and Hackermann [Aronowitz 1963] who examined the regime of secondary passivity, as defined by Frankenthal. Aronowitz concluded that the passivation process was irreversible. Other researchers argue that the passive film is either a bulk oxide or hydrated oxide, which that acts as a barrier [e.g. Okamoto 1973], and which may be amorphous or crystalline in structure. The passive film as a barrier is discussed more fully in §[3.4].

3.2.2. Metal ions in the passive film

For Fe, thermodynamic arguments show that Fe$_2$O$_3$ cannot be in equilibrium with the bare Fe metal substrate [Vetter 1967]. Many investigators consequently propose a ‘sandwich’ or bi-layer structure for the passive film on Fe. This bi-layer is usually proposed to be an inner Fe$_3$O$_4$ layer and an outer α-Fe$_2$O$_3$ layer. Experimental evidence supporting the bi-layer theory exists in the literature [Nagayama 1962, Nagayama 1963, Dvoracec 1970, Cohen 1974 (b)], but experimental evidence contradicting the existence of a bi-layer structure has been presented more recently [Chen 1982].

Comparison of the constituent polarisation curves lead some researchers [Okamoto 1973, Kolotyrkin 1978] to conclude that the components in a stainless steel enrich in the passive film, according to their relative stability at each potential. This behaviour is schematically illustrated in figure [3.6.7]. Cr is thus expected to enrich in the passive film in the lower potential regime, while Fe is expected to enrich in the passive film in the secondary passive regime. This prediction is closely related to the thermodynamic arguments as presented in §[3.1]. Evidence confirming this hypothesis exists [Yaniv 1977, Kolotyrkin 1978, Hara 1979, Leygraf 1979, Hultquist 1987], but other investigators found no evidence to confirm this [Kolts 1978].
Several investigators reported a ‘threshold’ percentage of Cr in the alloy, below which Cr did not enrich in the passive film. Hara concluded that alloys with less than 20 wt% Cr behave essentially like Fe, while higher % Cr leads to Cr like behaviour [Hara 1979]. Tjong found this threshold to be 3 wt% [Tjong 1982], while Asami found it to be ~10 wt% [Asami 1978]. Kirchheim and co-workers [Kirchheim 1989] found that Cr was enriched in the passive regime even at very low wt% Cr in the alloy. He proposed a model that accounted for this enrichment by the lower mobility of Cr versus Fe, and consequently preferential corrosion of the Fe. Surface treatment was shown to be extremely important [Asami 1977, Asami 1984]. Differences in surface preparation could explain why such widely differing results are documented in the literature.

Uncertainty on the distribution of the Fe and Cr in the passive film still exists. Angular resolved X-ray photoelectron spectroscopy indicated that a well pronounced change of composition with depth exists [Strehblow - this article has not yet been published at the time of writing of this thesis, but is referred to by Calinski/Strehblow 1989]. This depth dependent composition is especially present in alkaline electrolytes. An Fe(III) over layer is suggested which is a consequence of the reduced solubility of Fe(III) ions under alkaline conditions. Ion scattering spectroscopy (ISS) has been especially useful in determining the depth distribution of elements in the passive film, because of this method’s unique monolayer sensitivity. Using ISS, Calinski and Strehblow showed that in 1 N NaOH an Fe rich over layer lies on top of a Cr rich layer [Calinski 1989]. In 0.5 M H2SO4 Calinski found greater Cr enrichment in the passive film, and attributed it to the greater solubility of the Fe in the acid electrolyte.

Calinski and Strehblow [Calinski 1989] found the same bi-layer structure discussed above, consisting of an Fe rich over layer on top of a Cr rich inner layer, in acid electrolytes. It was postulated that at long times the Fe rich layer will be displaced by an outward moving Cr rich layer, because of the greater dissolution of the Fe. At long times, an enrichment of Cr even at the surface is thus expected. This experimental evidence showing a bi-layer structure is supported by the work of Coad [Coad 1974], who found that Cr is depleted in the outside layer of the air formed film on Fe-Cr alloys. Cr depletion was also reported by Tjong [Tjong 1982]. A similar bi-layer structure was also postulated by Haupt [Haupt
1986] for Fe-Cr alloys, and by König [König 1988] for Fe-Cr alloys containing greater than 9 wt% Cr. Mitrovic-Scepanovic [Mitrovic-Scepanovic 1984] examined an Fe-26 wt% Cr alloy in a pH 2 acidified sulphate solution, and concluded that the passive film consists of either an \((\text{Fe},\text{Cr})_2\text{O}_3\) type of oxide, or an inner layer of \(\text{FeCr}_2\text{O}_4\) and an outer layer of \((\text{Fe},\text{Cr})_2\text{O}_3\). The latter bi-layer structure indicates an inner layer that is relatively more enriched in Cr than the outer layer.

3.2.3. The role of water in the passive film

The role of water on the passivation process is usually investigated using mixed organic solvent/aqueous electrolytes. It has been shown that Fe does not passivate in water free solutions (<0.1% \(\text{H}_2\text{O}\)) of sulphuric acid and dimethylformamide (DMF), but that the current density increased continuously with increasing anodic potential [Schwabe 1981]. Schwabe showed that the potential for passivation increased as the water content decreased (for 1% \(\text{H}_2\text{O}\) the passivation potential was 500 mV more anodic than for 100% water). In dimethylsulfoxide (DMSO)-\(\text{H}_2\text{O}-\text{H}_2\text{SO}_4\) mixtures a solid state reaction gave a salt layer. The results showed that water is not necessary to give dissolution.

Banas investigated both Fe-Cr alloys, as well as Cr in organic water free and water containing solvents [Banas 1982 (a), Banas 1982 (b), Banas 1982 (c)]. His work utilizing a RDE with a commercial X20Cr13 alloy showed that in DMF-\(\text{H}_2\text{O}-\text{H}_2\text{SO}_4\) solutions, sulphate ions or sulphuric acid participates in formation of a salt film [Banas 1982 (a)]. In \(\text{CH}_3\text{OH-CH}_2\text{O-CH}_2\text{SO}_4\) it was difficult to obtain completely water free solutions. \(\text{CH}_3\text{OH}\) has protolytic activity which favours acid dissolution, so that an increase in the acid concentration increases the dissolution. He showed that in the \(\text{Fe}^{2+}\) dissolution regime, a salt film formed, while \(\text{Fe}^{3+}\) salts that are more soluble did not act protectively.

Work on a series of Fe-Cr alloys indicated that in DMF no true passivity was observed, although increased Cr content caused the observed current densities to be lower [Banas 1982 (b)]. Very little water was enough to cause passivity. Banas showed that the films on alloys with less than 18 wt% Cr were not stable if the water concentration was increased. In solutions of \(\text{CH}_3\text{OH}\) the residual water present was enough to cause
passivity in alloys containing more than 11 wt% Cr. For pure Cr, Banas found that a solid state reaction in a DMF-H₂O-H₂SO₄ electrolyte deposited a protective Cr₂(SO₄)₃ film [Banas 1982 (c)].

In summary it is concluded that current limiting mechanism in the absence of water is due to deposition of an insoluble, amorphous salt film formed by a solid state reaction. Solid state deposition reactions form more protective films in the regimes where Fe dissolves as Fe²⁺. The addition of Cr to the alloy decreases the amount of water that is required for true passivity. With the addition of water the dissolution of the deposited salt films is enhanced, and they cease to be protective, so that for passivity in these conditions a normal passive film is required. Water is in all cases required in order to produce a ‘true’ passive film.

3.3. Theories on the critical percentage chromium for passivity

3.3.1. D-orbital theory of passivity

Chemical theory of adsorption relates the typical strong chemical bonds of adsorbates to transition metals to the unfilled d-level orbitals. This theory led Uhlig [Uhlig 1958] to propose that the effects observed in the Fe-Cr system were due to the elimination of filled d-orbital configurations. From this he was able to show that the transition of ‘iron like’ to ‘chromium like’ behaviour should occur at a concentration of ~15.7 at% Cr, thus corresponding fairly closely to the 12 wt% of Cr commonly assumed to be the critical percentage for stable passivity.

3.3.2. Percolation theory of passivity

For the reader unfamiliar with percolation phenomena, it is recommended that the summary of percolation theory given in §[12.2.2.] is first reviewed. For a more thorough discussion of percolation theory the reader is referred to the work of Zallen [Zallen 1983].

Recently Sieradzki and Newman [Sieradzki 1986] applied geometrical percolation theory to explain the observed phenomenon that alloys with less than the critical amount of Cr show
an inability to have Cr enrichment in the passive film, and consequently do not show enhanced passive behaviour. Referring to the data of Frankenthal [Frankenthal 1967], as discussed in §[3.2.1.], which implied that the passive film on iron consists of an initial absorbed oxygen film, followed by subsequent irreversible oxide growth, Newman and Sieradzki postulated that the adsorbed oxygen must bridge the chromium atoms, in what is to become the oxidized chromium surface.

Based on the hard sphere ionic radii, for Cr\(^{3+}\) (0.69 Å) and O\(^{2-}\) (1.4 Å), the maximum separation consistent with continuity was found to be 4.18 Å. The third nearest neighbour distance in the Fe–Cr lattice is \(\sqrt{2}\) a. For a \(\sim 2.87\) Å this distance is 4.06 Å. This distance is just slightly less than the maximum separation consistent with continuity as determined above. The \(p_c\) in the BCC lattice is 9.5 wt%. At this critical percentage it becomes possible for a chain of chromium oxyhydroxide to span from one end of the surface to the other. This fraction is close to the observed ‘transition’ from ‘Fe like’ to ‘Cr like’ behaviour at 12 wt% documented in the literature [King 1959]. If second neighbour percolation is considered, \(p_c\) in the BCC lattice is 17.5 wt%.

Incomplete passivation, according to this model, therefore corresponds to finite clusters, around which dissolution in the incompletely passivated state should proceed. Experimental confirmation [Newman 1988] of this theory was obtained by comparing current passed with weight loss, and noting that the weight loss was higher than the predicted current. Microscopy also revealed the detachment of small ferromagnetic particles (<100 nm) in the case of incomplete passivity on a 10.9 wt% Cr alloy, while no grain detachment occurred. Qian and Newman also carried out two dimensional computer modelling to show how enrichment would take place in an Fe-Cr binary alloy according to this mechanism [Qian 1990].

3.4. Mechanism of protection of the passive film

There are in essence two fundamental opposing views of the mechanism by which the passive film in the Fe-Cr system serves to inhibit the corrosion. The first of these postulates that passivity is primarily conferred by an adsorbed oxygen film. Uhlig is the
primary advocate of this theory [Uhlig 1946, King 1959, Uhlig 1979]. Most of the other theories consider the passive film to inhibit corrosion by acting as a barrier to one or more species. In the following sections brief overviews of some of the most important theories are given.

3.4.1. Adsorbed oxygen model

Following a history in which the passive films on some materials were postulated to be adsorbed oxygen films, as opposed to being diffusion limiting bulk oxides [Fredenhagen 1903, Flade 1911, Langmuir 1916], Uhlig proposed [Uhlig 1946] that an adsorbed oxygen film, sometimes less than a monolayer in thickness, is the primary source of passivity in the transition metals and their alloys. Later he proposed that the mechanism of such an adsorbed film is to reduce the value of the exchange current density of the metal dissolution reaction [Uhlig 1979]. He postulated that Cl- destroys passivity by displacing O at adsorbed sites, thus leading to a decrease in anodic polarisation.

Uhlig accounted for the observed three dimensional oxides, by postulating multi layer adsorption of oxygen at higher potentials. This multi layer adsorption is followed, in time, by non-stoichiometric oxides, which ultimately nucleate stoichiometric oxides. Uhlig maintains, however, that thin non-stoichiometric adsorbed complexes next to the metal surface confer primary passivity, while the over layer acts as a further diffusion barrier. Uhlig [Uhlig 1958] linked this model of passivity with the 'critical' wt% Cr in the Fe-Cr system, by postulating that the adsorption of oxygen is enhanced by specific d-orbital electron configurations, thus enhancing the passivity. King and Uhlig [King 1959] compared the free energy of adsorption reaction with the free energy corresponding to the Flade potential (via $\Delta G = -nF\Delta\phi$), and found it to correspond more closely than the free energy for the oxidation reaction, thus lending substance to the postulation that adsorption and not oxidation is present at the onset of passivity. See also the discussion of the d-orbital model of the critical transition in the Fe-Cr alloy system in §[3.3.1.].
3.4.2. Point defect model

The point defect model was developed to explain the logarithmic and inverse logarithmic film growth kinetics that are commonly observed in the study of passive films [Chao 1981, Lin 1981, Chao 1982]. The model starts out by pointing out that the Mott-Cabrera model [Cabrera 1948-49], which assumes that the film growth is by metal ions, is not in accord with tracer studies carried out by the Chalk River Nuclear Laboratories [Davis 1965, Whitton 1968, Brown 1973, Mackintosh 1976, Mackintosh 1977], which shows that anion transportation is largely responsible for film growth in the anodic films on a wide variety of materials. Chao [Chao 1981] also points out that equilibration measurements of the reaction [Vetter 1954, Weil 1955]:

$$\text{O}_{\text{oxide}} + 2\text{H}^+_{(aq)} + 2\overline{e} \rightarrow \text{H}_2\text{O} \quad [3.1.]$$

showed that equilibrium is rapidly established. The Felner-Mott model [Fehlner 1970], which assumes the rate limiting step at the film/electrolyte interface, is not supported by these results.

Chao assumes that the passive film behaves like an incipient semiconductor, on the verge of dielectric breakdown. The field strength is therefore not a function of the thickness of the passive film, but only a function of the passive film material properties. By considering the chemical equilibrium at the metal/film and the film/electrolyte interface, Chao shows that oxide vacancies are produced at the metal/film interface which then migrate to the film/electrolyte interface. In the same manner, metal vacancies are produced at the film/electrolyte interface and are consumed at the metal/film interface. According to this model, diffusion of metal vacancies contributes to corrosion only, while the diffusion of oxygen vacancies is associated with the growth of the film. The growth rate of the film is thus equal to the diffusional flux of oxygen vacancies in the concentration and potential gradient that exists in the passive film. The passive film, in order to be protective according to this model, therefore, has to function as a barrier against metal vacancy diffusion.
In a subsequent paper, the same group of investigators postulated that film breakdown, by
the point defect model, occurs when the metal vacancy arrival rate at the metal/film interface
is greater than the rate of disappearance of metal vacancies into the bulk metal [Lin 1981].
Void formation associated with the coalescence of vacancies follows, and the passive film
collapses locally. Because the proposed model is based on a diffusional process, the
diffusional process should be discernible by means of low frequency impedance
measurements. Such measurements should exhibit a Warburg impedance element. Results
of this kind for passive films on Ni and 304 SS were presented by Chao [Chao 1982].

3.4.3. Chemi-conductor model

It is generally recognised that the passive film on Fe is primarily an Fe$^{3+}$ oxide. It was
pointed out in §[3.2.2], that from thermodynamic arguments it follows that the Fe$^{3+}$ cannot
exist in thermodynamic equilibrium with the metal substrate [Vetter 1967], and that for this
reason several investigators have postulated a bi-layer film, consisting of an inner Fe$_3$O$_4$
film, and an outer $\alpha$-Fe$_2$O$_3$ film [Nagayama 1962, Foley 1967, Cohen 1974 (a), Cohen
1974 (b)].

Chen and Cahan [Chen 1982] could not find evidence from ellipsometric measurements
that the passive film consists of a bi-layer, although they speculated about deposition of an
over layer under certain specific conditions. In a subsequent paper [Cahan 1982 (a)] they
examined the passive film by means of AC impedance spectroscopy. They observed the
same frequency dispersion of the capacity values that has been documented by other
investigators [Stimming 1976, Stimming 1983]. To model this observed data and to
integrate it with the ellipsometric data which indicated a single Fe$_2$O$_3$ phase, Chen and
Cahan postulated a model in which the passive film consists of primarily Fe$^{3+}$, in which a
gradient of Fe$^{2+}$ exists [Cahan 1982 (b)].

In Cahan’s model, it is recognised that thermodynamics dictate an Fe$^{2+}$ concentration at the
metal/film interface. Under the influence of a potential gradient such as is present under
polarisation, Fe$^{2+}$ has to establish a chemical potential that balances the electrostatic
potential in order to maintain equilibrium. The linear potential gradient therefore
corresponds to an exponential Fe$^{2+}$ distribution in the film. If the potential is increased, the concentration gradient of Fe$^{2+}$ that has to be maintained becomes steeper. The Fe$^{2+}$ is therefore progressively replaced by Fe$^{3+}$ as the potential is increased. This situation is schematically illustrated in figure [3.6.8]. Because the Fe$^{3+}$ oxides are much less soluble and have much slower kinetics of dissolution than the Fe$^{2+}$ oxides, this appearance of Fe$^{3+}$ at the interface film/electrolyte decreases the corrosion rate.

Local conductivity is postulated to be a function of the Fe$^{2+}$ species in the film. Similarly, at high potentials, Fe$^{4+}$ is introduced into the film. In this case, however, the Fe$^{4+}$ concentration extends back into the film from the film/electrolyte interface. The concentration of the Fe$^{4+}$ is also not fixed at the interface like the Fe$^{2+}$, but rather, is a function of the applied potential. This situation is schematically illustrated in figure [3.6.9]. Cahan shows that this model could exhibit the impedance response measured for the passive film, and that a linear fit for a $1/C$ or $1/C^2$ are special cases and are coincidental. Cahan calls this model the 'chemi-conductor' model, in which the stoichiometry can be varied by oxidative or reductive valence state changes. Cahan thus relates protectiveness of the passive film to the solubility and kinetics of dissolution of the passive film.

3.5. Electronic structure of the passive film

From the band theory for materials, it follows that electron bands may be formed if there is enough periodicity of electron terms. The thicker the polyatomic passive film, the better the approximation that the band model gives, so that for passive films with thicknesses greater than 10 Å, the band model becomes a good approximation [Schultze 1978]. Stimming [Stimming 1976] showed by a series of capacitance measurements that the passive film on iron behaves like a highly doped n-type semiconductor.

Stimming's results indicated that the capacity versus potential behaviour of the passive film on Fe can be divided into three potential ranges; (i) the first, a low potential range, in which the film behaves approximately as a semiconductor according to the Mott-Schottky equation, (ii) the second at intermediate potentials in which the passive film behaves like an
exhausted semiconductor, thus exhibiting dielectric behaviour, and (iii) the third at high anodic polarisation, in which the passive film shows phenomena associated with the onset of degeneracy.

In order to apply Mott-Schottky analysis, the following conditions have to be satisfied: (i) Donor concentration constant in the space charge layer (ii) Dielectric constant must be constant (iii) Space charge layer capacity $C_{sc}$ small in comparison to the Helmholtz capacity $C_h$ as well as (iv) The presence of only one fully ionised dopant species. Stimming pointed out that according to Wagner [Wagner 1973] the Fe$^{2+}$ concentration decreases with increasing distance from the metal. Also that according to Jantzen [Jantzen 1965] the dielectric constant varies from $\varepsilon = 10$ for $\gamma$-Fe$_2$O$_3$ to $\varepsilon = 250$ for Fe$_3$O$_4$ so that the dielectric constant is very susceptible to the amount of Fe$^{2+}$. Jantzen showed that even as little as 4% Fe$^{2+}$ changes the dielectric constant from ~10 to 56. Wisdom and Hackermann [Wisdom 1963] established, by means of a potentiostatic pulse method that the value of the dielectric constant for the passive film on Fe in a neutral borate solution changes from 54 to 21 with a change in the electrode potential from -0.1 to 0.75 V. This change in the dielectric constant violates assumption (ii) above. Simoes [Simoes 1990] has also experimentally observed the presence of two donors in a pure Fe film, visible as a slope change in the Mott-Schottky plot. Multiple donors in the passive film violates condition (iv) above. An inflection of the type that he describes was not observed on the Fe in this study as will be discussed in §[6.], even though films formed in the same potential range were investigated. Cahan [Cahan 1982 (a)] also showed that considerable frequency dispersion is present when capacitance values are measured as a function of excitation frequency. Due to these limitations, the capacitance response, in the low potential region (i), cannot be fully analysed in terms of the Mott-Schottky treatment, although it provides a useful simplified description of the behaviour.

In the intermediate potential regime Stimming [Stimming 1976] postulated an exhaustion of donors with increased potential. Donors can consequently not contribute to the capacitance, with the result that the passive film behaves like a dielectric. Similar behaviour was also shown for the passive film on iron in the work of Engell [Engell 1955] as well as the work of Moshtev [Moshtev 1968]. By similar reasoning, and theoretical modelling,
Khan [Khan 1980] has shown that for thin passive films, where the thickness of the space charge layer, $D_{sc}$, is of the same order of magnitude as the thickness of the passive film, $d$, that at potentials close to the flat band potential, $E_{fb}$, the charge is concentrated in the passive film. With increasing potential, the film is depleted of charge carriers, and the band bending extends over the entire thickness of the passive film. Upon further increase in the potential, the film becomes almost completely exhausted and acts like an insulator, so that the total capacitance is equal to that of a parallel plate capacitor. The capacitance then remains constant with an increase in potential until the valence band starts to participate. These calculations shows that the interpretation of Stimming [Stimming 1976, Stimming 1979] is mathematically feasible.

At even higher potentials an increase in the capacitance is observed (see figure [6.10.29.]). Stimming attributes this to an increase in the hole concentration in the valence band, yielding a dominating space charge concentration at the surface. Stimming also showed how degeneracy lowers the capacity from the theoretical prediction. Many other authors have also concluded that the passive film formed on Fe behaves like a highly doped n-type semiconductor [Hardee 1977, Stimming 1979, Wilhelm 1981, Abrantes 1983, Peat 1987, Searson 1988]. Photoelectrochemical measurements on Fe$_2$O$_3$ or oxidized Fe have also indicated that the oxide behaves like an n-type semiconductor [Yeh 1977, Hardee 1977, Anderman 1984].

For Cr the situation is a little more complex. Because of the thinness of the passive film on Cr, a photoelectrochemical investigation is difficult. A comparison of the behaviour of Cr passive films with bulk Cr$_2$O$_3$ is useful, because of the relative abundance of data of the conduction properties of Cr$_2$O$_3$, generated with a view towards understanding the high temperature corrosion resistance of Cr oxides. Pure thermally grown Cr$_2$O$_3$ has been reported to have a p-type conduction mechanism in some cases, and an n-type mechanism in other cases [Young 1985, Young 1987, Metikos-Hukovic 1987].

Young [Young 1985], showed that Cr$_2$O$_3$ sintered at high oxygen partial pressure gives a p-type conduction mechanism. This conduction mechanism indicates the presence of Cr interstitials. Kofstad [Kofstad 1980] also indicated the presence of Cr interstitials as the
dominant defect. This type of defect, if present, would lead to p-type behaviour. Young also showed that at low partial pressures, an n-type conduction mechanism results. Young showed that the oxides could reversibly be made either n-type or p-type. Reversibility indicates that behavioural change is not due to contamination. In a later paper [Young 1987], Young again showed that the n-p change could be made to take place reversibly, and refined the conditions under which each type of conduction mechanism is expected.

Metikos-Hukovic [Metikos-Hukovic 1987] investigated thermally formed oxides on Cr. In this paper, the conduction mechanisms were determined by photopotential measurements (positive photopotential corresponds to p-type behaviour, negative photopotential to n-type behaviour), and not by thermoelectric power as in the case of Young above. It was found that at low anodic potentials p-type behaviour was indicated, while at higher potentials the oxide behaved like an n-type semiconductor. It was also shown that the transition from n-p and p-n is a pH dependent reversible process. Examination of the passive film on Cr did not show any photopotential. Metikos-Hukovic ascribed this lack of a measurable response to the thinness of the passive film. Metikos-Hukovic concluded that the passive film on Cr is a Cr oxide with a continuously variable oxidation state.

Sugimoto [Sugimoto 1985] carried out photocurrent measurements on \( \text{Cr}_2\text{O}_3 \) deposited onto a Pt substrate by means of chemical vapour deposition (CVD). He also investigated the passive film on Cr. His measurements of the oxide electrode indicated that the photoresponse was p-type at the lower potentials, and n-type for higher potentials. For the Cr passive film, Sugimoto also concludes that p-type behaviour at low potentials is followed by n-type behaviour at higher potentials, however, in the opinion of this researcher, his data does not merit such a conclusion. Sugimoto’s data is shown in figure [3.6.10.], from which it is clear that the regime in which he postulates cathodic photocurrents, are in fact the regime in which the data is indicated as \( \pm 10^{-5} \text{ A/m}^2 \), and is therefore below the detection limit of his experimental set up, since he could not resolve a sign for the photocurrent. It is therefore uncertain whether the observed response is in fact noise, or represents an anodic, or a cathodic photocurrent.
Sunseri [Sunseri 1987] reported results of a photocurrent spectroscopic investigation of the passive film on three ferritic stainless steels and also a preliminary investigation of the passive film on Cr. The electrolyte was 0.5 M pH 6 H₂SO₄+Na₂SO₄. They showed anodic photocurrents on the ferritic stainless steels, indicating an n-type conduction mechanism, while the photocurrents on the Cr were initially anodic and decayed to steady state cathodic values. Cathodic photocurrent indicates p-type response. In a later paper [Sunseri 1990], it was shown that the results from a photoelectrochemical investigation of Cr indicates that the passive film on Cr is either isolating or slightly p-type.

Moffat [Moffat 1990], investigated the passive film on Cr, formed at various potentials in the passive regime, by means of a redox couple. From this measurement, it is possible to determine the conduction characteristics of the passive film. While not conclusive, the results reported by Moffat, are closer to that expected on a passive film with a p-type conduction mechanism. Moffat determined the exchange current density for the redox couple on the passive film on Cr, as well as on gold, at various film formation potentials. These results were then plotted as E_{form} versus log(i_o). A schematic of such a plot is shown in figure [3.6.11.]. Moffat’s results indicate that the intercept of the value for i_o on the passive Cr film equals the value for i_o on the gold electrode at the potential of the onset of passivity for Cr, E_{ps}. These results indicates that the passive film is (i) Electronically conductive, with a conductivity that is a function of the film thickness, or (ii) that the passive film functions as a barrier; that the electron transfer occurs via a tunneling mechanism. The change in the passive film thickness d, in the tunneling controlling equation is then responsible for the observed change in the value of i_o.

Searson [Searson 1990] investigated the photocurrent on both the air formed passive film and the passive film formed at 0.94 V versus SCE. The electrolytes employed were H₂SO₄ solutions of 0.1 and 1 N. The investigation showed that the photocurrent on this system was anodic, indicating n-type behaviour over the whole potential range investigated. Searson’s result is in contrast with the other results that has been presented here. It may be due to the fact that the passive films that Searson investigated, were formed at 0.94 V. This potential is very close to the breakdown potential for the passive film on Cr in acidic solutions of the kind employed (see also the polarisation data in §[5.], and
specifically in figure [5.10.5.]), so that at this potential the film might be n-type as Sugimoto [Sugimoto 1985] suggests. If the potential dependent measurements of Searson were carried out faster than the relaxation from n-p at lower potentials, the observed n-type behaviour might just be due to the high film formation potential.

The observed n-type behaviour measured by Searson may also be due to the fact that although the Cr investigated by him was low in metallic impurities, it contained many Cr$_2$O$_3$ particles due to the high oxygen content of the alloy. Searson estimates that these particles contributed about 50% of the observed photocurrent, however, since this is only an estimate, the particles may in reality contribute the bulk of the measured photocurrent. The oxygen partial pressure at the time of formation of these particles would then determine whether n or p-type response is exhibited. If the particles are n-type, this could give the observed behaviour, which is contrary to what is expected. Support for the postulate that the particles contribute the bulk of the photocurrent, comes from the fact that the oxide particles are normally formed at very low oxygen partial pressures. Under these formation conditions, thermal oxides of Cr have been shown to be n-type, which is in line with the observation by Searson.

Very little published work on the semiconductive properties of the passive film formed on Fe-Cr alloys exist in the literature. Sunseri [Sunseri 1987] investigated three ferritic stainless steels and concluded that the films exhibited n-type behaviour. Sunseri’s alloys, however, also contained Mo, Ni and smaller amounts of Mn, making these results more difficult to relate to binary Fe-Cr alloys. Sugimoto [Sugimoto 1985] examined the semiconducting properties of both the passive film formed on Fe-Cr alloys, as well as that of Fe$_2$O$_3$/Cr$_2$O$_3$ oxide electrodes, the latter CVD deposited onto a Pt substrate. Sugimoto concluded that alloys with less than 20 wt% Cr exhibits n-type behaviour, while alloys with more than this amount of Cr exhibits p-type behaviour. As in the case of pure Cr discussed above, a closer examination of Sugimoto’s data shows that the regime in which he postulates cathodic photocurrents, is in fact the regime in which the data is indicated as $\pm 10^{-5}$ A/m$^2$. The measurements in this regime is therefore likely below the detection limits of his experimental set up, since he could not resolve a sign for the photocurrent. Sugimoto’s results are shown in figure [3.6.10.].
Results on the oxide electrodes indicated n-type behaviour for electrodes with $X_{Cr} < 0.5$. Sugimoto also reports a change in the value of $E_g$ of oxide films, from 2.25 eV for $\gamma$-Fe$_2$O$_3$ to 2.48 eV for $X_{Cr}=0.42$. For alloys with $X_{Cr} > 0.8$, he reports p-type behaviour at low potentials and n-type behaviour at high potentials. Sugimoto also finds a linear relationship between $i_{ph}$ and the Cr content of the alloy, for alloys containing less than 20 wt% Cr. For alloys containing more than this amount of Cr, however, the photocurrent is almost constant as a function of the Cr concentration. This data, however, was taken at constant potential, so that if there is a shift in the flat band potential as a function of the Cr content of the material, the data is not taken at constant band bending.

In summary the following conclusions regarding the band structure of the passive film on Fe, Cr and Fe-Cr alloys can be drawn: (i) The passive film on Fe behaves like a highly doped semiconductor. (ii) The passive film on Cr is most likely p-type at low potentials, but becomes n-type at higher anodic polarisation potentials. (iii) The passive films on Fe-Cr alloys containing less than about 20-30 wt% Cr are n-type, while (iv) it is not certain what the conduction mechanism for the passive film on Fe-Cr alloys with a Cr concentration higher than 20-30 wt% is. The conduction mechanism for these alloys is expected in the limit, to approach that of pure Cr, and thus to exhibit a potential dependent conduction mechanism.
3.6. Figures - Literature review of passivity of Fe-Cr alloys
Figure [3.6.1.] Pourbaix diagram for the system Fe-H₂O, at 25 °C [Pourbaix 1974]. (Established considering as solid substances only Fe, Fe₃O₄ and Fe₂O₃.)
Figure [3.6.2.] Pourbaix diagram for the system Fe-H₂O, at 25 °C [Pourbaix 1974]. (Established considering as solid substances only Fe, Fe(OH)₂ and Fe(OH)₃.)
Figure [3.6.3.] Pourbaix diagram for the system Cr-H₂O, at 25 °C [Pourbaix 1974]. In solutions not containing chloride. (Established considering anhydrous Cr₂O₃.)
Figure [3.6.4.] Pourbaix diagram for the system Cr-H₂O, at 25 °C [Pourbaix 1974]. In solutions not containing chloride. (Established considering Cr(OH)₃.)
Figure [3.6.5.] Pourbaix diagram for the system Cr-H$_2$O, at 25 °C [Pourbaix 1974]. In solutions containing chloride. (Established considering Cr(OH)$_3$.nH$_2$O.)
Figure [3.6.6] E vs i for Fe-24 wt% Cr in 1 N H₂SO₄ [Fankenthal 1967]. (a) Reversible behaviour of the primary passivation film. (b) Hysteresis due to the secondary passive film.
Figure [3.6.7.]  Comparison of polarization curves for Fe, Cr, Ni and 18-8 stainless steel. Sketch in the upper part shows the composition and thickness of the passive film [Okamoto 1973].
Figure [3.6.8.] Schematic representation of Fe$^{2+}$ gradually replaced by Fe$^{3+}$ as the potential is increased [Cahan 1982 (b)].
Figure [3.6.9.]  Schematic representation of Fe$^{3+}$ gradually replaced by Fe$^{4+}$ as the potential is increased [Cahan 1982 (b)].
Figure [3.6.10.] $i_{\text{ph}}$ vs $E$ for the passive film formed on Cr and Fe-Cr alloys [Sugimoto 1985].
Figure [3.6.11.] Schematic representation of $E_{\text{cor}}$ vs $\log(i)$ for a redox couple on the passive film on Cr, as well as on a gold electrode.
4. RESEARCH OBJECTIVES

The literature available regarding the corrosion characteristics of Fe, Cr and its alloys is extensive. There are several models for the behaviour of Fe-Cr alloys, and the role that Cr has on passivity in this alloy system. Some aspects of the role of Cr have been discussed in the literature review, [3.]. Despite all the interest in this alloy system, several important aspects of the role of Cr on the corrosion characteristics of this alloy system remain unclear.

One of the interesting characteristics of the alloy system is that many articles report the existence of a critical threshold in Cr content, above which the corrosion characteristics of the alloy are greatly improved. The present investigation was directed at determining the fundamental aspects that underlie this transition. By electrochemical examination of a series of alloys with progressively increasing amounts of Cr, it was anticipated that the reason for the existence of such a threshold could be found, and that this knowledge could be used in the design of new corrosion resistant materials.

The electronic structure of the passive films on Fe-Cr alloys is very important in determining the chemical nature of these films. To examine the electronic structure of the passive films on these alloys, impedance spectroscopy and photoelectrochemistry can be utilised. Impedance spectroscopy and photoelectrochemistry allow the passive film to be studied in-situ. Using these techniques, one is therefore able to examine the film in the unperturbed state. It was hoped that by using the two techniques, the changes in the electronic characteristics of the passive film as a function of the amount of Cr in the alloy could be isolated. By using the two techniques in tandem, some parameters may be determined in two ways, so that the consistency of the two methods may be checked. The photoelectrochemical and impedance techniques not only permit the examination of the band structure of the passive film, but can also be used to elucidate the compositional changes of the passive film in-situ. Changes that occur in the passive film in conventional ex-situ investigation methods, and which may give rise to artifacts, may thus be avoided.
In summary, the research will therefore attempt to answer the following questions regarding passivity in the Fe-Cr system:

(i) Does a discontinuity in the corrosion characteristics of Fe-Cr alloys occur at ~12 wt% Cr?
(ii) If the discontinuity in (i) exists, why does it exist?
(iii) What is the role of Cr enrichment in the passive film on the corrosion characteristics?
(iv) Can the passive film be treated as a semiconductor?
(v) What is the composition of the passive films?
(vi) How does Cr affect the electronic properties of the passive film?
(vii) How does the change in electronic properties affect the corrosion characteristics of the alloy?
(viii) How do the properties of the passive film as determined by in-situ photocurrent spectroscopy differ from ex-situ determinations?
5. DC AND OPEN CIRCUIT MEASUREMENTS

5.1. Materials

The nominal compositions of the alloys investigated are shown in table [5.9.1.]. The alloys 5 - 30 wt% Cr were prepared from electrolytic chromium and pure iron by melting in a vacuum to form ingots of ~ 3 kilogram each. The pure elements were purchased from Aesar® Johnson Matthey. Because it was found that the chromium from Aesar® contained a lot of Cr₂O₃ inclusions, chromium containing low amounts of oxidized metallic species were obtained from the Ames Laboratory Materials Preparation Centre at Iowa State University. An analysis of a similar finger of Cr, supplied by the same laboratory is given in table [5.9.2.].

The ingot as described above were cut into strips ~ 22 x 22 mm x length of the ingot. These specimens were cut and then machined into bars ~ 16 mm in diameter. The bars were encapsulated in quartz, using tantalum to bind oxygen. The capsules were filled with argon to further avoid any oxidation. The encapsulated specimens were homogenized at 1100 °C for 24 hours in some cases and 96 hours in others. The latter heat treatment was carried out in order to serve as a comparison of the effect of heat treatment. No differences in the electrochemical characteristics could be resolved between the two types of heat treatment. After cooling the specimens were machined to a diameter of 11.28 mm. The specimens were subsequently abraded with 600 grit Carbimet® silicon carbide grinding paper, to form cylinders with a cross sectional area of 1 cm². The latter procedure was followed in order to ensure that oxidized parts as well as parts contaminated by the machining tools were completely removed.

The phase diagram for the iron-chromium system is shown in figure [5.10.1] [Ageev 1962]. The phase diagram shows that except for the high wt% Cr alloys, the expected phase is the α phase, although some evidence exists in the literature to suggest that the equilibrium reaction is a separation into a bi-phase structure, with iron and chromium as the structural constituents [Lihl 1955, Maykuth 1955]. The materials were examined by X-ray diffraction to ensure that a solid solution resulted from the heat treatment described above.
Results showed that the alloys were single phase, with the exception of the higher wt% Cr alloys, which showed a small percentage of the retained δ-phase as expected from the phase diagram.

From the cylinders as prepared above, ~ 1 cm lengths were cut and used to prepare the specimens for the polarisation data reported. Electrical contact to the specimen was made by attaching a 24 gauge copper wire to the back of the specimen by means of silver paint. To ensure mechanical integrity this contact was covered with a spot of 5 Minute Epoxy®. The electrical resistance of the joint was measured to ensure that it was smaller than 1 ohm. A small value of the resistance was necessary to ensure that no significant potential drop resulted due to the mounting scheme. The specimens were subsequently painted with two or three layers of Amercoat® 90, utilizing a 48 hour drying period between coats. For ease of polishing, the specimens were encapsulated in Epon® 828 resin, using Triethylenetetramine as curing agent. A glass tube shielding the copper wire from the solution was also affixed to the specimen during this step, using Epoxi-Patch®. In this way, an electrode was created that exposed only one cylindrical surface of 1 cm² to the electrolyte. Upon completion, the electrode was cured for a minimum of seven days before use. The design ensured that the specimen could be re-used by polishing the exposed surface. A schematic diagram of the completed electrode assembly is shown in figure [5.10.2].

5.2. Electrolytes

All electrolytes were prepared using high purity water (Barnstead Nanopure System). The electrical resistance of the pure water was greater than 18 MΩ.cm, as determined by a Barnstead resistivity meter. Acidic electrolytes were prepared using Malinckrodt® analytical grade H₂SO₄ diluted to 0.5 M. This electrolyte will be referred to as ‘acid’ in the rest of the document. For pH 4 and pH 6 electrolytes an aqueous solution of Malinckrodt® Na₂SO₄ of 0.5 M strength was titrated with the acid prepared as above. These electrolytes will be referred to as ‘pH 4’ and ‘pH 6’, respectively, in the rest of this document. Neutral electrolytes were prepared by mixing equal volumes of 0.1 M Na₂B₄O₇·10H₂O and 0.1 M H₃BO₃ solutions prepared from Malinckrodt® analytical grade reagents. This
electrolyte will be referred to as 'borate' in the rest of this document. Basic electrolytes of 0.1 M strength were prepared from Malinckrodt® analytical grade crystalline NaOH. This electrolyte will be referred to as 'hydroxide' in the rest of this document.

5.3. Equipment

5.3.1. Polarisation studies

The electrochemical cell was an airtight unit, based on a modified Pyrex® glass Florence flask. A schematic diagram of the cell is shown in figure [5.10.3]. The functions of the relevant ports used are labelled in this diagram. A Cole-Parmer ceramic junction saturated calomel electrode (SCE) was used as the reference electrode, and all potentials, unless otherwise indicated, are reported with respect to this electrode. Electrical continuity to the reference was established using a Luggin capillary arrangement to minimize the effect of electrolyte resistance. The counter electrode consisted of a platinum foil with a surface area of 12 cm².

The temperature in the cell was maintained at 30 °C by a Cole-Parmer Lab Monitor® III thermoregulator, used in conjunction with a nichrome resistance wire heating coil, and a Staco Energy Products type 3P1010 variable auto transformer set at 10-15 V AC. The Lab Monitor® III unit was modified to switch the output from the auto transformer, and not the power input to the auto transformer, in order to minimize electrical noise.

Polarisation runs were generally conducted using a PAR 173 potentiostat equipped with a PAR 376 linear/logarithmic converter, in combination with a PAR 175 universal programmer. In a few cases a PAR 273 potentiostat were also used. The scan rate utilized was 1 mV/s, and the slew rate (in the case of the PAR 173) was set at 10 ms. The accuracy of the current metering systems of the potentiostats were checked over the ranges utilized by means of a series of standard resistors. Metered currents were shown not to deviate more than 10% from the true currents, even when measuring currents in the nA range.
The output from the potentiostat was recorded using an Apple Macintosh® II microcomputer equipped with a National Instruments™ NuBus® NB-MIO16 analog to digital converter. The software for the data acquisition were developed using LabDriver® and Microsoft QuickBasic®. The software listing is given as §[12.3.1.]. The sample interval was 10 seconds, corresponding to one reading every 10 mV. A Hewlett Packard model 7044 B X-Y recorder was used as a secondary means of recording data. The results were not corrected for IR drop.

5.3.2. Open circuit measurements

The electrochemical cell and reference system was similar to the cell described in §[5.3.1.], with the exception that no counter electrode was provided. The potential of the specimen with respect to the reference electrode was logged using a Keithley model 197 digital microvolt digital multimeter.

5.4. Experimental procedures

5.4.1. Anodic polarisation scans

All runs were conducted with the electrolyte deaerated/aerated for at least 30 minutes before the start of the experiment. The deaerating gas was pre-purified grade Airco® H₂ and in some cases Airco® N₂. A check for deaeration was carried out by monitoring the potential of the platinum electrode against the reference electrode in the cases that H₂ was used as deaerating gas. No differences in the electrochemical behaviour could be observed in experiments in which the only variable was the deaerating gas used. Before each run the specimen prepared as described in §[5.1.] was polished to a 600 grit finish using Carbimet® disks.

Prior to generating the polarisation diagrams, the electrodes were allowed to stabilize to their corrosion potentials. All anodic polarisation scans were initiated at the corrosion potential, and terminated at 1.5 V. Three identical scans were conducted in the acid, pH 4, borate and hydroxide solutions, in order to check for reproducibility. At least two different
electrodes were used. In the case of the pH 6 solution, only two runs were conducted because behaviour was very similar to the pH 4 case. The results were very reproducible in all cases.

5.4.2. Cathodic polarisation scans

Aeration was carried out with Airco® compressed air for at least 30 minutes before the start of the experiment. Before each run the specimen prepared as described in §[5.1.] was polished to a 600 grit finish using Carbimet® disks with the exception of the gold electrode which was polished to a 0.3 μm finish by polishing with alumina paste on Microcloth®.

In the case of gold, the electrode was allowed to stabilize at the open circuit potential, and the scan was initiated from this point. In the case of the 100, 30 and 15 wt% Cr, Fe-Cr alloys, the electrode was stabilized at a potential of 0.5 V and the passive film allowed to form for a period of 1800 seconds, before the scan was initiated from this potential. The latter procedure was necessary because not all of the alloys exhibited a corrosion potential in the passive regime, so that if this procedure was not followed, the oxygen reduction reaction diffusion limiting current density might have been obscured by the ‘nose’ of the active passive transition. Two identical runs were carried out in all cases in order to check for reproducibility.

5.4.3. Open circuit measurements

Aeration was carried out with Airco® compressed air for at least 30 minutes before the start of the experiment. Before each run the specimen prepared as described in §[5.1.] was polished to a 600 grit finish using Carbimet® disks.

The potential of the specimen with respect to the reference electrode was monitored with 1 hour intervals for a period of 24 hours, using the data logging function of the multimeter. The data was subsequently retrieved from the memory of this unit, and transferred to an Apple Macintosh® II microcomputer.
5.5. Data treatment and presentation

In all graphical representations of data, only enough data sets are shown to unambiguously define the trends. Elimination of some of the data sets was done in order to avoid visual clutter in graphs which was distracting when all eight data sets were shown in one graph. The experiments, however, were carried out on all eight different specimens (0, 5, 7.5, 10, 12.5, 15, 30 and 100 wt% Cr).

5.5.1. Cathodic and anodic polarisation scans

The complete data treatment procedure is given as §[12.1.1.]. The listing of the software used for collection of the data is given as §[12.3.1.], while the program used to interpolate the current values to the same potential increments, is given as §[12.3.2]. Note that the results presented for the anodic scans in acid, pH 4, borate and hydroxide are the averages of three runs, while in the case of the anodic scans in pH 6, as well as the cathodic scans the data shown is a representative set chosen from the two runs conducted.

5.5.2. Open circuit measurements

No further treatment was carried out.

5.6. Results

5.6.1. Limitations of potentiodynamic polarisation methods

It is important to realise that potentiodynamic scans exhibit scan rate dependency. The slower the scan rate, the more closely the results of the scan correspond to true steady state conditions. Investigation showed that the current density in the passive regime for Cr and Fe, the constituents of the alloys investigated, would still be decreasing after polarisation times of 24 hr or longer. Over a practical time scale, true steady state can therefore not be achieved. Figure [5.10.4.] from the work of Moffat [Moffat 1989] shows the effect of scan rate on the polarisation behaviour of Cr. Other problems may also occur if very slow
scan rates are employed. If the solution is not buffered, even a relatively small amount of metal dissolution may cause a pH change in the solution in the corrosion cell. The reason for this pH change can best be understood by considering the metal dissolution reaction:

\[ M \rightarrow M^{x+} + xe^- \quad [5.1.] \]

The metal dissolution reaction has to be balanced by a cathodic reaction; in the case of deaerated solutions this is the cathodic hydrogen reaction:

\[ 2H^+ + xe^+ \rightarrow H_2 \quad [5.2.] \]

The nett result of reactions [5.1.] and [5.2] is, therefore, to consume the $H^+$ ions in the electrolyte, which raises the pH of the solution if the solution is unbuffered. A pH change in the solution, in turn, affects the corrosion characteristics of the metal. Buffering solutions are not desirable because buffering changes the corrosive characteristics of the electrolyte. Since the total amount of dissolution generally becomes greater when the scan rate is decreased, pH changes during the course of an experiment may become problematic at low scan rates.

The fact that one can never approach steady state is not as severe a restriction on the usefulness of data obtained by potentiodynamic methods as one would expect. Polarisation data are very useful, provided that data are never used to calculate absolute values of parameters like lifetime of a given alloy. Polarisation data are very useful to establish patterns or trends in the phenomenon investigated. In this investigation, a scan rate of 1 mV/s was chosen as a good compromise between duration of experiment and visibility of the phenomenon investigated. At this chosen scan rate, the bulk pH of the unbuffered solutions employed did not change by more than 0.5 pH units over the duration of the experiment.
5.6.2. Anodic polarisation scans

Graphs comparing the anodic polarisation behaviour for the different alloys in the electrolytes utilised are shown as figures [5.10.5.] to [5.10.9.]. Important electrochemical parameters are summarised in tables [5.9.3.] to [5.9.6.]. The alloys studied show a well developed active to passive transition in the solutions investigated, although in some cases, in the higher pH solutions, spontaneous passivity under deaerated conditions existed. This condition is indicated as "< $E_{corr}$" in the tables where relevant.

The values of the passive current densities as well as the critical current densities for the alloys decrease as the pH of the solution is increased. In the acidic solution, the 5 wt% Cr, Fe-Cr alloy showed a current density that was lower than some of the alloys containing more Cr. This phenomena was reproducible, but no explanation could be found for this behaviour. The values of the passive and critical current densities decrease as the wt% Cr in the alloy is increased. The pseudo steady state data of Kirchheim [Kirchheim 1989] provide a good comparison of how the parameters as determined by the potentiodynamic technique correspond to steady state results. Kirchheim's data shown in figure [5.10.10.] show that the values for the critical current density $i_{crit}$, as determined by potentiodynamic polarisation, correspond closely to the steady state results. Kirchheim's data also shows that there is greater separation between the passive current densities as a function of Cr concentration of the materials at steady state conditions. Kirchheim's data, the current set of data, and the data of El-Basiouny [El-Basiouny 1976] closely correspond in trends if not in absolute values, indicating that the trends obtained in the current study are accurate.

For the 0, 5 and 7.5 wt% Cr, Fe-Cr alloys in the 0.5 M H$_2$SO$_4$ electrolyte oscillatory behaviour in the current density was observed as the critical potential was approached. The potential at which the onset of passivity occurred, $E_{ps}$, was not an easily reproducible value, but varied by as much as 0.2 - 0.3 V from one experiment to the next. The oscillation frequency was $\sim$ 2 Hz. The oscillatory behaviour of the current density is a well known phenomenon, first documented by Franck [Franck 1961]. This behaviour was examined by other researchers [Epelboin 1977, Sato 1981, Russel 1983], who attributed it to mass transfer limitations. Epelboin showed that, at a given potential in the regime where
the oscillations occur, the electrode could be either in the active or the passive state as a result of a Z-shaped polarisation curve. A schematic of such a curve is shown in figure [5.10.11]. Evaluation of the full Z-shaped polarisation characteristics is not possible using a conventional potentiostat, but requires a device with a variable load line.

Visual examination of the electrode in the potential regime where the current oscillations occurred, showed an oscillating 'wave' of passive film that could be seen with the unaided eye. The current density oscillated in unison with the surface fraction of the specimen covered by the passive film. As the critical potential was approached, the 'wave' covered progressively more and more of the surface, until one oscillation of the 'wave' reached the edges of the specimen and the specimen abruptly passed from the active state with a current density nearly 1 A/cm², to the passive state with a current density ~ 1 x 10⁴ A/cm². This observation is very important, as it visually demonstrates that the onset of passivity is characterized by the formation of a film.

Certain aspects of the polarisation behaviour of the pure elements can be observed to persist in the polarisation behaviour of the alloys. Examples include breakdown and subsequent repassivation to form a secondary passive regime that is observed in all the electrolytes investigated. This breakdown/repassivation corresponds to the regime where Cr dissolves transpassively, while Fe is still in the passive state. An example of this type of behaviour can be seen in figure [5.10.5]. The breakdown/repassivation behaviour is in accordance with what is expected from thermodynamic arguments, as has been discussed in §[3.1.] and §[3.2.2.]. The observed 'double' passivity is also described by Heumann for alloys above 11 wt% Cr [Heumann 1963]. From the experimental work described here, it is clear that it also occurs in alloys containing less Cr than this amount.

5.6.3. Cathodic polarisation scans

Cathodic polarisation diagrams of the 15 wt%, 30 wt%, pure Cr as well as for a gold electrode in the pH 4 solution is shown in figure [5.10.12]. As can be seen, the electrodes all exhibit a diffusion limited current density for the oxygen reduction reaction on the order of 2.5 x 10⁻⁴ A/cm². The diffusion limited current density for all the alloys do not differ
substantially from that on a gold electrode. The value of the diffusion limited current density in the pH 4 solution, under natural convection, corresponds closely to the value for the diffusion limited oxygen current density as determined by Hihara on a gold electrode in a neutral sulphate medium [Hihara 1989].

The results show that the whole surface of all the electrodes investigated are catalytically active for the cathodic oxygen reduction reaction. A value of \( i_{\text{ox, diff}} \) close to that on gold is expected, since the passive films on iron is electronically conductive [Faraday 1965], and it is thus possible for the reaction to be supported on the entire surface. In this respect the films on Fe-Cr alloys differ from, for instance, the aluminium passive film, which is non-conductive. For aluminium the passive film is only catalytically active for the cathodic oxygen reaction at flaws [Hihara 1989]. As a result, the observed diffusion limited current density is typically more than an order of magnitude lower on aluminium than on a gold electrode.

The anodic loops in the cathodic polarisation behaviour of the 15% alloy shown in figure [5.10.12.], can be attributed to multiple intersection of the cathodic reaction with the anodic characteristics of the alloy. In these potential regimes the anodic dissolution current of the alloy exceeds the oxygen reduction reaction current. In the case of the 30% alloy, as well as the pure Cr, there is no cathodic loop, because there is only one intersection with the anodic characteristic. In these cases the anodic dissolution current of the alloy never exceeds the oxygen reduction reaction current. Note, however, the decrease in the cathodic current density in the case of the 30 wt% alloy in the potential regime where the 15% alloy exhibits a net anodic current. It can be seen that the anodic process here, severely lowers the observed total cathodic current, giving rise to the 'backwards bending' of the cathodic curve for this alloy in this potential regime.

It can be confirmed that the observed loops are in fact due to the anodic and cathodic half reactions intersecting. This confirmation can be made by synthesizing a composite curve from the known anodic characteristic of the material under interest and the cathodic reaction on a surface that only serves to catalyse the cathodic oxygen reduction reaction. A clean polished gold surface was used in the experiments presented, and is an example of such a
catalytic surface. Note that the synthesized curve will differ somewhat from the experimental curve obtained for the following reasons: (i) The passive film on the alloy will be reduced while the scan is conducted, thus giving additional processes that contribute to the experimentally observed behaviour. (ii) The kinetic characteristics for the oxygen reduction reaction on the alloy under interest in the non-diffusion limited regime may not be the same as that on a gold electrode. Examples of the latter parameters are the exchange current density for the oxygen reaction on gold versus the exchange current density on the alloy, and differences in the Tafel slopes for the reaction on the gold and on the alloy.

Figure [5.10.13.] is an overlay of the cathodic polarisation diagram of gold with the anodic characteristics of the other alloys in the pH 4 solution. It can be seen that the cathodic curve for gold intersects the curve for the 12.5 wt% alloy in 2 places. The nett current that will flow is synthesized by subtracting the cathodic current (when the gold electrode is cathodically polarised) from the anodic dissolution current of the alloy. This synthesis is shown in figure [5.10.14.]. As can be seen, anodic loops and other characteristics similar to the experimentally observed phenomenon are present, confirming that the loops are indeed cathodic loops formed when the magnitude of the oxygen reduction reaction exceeds the anodic dissolution reaction.

5.6.4. Open circuit measurements

The results from the open circuit measurements over a period of twenty four hours are shown in figures [5.10.15.] to [5.10.18.]. As can be seen from these graphs some alloys required considerable time to reach a pseudo steady state corrosion potential. In tables [5.9.7.] to [5.9.10.] the regime in which each of the alloys stabilize in the aerated media are tabulated. The wt% Cr at which the material will settle in the stable passive regime in an aerated solution becomes lower as the pH of the solution increases. In the acid solution, only pure Cr is spontaneously passive. For the pH 4 solution the 30 wt% Cr alloy also spontaneously passivates. As the pH is further increased to pH 6 the 15 wt% Cr alloy also passivates. At pH 8.6, even pure Fe passivates spontaneously.
The 12.5 wt% Cr alloy closely corresponds to the amount of Cr that is often quoted as 'critical' in the literature, and the open circuit characteristics of this alloy therefore merit special attention. A 12.5 wt% Cr alloy will corrode actively in the acid and pH 4 electrolytes, and is still in the active corrosion regime at pH 6, although corroding slowly. This alloy only passivates when the pH is increased to 8.6. Addition of 12.5 wt% Cr to Fe is therefore not enough to confer spontaneous passivity in acidified solutions.

5.7. Discussion

The discussion of the DC polarisation results and the open circuit corrosion potential measurements will be limited mainly to the acid and the acidified pH 4 and pH 6 electrolytes. The data in the acidic electrolytes are the pertinent results to be examined when the validity of present models for passivity in the Fe-Cr system are investigated. The experimental results for the borate electrolyte and hydroxide electrolyte are also briefly presented in this chapter for the sake of completeness. The results in the neutral borate media will be referred to extensively when comparisons with the AC measurements in §[6.] and with the photoelectrochemical results in §[7.] are made.

5.7.1. Effect of Cr on the $i_{\text{crit}}$ and $E_{\text{crit}}$

Two of the most important parameters dictating the ease with which an alloy may be passivated are the critical current density, $i_{\text{crit}}$, and the critical potential, $E_{\text{crit}}$. The effect of Cr addition on these parameters is therefore of great importance. The change in these parameters will now be examined for the different electrolytes investigated.

The change in $E_{\text{crit}}$ is, for the alloys investigated, a pronounced function only of the wt% Cr in the alloy in the acid solution. In all other solutions investigated, the $E_{\text{crit}}$ value is only weakly affected by the addition of Cr. These trends are summarised in tables [5.9.3.] to [5.9.6.]. It can also be visually seen in figures [5.10.5.] to [5.10.9.]. The shifting of the potential $E_{\text{crit}}$ is therefore only important in the very acidic electrolytes. The change in the critical current density $i_{\text{crit}}$ is very pronounced in the acidified solutions. The results of polarisation studies in the acid, as shown in figure [5.10.5.] and table [5.9.3.] show that
the addition of 30 wt% Cr to Fe reduces the value of $i_{\text{crit}}$ by two orders of magnitude, while it is shown in figure [5.10.6.] and table [5.9.4.] that in the pH 4 solution a decrease in $i_{\text{crit}}$ of four orders of magnitude results. In the near neutral borate, addition of 30 wt% Cr decreases $i_{\text{crit}}$ by less than one order of magnitude.

Figure [5.10.19.] shows corrosion rates in mm/year versus potential for the 0.5 M H$_2$SO$_4$ solution. Since the corrosion rate is directly proportional to the corrosion current, these plots represent plots of potential versus linear corrosion current, as compared to the Evans plot which plots potential versus log corrosion current. On these 'linear plots', the extent to which Cr extends the range where the corrosion rate is smaller than an arbitrary cut-off point, is even more visible than on the Evans plots.

The nett effect of the Cr addition is therefore to increase the ease with which the alloys are passivated, by decreasing both the critical potential $E_{\text{crit}}$ (especially in acid solutions), as well as the critical current density, $i_{\text{crit}}$.

5.7.2. Cathodic reaction responsible for passivity

In §[2.2.] it was pointed out that in the absence of other oxidizers, the cathodic hydrogen reaction or the the cathodic oxygen reaction is responsible for raising the potential of the corroding electrode into the passive regime. It was shown that the limiting point that must be overcome in order to induce passivity, $E_{\text{crit}}$, may be situated in a regime where: (i) the cathodic hydrogen reaction (ii) the cathodic oxygen reduction reaction in the non-diffusion limited regime or (iii) the cathodic oxygen reduction reaction in the diffusion limited regime is the reaction supplying the majority of the cathodic component. The next discussion will focus on elucidating which of the cathodic reactions is controlling for the Fe-Cr alloy system in the electrolytes investigated, since this is of paramount importance.

In figure [5.10.5.] it is clear that all the alloys corrode, under deaerated conditions, in the active regime when immersed in the 0.5 M sulphuric acid solution. It can most easily be seen that the alloys are actively corroding, by noting that the alloys exhibit a well defined active to passive transition, when polarisation is initiated from the corrosion potential. It is
concluded, therefore, that in the acid electrolytes, case (i) above does not hold, and that in the acidic electrolytes the cathodic oxygen reaction is necessary for spontaneous passivity. Case (ii) or (iii) as defined above is therefore, in the absence of additional oxidizers, the only possible reactions for establishing a corrosion potential in the passive regime for Cr concentrations of up to 30 wt%.

The result that the hydrogen reaction alone is not enough to stably passivate Fe-Cr alloys of up to 30 wt% Cr, is also confirmed by studies of cathodically modified alloys. For these alloys, noble metal additions that boost the hydrogen reaction kinetics are required to stably passivate a 40 wt% Fe-Cr alloy in acidic media [Higgenson 1989], and also by polarisation studies carried out on a 24 wt% Cr Fe-Cr alloy [Frankenthal 1967] that showed that two open circuit potentials exist, one in the active and one in the passive regime. It is also confirmed by the work of Moffat [Moffat 1989], which showed that pure Cr in a sulphuric acid solution shows two open circuit potentials. The latter two cases indicate an intersection of the anodic and cathodic characteristics of the form of the unalloyed Cr showed in figure [2.4.3.]. For the alloys with less than 30 wt% Cr, where case (i) holds, the critical current density is therefore in all cases higher than the cathodic hydrogen reaction can sustain.

From the cathodic polarisation studies conducted, it is concluded that in cases (ii) and (iii), the maximum cathodic process that can be sustained is equivalent to $2.5 \times 10^{-4}$ A/cm$^2$, the diffusion limited current density for the oxygen reduction reaction. Therefore, if situation (ii) or (iii) holds, and the critical current density is greater than $2.5 \times 10^{-4}$ A/cm$^2$, the material will not spontaneously passivate. Since it has been showed that situation (ii) or (iii) does hold in the acidified electrolytes it is concluded that the alloys will not be spontaneously passive unless the critical current density is less than $-2.5 \times 10^{-4}$ A/cm$^2$.

Because oxygen has no effect on the anodic characteristic of Fe-Cr alloys [Stokkers 1983, Greene 1960], the anodic characteristic of the material may be measured under deaerated conditions, and the corrosion potential in the aerated solution superimposed on this curve, in order to identify the regime in which the material will be under aerated conditions. These open circuit measurements can then be used to validate the postulation that the alloys will

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only passivate when the oxygen reduction reaction current density exceeds the anodic
dissolution current at $i_{\text{crit}}$. The corrosion potential experiments, summarised in tables
[5.9.7.] to [5.9.10.] show that in the acidic media greater than 30 wt% Cr is needed to
ensure spontaneous passivation, since all the measured corrosion potentials in both the
aerated and deaerated acid solution is situated in the active corrosion regime. It is therefore
concluded that the Fe-Cr alloys in acidified solutions require the cathodic oxygen reduction
reaction in order to passivate, and that the cathodic hydrogen reaction alone is not sufficient
to ensure spontaneous passivity. It has been shown that in acidified solutions, an Fe-Cr
alloy will only passivate when the critical anodic current density is lower than $\sim 2.5 \times 10^{-4}$
A/cm$^2$. The results indicate that in the acid solution, even 30 wt% Cr is not enough to
cause passivity under aerated conditions, and that a 12 wt% Cr, Fe-Cr alloy will thus not be
spontaneously passive under these conditions.

5.8. Conclusions

5.8.1. Validity of the d-orbital model

If one considers the original work of King and Uhlig [King 1959, Uhlig 1958] in which an
explanation of the critical %Cr is attributed to d-orbital configurations, it is clear that the
'critical' transition described is for neutral aerated media only. From later publications by
Uhlig [Uhlig 1961], it is clear that the author was well aware that a critical wt% Cr exists
for every pH which is also borne out by the experimental data presented in this document.

Uhlig originally tried to explain this observed phenomenon, namely that a different critical
%Cr exists for each pH, by a model that could at best explain behaviour at a single pH,
namely at pH 7. In the discussion in §[5.7.2.], it was shown that the spontaneous
passivity of the alloys in the Fe-Cr system is usually associated with the oxygen cathodic
reduction reaction. The limiting current density of this reaction places, in the majority of
cases, the limitation on which alloys will passivate, and which alloys will not. The
magnitude of this reaction is diffusion limited, with the kinetics on the catalysing surface
(in our case the passive film), not rate controlling. The diffusion limiting current density,
provided that the catalysing surface is electronically conductive, is normally a function of
the hydrodynamic conditions only. Figure [5.10.12] shows that the diffusion limited oxygen reduction reaction current density is the same on gold than it is on Fe-Cr alloys containing 15 and 30 wt% Cr respectively. Under the experimental conditions, the diffusion limiting current density is, therefore, only a function of the hydrodynamic conditions, and not of the %Cr in the alloy.

The Uhlig explanation of a critical transition is by electronic theory of the catalysing surface. The above discussion clearly illustrates that the dissolution current of the anodic reaction is only one half of the explanation, because, as has been shown in the preceding discussion, the magnitude of the balancing cathodic half reaction is just as important. It is not clear how a model like the d-orbital model makes a perceived 'critical' transition more understandable by implicitly relating the electronic structure of the catalysing surface to a hydrodynamically controlled parameter, namely, the diffusion limited oxygen reduction reaction current density. As has been shown, the diffusion limited oxygen reduction reaction current density is the controlling reaction, and is not in any way related to the properties of the catalysing surface, provided that the diffusional step is the slow reaction step. It can therefore only be concluded that the electronic configuration model of passivity in the Fe-Cr alloy system is not convincing as a possible explanation.

5.8.2. Validity of the percolation model

Sieradzki and Newman [Sieradzki 1986], in their percolation model, try to predict a critical transition at ~12 wt% Cr. In order to do this, they considered the passivation potential data of Kolotyrkin which is shown in figure [5.10.20.] [Kolotyrkin 1977]. The latter data set was generated in 0.1 N H₂SO₄, and shows a large change in the passivation potential Eₚₚ. This large change in Eₚₚ was shown in §[5.7.1.] to occur only in acid electrolytes. In their experimental confirmation [Newman 1988], in which the experiments were carried out in 1 M H₂SO₄ it would seem that the percolation model tries to predict a critical transition at 12 wt% in acidic solutions, or for electrolytes also including acidic electrolytes. It is therefore concluded that Sieradzki and Newman try to predict a critical transition at 12 wt% in an acidic medium, or in dilute solutions including acidic media, and that they base their model for a critical transition on the large change in Eₚₚ at ~ 12 wt% in acid solutions.
The ~ 12 wt% transition they try to predict, is in fact a special case in pH 7 media only as was shown by Uhlig [Uhlig 1961], and also by the results of the present investigation. A critical transition from active corrosion at lower than 12 wt%, to spontaneous passivation at greater than 12 wt% does not occur in the acidic electrolytes that they use for their investigation, as is clearly evident from figures [5.10.5] and [5.10.15], where it is shown that a 12.5 wt% Cr, Fe-Cr alloy corrodes actively in the absence and presence of oxygen. Because the critical wt% Cr for passivity in aerated media varies with pH as has been indicated above, the percolation model has a parameter, namely the number of neighbours the Cr atoms should be removed from each other in order to still ensure passivity, that will vary as the pH of the media is varied. The usefulness of this model, that unsuccessfully tries to model a critical phenomenon that as has been shown in §[5.7.2.] and as will be shown in §[7.7.2.] does not exist, is doubtful.

In the experimental modelling of dissolution by this mechanism [Qian 1990], Qian and Sieradzki again state that they are trying to model dissolution in acidic media. In this model, two dimensional percolation with a percolation threshold \( p(1,2) = 41.5\% \) is investigated. In the latter paper the authors introduce two new variables, the probability of dissolution of Cr, \( q_{\text{diss}}(\text{Cr}) \), and the probability of dissolution of Fe, \( q_{\text{diss}}(\text{Fe}) \). These parameters are intended to simulate the difference in corrosion rates of the elemental constituents, Fe and Cr, in those potential regimes where the one component is passive while the other is actively corroding. The requirements are schematically illustrated in figure [5.10.21.] taken from the paper by Qian. These two slack parameters, however, can be manipulated to give a critical transition at whatever wt% Cr desired.

It is well known that potential regimes in which the above requirement are met, are present in the anodic polarisation of Fe and Cr. A potential regime such as this, is shown in the data presented in this current study, see for example figure [5.10.5.] between -0.4 and 0.5 V versus SCE, where Cr is passive, but Fe not. The data of Kolotyrkin shown in figure [5.10.22.] illustrates the same between -0.2 and 0.5 V versus NHE. Both Okamoto and Kolotyrkin stated in the 1970’s that the element that has the smallest corrosion rate under the conditions of interest can be expected to enrich in the passive film [Okamoto
1973, Kolotyrkin 1977]. This enrichment has also recently been experimentally illustrated by Kirchheim who examined enrichment of Cr in Fe-Cr alloys [Kirchheim 1989]. What distinguishes the percolation model of Newman and Sieradzki, however, from the earlier work of Okamoto, Kolotyrkin and other workers, is that the percolation model takes the rationale one step further, and tries to use the differential solubility of the constituent elements in order to predict the perceived critical threshold in the corrosion behaviour of Fe-Cr alloys by means of an enrichment model. It is the latter result that the present investigation calls into question.

At the present level of reasoning, the percolation model therefore holds no more information that has not been known for a long time, namely that the critical transition in pH 7 solutions takes place at a lower wt% Cr than is necessary for the Cr atoms to touch [Tamman 1928]. Touching of Cr atoms corresponds to nearest neighbour percolation. The percolation model does not take into account that the alloy polarisation curve cannot be synthesized from the constituent element polarisation curves even if enrichment is taken into account [Steigerwalt 1962], and that some perturbation effects must be included [Keddam 1986]. The latter experimental evidence implies that there is some chemical effects of mixing, so that the atoms can not be considered as mere hard balls. It was shown that the basis for the threshold that the percolation model tries to predict is wrong. It will also be shown in §[7.] that the results from the photoelectrochemical experiments carried out as part of this investigation do not support a critical transition by a percolation mechanism at 12 wt% Cr, in agreement with the conclusions reached from the DC polarisation data presented here.

5.8.3. New thoughts on passivity in the Fe-Cr system

From the experimental data, and bearing in mind the criticisms of the models presented above, it is concluded that a discontinuity in the corrosion behaviour of Fe-Cr alloys does not exist. This view has also recently been expressed by Kirchheim [Kirchheim 1989], who found that Cr enriched in passive films even at very low wt% Cr in the bulk alloy. Also the recent work of Calinski [Calinski 1989] with ion scattering spectroscopy has indicated that the amount of Cr in the passive film is a linear function of the amount of Cr in
the base alloy, and that no critical Cr concentration was found. It will also be shown in §[7.] that the photoelectrochemical investigation carried out as part of this current research confirms that no discontinuity in the Fe concentration in the passive film occurs at 12.5 wt% Cr.

The only easily characterizable parameter which shows a significant discontinuity at 12 wt% Cr is the passivation potential $E_{ps}$. The change in the potential at which the passivity starts, is clearly visible in figure [5.10.5.]. Note, however, that this discontinuous behaviour is only observed in very acidic electrolytes; no such discontinuity exists in pH 4 or pH 6 electrolytes, as can be seen in figures [5.10.6.] and [5.10.7.]. Although the $E_{ps}$ for the alloy system, as considered by Kolotyrkin [Kolotyrkin 1977] and subsequently Sieradzki and Newman [Sieradzki 1986] is one important parameter in determining the ease with which the system can be passivated, other parameters such as the critical current density $E_{crit}$ and also the relevant cathodic half reaction, are as important. This has also been pointed out in the discussion of experimental results in §[5.7.1.] and §[5.7.2.],

From the polarisation and open circuit data presented, it is evident that for Fe-Cr alloys with less than 30 wt% Cr, the cathodic oxygen reduction reaction is responsible for establishing the corrosion potential in the passive regime in acidified electrolytes. The critical current density/critical potentials for alloys containing less than 30 wt% Cr, is such that spontaneous passivation in acidic media by the cathodic hydrogen reaction alone is not possible. Because $E_{corr} > E_{crit}$ for stable passivity, an Fe-Cr alloy will, therefore, only achieve spontaneous stable passivity in an aqueous aerated electrolyte if the prevailing cathodic reaction on the surface of the specimen under interest has sufficient driving force to exceed the current density along each point of the anodic characteristic of the material, up to the corrosion potential. In practice the cathodic reaction is usually the oxygen reduction reaction. In natural convection this implies that only for $i_{crit} < i_{oxdiff} = 2.4 \times 10^{-4}$ A/cm$^2$, can the alloy passivate spontaneously.
The critical wt% Cr for stable passivity is therefore a function of surface pre-treatment, degree of agitation, oxygen partial pressure in the system, microstructure of the specimen, etc. The observed 12 wt% transition is the wt% Cr in a neutral media at which the critical current density of an Fe-Cr alloy is approximately equal to the diffusion limited oxygen reduction reaction.
5.9. Tables - DC and open circuit measurements
Nominal analysis of the materials investigated.

<table>
<thead>
<tr>
<th>Alloy #:</th>
<th>Aim analysis</th>
<th>Actual analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt% Fe</td>
<td>wt % Cr</td>
</tr>
<tr>
<td>1</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>95.0</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>92.5</td>
<td>7.5</td>
</tr>
<tr>
<td>4</td>
<td>90.0</td>
<td>10.0</td>
</tr>
<tr>
<td>5</td>
<td>87.5</td>
<td>12.5</td>
</tr>
<tr>
<td>6</td>
<td>85.0</td>
<td>15.0</td>
</tr>
<tr>
<td>7</td>
<td>70.0</td>
<td>30.0</td>
</tr>
<tr>
<td>8</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table [5.9.1.] Nominal analysis of the materials investigated.
<table>
<thead>
<tr>
<th>Element</th>
<th>Level (at. ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>60</td>
</tr>
<tr>
<td>N₂</td>
<td>24</td>
</tr>
<tr>
<td>O₂</td>
<td>48</td>
</tr>
<tr>
<td>Na</td>
<td>0.2</td>
</tr>
<tr>
<td>Mg</td>
<td>0.07</td>
</tr>
<tr>
<td>Si</td>
<td>12</td>
</tr>
<tr>
<td>S</td>
<td>1</td>
</tr>
<tr>
<td>Cl</td>
<td>0.06</td>
</tr>
<tr>
<td>K</td>
<td>0.2</td>
</tr>
<tr>
<td>Ca</td>
<td>0.4</td>
</tr>
<tr>
<td>Ti</td>
<td>0.3</td>
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<tr>
<td>V</td>
<td>4</td>
</tr>
<tr>
<td>Fe</td>
<td>18</td>
</tr>
<tr>
<td>Ni</td>
<td>3</td>
</tr>
<tr>
<td>Cu</td>
<td>8</td>
</tr>
<tr>
<td>As</td>
<td>0.2</td>
</tr>
<tr>
<td>Y</td>
<td>0.5</td>
</tr>
<tr>
<td>Zr</td>
<td>0.2</td>
</tr>
<tr>
<td>Mo</td>
<td>0.1</td>
</tr>
<tr>
<td>Cd</td>
<td>0.07</td>
</tr>
<tr>
<td>Sb</td>
<td>0.7</td>
</tr>
<tr>
<td>Ba</td>
<td>0.1</td>
</tr>
<tr>
<td>W</td>
<td>70</td>
</tr>
<tr>
<td>Th</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table [5.9.2.] Solid Source Mass Spectroscopic Analysis of Cr [Cotell 1988].
These alloys also exhibited a secondary passive regime.

The potential for the onset of the main passive region was taken for these alloys.

Table [5.9.3.] Parameters for anodic scans in 0.5 M H₂SO₄.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>E_{crit}</th>
<th>i_{crit}</th>
<th>E_{ps}</th>
<th>E_{pe}</th>
<th>i_{pass}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.25</td>
<td>3.66×10⁻¹</td>
<td>0.50</td>
<td>&gt;1.5</td>
<td>4.90×10⁻⁵</td>
</tr>
<tr>
<td>5</td>
<td>0.35</td>
<td>3.54×10⁻¹</td>
<td>0.50</td>
<td>1.00</td>
<td>2.19×10⁻⁵</td>
</tr>
<tr>
<td>7.5</td>
<td>0.10</td>
<td>1.49×10⁻¹</td>
<td>0.50</td>
<td>1.00</td>
<td>4.79×10⁻⁵</td>
</tr>
<tr>
<td>10</td>
<td>-0.30</td>
<td>6.50×10⁻²</td>
<td>0.20</td>
<td>1.00</td>
<td>3.16×10⁻⁵</td>
</tr>
<tr>
<td>12.5</td>
<td>-0.35</td>
<td>5.37×10⁻²</td>
<td>0.20</td>
<td>1.00</td>
<td>1.58×10⁻⁵</td>
</tr>
<tr>
<td>15</td>
<td>-0.38</td>
<td>2.99×10⁻²</td>
<td>0.20</td>
<td>1.00</td>
<td>9.55×10⁻⁶</td>
</tr>
<tr>
<td>30</td>
<td>-0.48</td>
<td>8.51×10⁻³</td>
<td>-0.30</td>
<td>1.00</td>
<td>6.31×10⁻⁶</td>
</tr>
<tr>
<td>100</td>
<td>-0.58</td>
<td>5.75×10⁻³</td>
<td>-0.40</td>
<td>1.00</td>
<td>3.63×10⁻⁶</td>
</tr>
</tbody>
</table>

† These alloys exhibited a secondary passive regime.

‡ The potential for the onset of the main passive region was taken for these alloys.

Table [5.9.4.] Parameters for anodic scans in pH 4, 0.5 M H₂SO₄+0.5 M Na₂SO₄.
These alloys exhibited a poorly defined secondary passive regime, which grew more pronounced as the \%Cr increased. \( E_{\text{pe}} \) potentials reported are those at the end of this poorly defined secondary passive regime.

**Table [5.9.5.]** Parameters for anodic scans in pH 8.6, 0.1 \( \text{M} \) \( \text{H}_2\text{BO}_3 \)+0.1 \( \text{M} \) \( \text{Na}_2\text{B}_4\text{O}_7 \).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( E_{\text{crit}} )</th>
<th>( i_{\text{crit}} )</th>
<th>( E_{\text{ps}} )</th>
<th>( E_{\text{pe}} )</th>
<th>( i_{\text{pass}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.70</td>
<td>2.45\times10^{-5}</td>
<td>-0.70</td>
<td>0.90</td>
<td>5.25\times10^{-6}</td>
</tr>
<tr>
<td>5</td>
<td>-0.70</td>
<td>1.29\times10^{-5}</td>
<td>-0.70</td>
<td>0.90</td>
<td>5.01\times10^{-6}</td>
</tr>
<tr>
<td>7.5</td>
<td>-0.70</td>
<td>1.07\times10^{-5}</td>
<td>-0.70</td>
<td>0.90</td>
<td>4.90\times10^{-6}</td>
</tr>
<tr>
<td>10</td>
<td>-0.70</td>
<td>9.33\times10^{-6}</td>
<td>-0.70</td>
<td>0.90</td>
<td>4.79\times10^{-6}</td>
</tr>
<tr>
<td>12.5</td>
<td>-0.70</td>
<td>8.51\times10^{-6}</td>
<td>-0.70</td>
<td>0.90</td>
<td>4.37\times10^{-6}</td>
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<tr>
<td>15</td>
<td>-0.70</td>
<td>7.59\times10^{-6}</td>
<td>-0.70</td>
<td>0.90</td>
<td>4.27\times10^{-6}</td>
</tr>
<tr>
<td>30</td>
<td>-0.70</td>
<td>5.13\times10^{-6}</td>
<td>-0.70</td>
<td>0.90</td>
<td>4.17\times10^{-6}</td>
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<tr>
<td>100</td>
<td>(&lt; E_{\text{corr}} )</td>
<td>(&lt; E_{\text{corr}} )</td>
<td>0.25</td>
<td>3.72\times10^{-6}</td>
<td></td>
</tr>
</tbody>
</table>

\( \dagger \) These alloys exhibited a poorly defined secondary passive regime, which grew more pronounced as the \%Cr increased. \( E_{\text{pe}} \) potentials reported are those at the end of this poorly defined secondary passive regime.

**Table [5.9.6.]** Parameters for anodic scans in 0.1 \( \text{NaOH} \).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( E_{\text{crit}} )</th>
<th>( i_{\text{crit}} )</th>
<th>( E_{\text{ps}} )</th>
<th>( E_{\text{pe}} )</th>
<th>( i_{\text{pass}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.90</td>
<td>1.29\times10^{-5}</td>
<td>-0.90</td>
<td>0.60</td>
<td>4.37\times10^{-6}</td>
</tr>
<tr>
<td>5</td>
<td>-0.90</td>
<td>1.20\times10^{-5}</td>
<td>-0.90</td>
<td>0.60</td>
<td>5.75\times10^{-6}</td>
</tr>
<tr>
<td>7.5</td>
<td>-0.90</td>
<td>1.17\times10^{-5}</td>
<td>-0.90</td>
<td>0.60</td>
<td>5.13\times10^{-6}</td>
</tr>
<tr>
<td>10</td>
<td>-0.90</td>
<td>6.92\times10^{-6}</td>
<td>-0.90</td>
<td>0.60</td>
<td>6.03\times10^{-6}</td>
</tr>
<tr>
<td>12.5</td>
<td>-0.90</td>
<td>1.12\times10^{-5}</td>
<td>-0.90</td>
<td>0.60</td>
<td>6.31\times10^{-6}</td>
</tr>
<tr>
<td>15</td>
<td>-0.90</td>
<td>8.91\times10^{-6}</td>
<td>-0.90</td>
<td>0.60</td>
<td>6.31\times10^{-6}</td>
</tr>
<tr>
<td>30</td>
<td>-0.90</td>
<td>6.17\times10^{-6}</td>
<td>-0.90</td>
<td>0.60</td>
<td>5.50\times10^{-6}</td>
</tr>
<tr>
<td>100</td>
<td>(&lt; E_{\text{corr}} )</td>
<td>(&lt; E_{\text{corr}} )</td>
<td>0.00</td>
<td>3.16\times10^{-6}</td>
<td></td>
</tr>
</tbody>
</table>

\( \dagger \) These alloys exhibited a poorly defined secondary passive regime, which grew more pronounced as the \%Cr increased. \( E_{\text{pe}} \) potentials reported are those at the end of this poorly defined secondary passive regime.
### Table [5.9.7.] Open circuit potentials in 0.5 M H₂SO₄.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>E\textsubscript{corr}</th>
<th>E\textsubscript{ps}</th>
<th>Regime</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>-0.76</td>
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<tr>
<td>5</td>
<td>-0.69</td>
<td>0.30</td>
<td>active</td>
</tr>
<tr>
<td>7.5</td>
<td>-0.69</td>
<td>0.15</td>
<td>active</td>
</tr>
<tr>
<td>10</td>
<td>-0.68</td>
<td>0.15</td>
<td>active</td>
</tr>
<tr>
<td>12.5</td>
<td>-0.54</td>
<td>0.15</td>
<td>active</td>
</tr>
<tr>
<td>15</td>
<td>-0.48</td>
<td>0.15</td>
<td>active</td>
</tr>
<tr>
<td>30</td>
<td>-0.20</td>
<td>-0.40</td>
<td>active</td>
</tr>
<tr>
<td>100</td>
<td>0.02</td>
<td>-0.40</td>
<td>passive</td>
</tr>
</tbody>
</table>

### Table [5.9.8.] Open circuit potentials in pH 4, 0.5 M H₂SO₄+0.5 M Na₂SO₄.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>E\textsubscript{corr}</th>
<th>E\textsubscript{ps}</th>
<th>Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.51</td>
<td>0.50</td>
<td>active</td>
</tr>
<tr>
<td>5</td>
<td>-0.51</td>
<td>0.50</td>
<td>active</td>
</tr>
<tr>
<td>7.5</td>
<td>-0.50</td>
<td>0.20</td>
<td>active</td>
</tr>
<tr>
<td>10</td>
<td>-0.50</td>
<td>0.20</td>
<td>active</td>
</tr>
<tr>
<td>12.5</td>
<td>-0.54</td>
<td>0.20</td>
<td>active</td>
</tr>
<tr>
<td>15</td>
<td>-0.50</td>
<td>0.20</td>
<td>active</td>
</tr>
<tr>
<td>30</td>
<td>-0.53</td>
<td>-0.30</td>
<td>active</td>
</tr>
<tr>
<td>100</td>
<td>0.02</td>
<td>-0.40</td>
<td>passive</td>
</tr>
</tbody>
</table>
Table [5.9.9.]
Open circuit potentials in pH 6, 0.5 M H₂SO₄+0.5 M Na₂SO₄.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Eₜₚ₀</th>
<th>Eₜₚₐ</th>
<th>Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>-0.65</td>
<td>0.40</td>
<td>active</td>
</tr>
<tr>
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<td>-0.59</td>
<td>0.10</td>
<td>active</td>
</tr>
<tr>
<td>12.5</td>
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<td>0.10</td>
<td>active</td>
</tr>
<tr>
<td>15</td>
<td>-0.42</td>
<td>0.10</td>
<td>active</td>
</tr>
<tr>
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<td>-0.21</td>
<td>-0.65</td>
<td>passive</td>
</tr>
</tbody>
</table>

Table [5.9.10.]
Open circuit potentials in pH 8.6, 0.1 M H₃BO₃+0.1 M Na₂B₄O₇.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Eₜₚ₀</th>
<th>Eₜₚₐ</th>
<th>Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>-0.70</td>
<td>passive</td>
</tr>
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<td>-0.24</td>
<td>-0.70</td>
<td>passive</td>
</tr>
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<td>7.5</td>
<td>-0.30</td>
<td>-0.70</td>
<td>passive</td>
</tr>
<tr>
<td>10</td>
<td>-0.20</td>
<td>-0.70</td>
<td>passive</td>
</tr>
<tr>
<td>12.5</td>
<td>-0.21</td>
<td>-0.70</td>
<td>passive</td>
</tr>
<tr>
<td>15</td>
<td>-0.23</td>
<td>-0.70</td>
<td>passive</td>
</tr>
</tbody>
</table>
5.10. Figures - DC and open circuit measurements
Figure [5.10.1.] Iron-chromium phase diagram [Ageev 1962].
Electrode design for DC, open circuit and impedance measurements.

Figure [5.10.2.]
Figure [5.10.3.] Schematic diagram of the electrochemical cell used
Figure [5.10.4.] Scan rate dependence of the anodic behaviour of Cr in 1 N sulphuric acid, 30°C [Moffat 1989].
Anodic polarisation characteristics for 5-30 wt% Cr, Fe-Cr alloys, Cr and Fe in 0.5 M H$_2$SO$_4$ at 30 °C. Scan rate 1 mV/s.
Figure [5.10.6.] Anodic polarisation characteristics for 5-30 wt% Cr, Fe-Cr alloys, Cr and Fe in pH 4, 0.5 M H₂SO₄+0.5 M Na₂SO₄ at 30 °C. Scan rate 1 mV/s.
Figure [5.10.7.] Anodic polarisation characteristics for 5-30 wt% Cr, Fe-Cr alloys, Cr and Fe in pH 6, 0.5 M H₂SO₄+0.5 M Na₂SO₄ at 30 °C. Scan rate 1 mV/s.
Figure [5.10.8.] Anodic polarisation characteristics for 5-30 wt% Cr, Fe-Cr alloys, Cr and Fe in a 0.1 M borate buffer at 30 °C. Scan rate 1 mV/s.
Figure [5.10.9.] Anodic polarisation characteristics for 5-30 wt% Cr, Fe-Cr alloys, Cr and Fe in 0.1 M NaOH at 30 °C. Scan rate 1 mV/s.
Figure [5.10.10.] Pseudo steady state anodic behaviour of Cr and Fe-Cr alloys in $1 \text{N} \text{H}_2\text{SO}_4$ [Kircheim 1989].
Figure [5.10.11.] Schematic current E vs i curve for Fe in 1 M H₂SO₄. a-b-c-e-f-b-a obtained by potentiostat, a-b-c-d-f-d-c-b-a obtained by a negative output resistance device [Epelboin 1977].
Figure [5.10.12.] Cathodic polarisation characteristics for 15 and 30 wt% Cr, Fe-Cr alloys, Cr and gold in pH 4, 0.5 M H₂SO₄+0.5 M Na₂SO₄ at 30 °C. Scan rate 1 mV/s.
Figure [5.10.13.]

Cathodic characteristics for Au overlaid on anodic characteristics of 10-15 wt% Cr, Fe-Cr alloys, Cr and Fe in pH 4, 0.5 M H₂SO₄ + 0.5 M Na₂SO₄ at 30 °C. Scan rate 1 mV/s.
Figure [5.10.14.] Simulated cathodic polarisation characteristics for a 12.5 wt% Cr, Fe-Cr alloy in pH 4, 0.5 M H₂SO₄+0.5 M Na₂SO₄ at 30 °C. Scan rate 1 mV/s.
Figure [5.10.15.] Corrosion potentials for 5-30 wt% Cr, Fe-Cr alloys as well as Fe in 0.5 M H₂SO₄ at 30 °C.
Figure [5.10.16.] Corrosion potentials for 5-30 wt% Cr, Fe-Cr alloys, Fe as well as Cr in pH 4, 0.5 M $\text{H}_{2}\text{SO}_{4}$+0.5 M $\text{Na}_{2}\text{SO}_{4}$ at 30 °C
Figure [5.10.17.] Corrosion potentials for 7.5-30 wt% Cr, Fe-Cr alloys in pH 6, 0.5 M H$_2$SO$_4$+0.5 M Na$_2$SO$_4$ at 30 °C
Figure [5.10.18]  Corrosion potentials for 7.5-30 wt% Cr, Fe-Cr alloys in a 0.1 M borate buffer at 30 °C.
Figure [5.10.19.] Corrosion rates for 5-30 wt% Cr, Fe-Cr alloys, as well as Fe and Cr in 0.5 M H₂SO₄ at 30 °C.
Figure [5.10.20.] Dependence of the passivation potential on the Cr content of Fe-Cr alloys. Electrolyte was 0.1 N sulphuric acid [Kolotyrkin 1977].
Figure [5.10.21.] Schematic partial anodic polarization curves for Fe and Cr, showing behaviour required by the simulations of Qian [Qian 1990].
FIGURE 1 — Anodic polarization curves for iron (1), chromium (2), and nickel (3) in 1N H₂SO₄.

Figure [5.10.22.] Anodic polarization curves for iron (1), chromium (2) and nickel (3) in 1 N H₂SO₄ [Kolotyrkin 1977].
6. IMPEDANCE MEASUREMENTS

6.1. Materials

The materials utilized for the impedance experiments were the same as those described in §[5.1.]. The electrodes were prepared in the same way as described in §[5.1.], with the exception that electrodes with a surface area of 0.2 cm² were also prepared.

6.2. Electrolytes

The testing was conducted in the 0.1 M borate buffer, prepared as described in §[5.2.]. For the purposes of this chapter, this solution will be referred to as borate.

6.3. Equipment

The electrochemical cell was the same as the unit described in §[5.3.1.], with the exception that the counter electrode consisted of a 80 mesh platinum gauze of 10 x 5 cm. For the AC frequency sweep experiments, which typically lasted for more than three days, migration of Cl⁻ ions from the reference electrode to the working electrode proved to be a problem. In order to eliminate this problem, a K₂SO₄ salt bridge arrangement was used in all of the experiments. In this arrangement the reference electrode was separated from the Luggin reservoir by means of a salt bridge consisting of a saturated K₂SO₄ solution which was gelled by means of Agar. The reference electrode itself was placed in a third compartment filled with saturated K₂SO₄. This arrangement is schematically shown in figure [6.10.1.]. The temperature controlling system was similar to that described in §[5.3.1.].

A Schlumberger Solartron® 1286 electrochemical interface (potentiostat/galvanostat) was utilized in combination with a Schlumberger Solartron® 1250 frequency response analyzer. Data output from these instruments were recorded via the GPIB interface bus of a Hewlett-Packard 9216 microcomputer. The software was written in HP Basic 3.0, and was a modification of an earlier program in use by the H. H. Uhlig laboratory. The essential modifications entailed the writing of code to automate the potential stepping and data
collection functions for the frequency sweep measurements and the potential sweep experiments without interaction from the user during operation. Routines to measure the impedance response at a single frequency during fast potential scans were also added.

Because of the greater flexibility for producing graphical hard copy of the results, the data as obtained above were transferred to an Apple Macintosh® II microcomputer. Data transfer was done via the serial ports of the two machines, using a routine of the AC impedance data acquisition program on the Hewlett-Packard 9816 Microcomputer, and a program written in Microsoft QuickBasic® on the Apple Macintosh®. The latter program is given in §[12.3.3.].

6.4. Experimental procedure

6.4.1. Frequency sweep experiments

All runs were conducted with the electrolyte deaerated/aerated for at least 30 minutes before the start of the experiment. The deaerating gas was pre-purified grade Airco® H₂. In some cases Airco® N₂ was used in place of H₂. A check for deaeration was carried out by monitoring the potential of the platinum electrode against the reference electrode in the cases that H₂ was used as deaerating gas. No differences in the electrochemical behaviour could be observed in experiments in which the only variable was the type of deaerating gas used.

The electrodes, prepared as described in §[6.1.] were polished to a 0.3 μm finish using alumina paste and Microcloth® just before the start of each experiment. Cathodic reduction of the specimen at a current density of 10 μA was carried out for a period of 1800 seconds in order to reduce the air formed film on the surface.

The excitation wave form for the impedance measurements was a sine wave of 2 V (RMS) generated by the Solartron® 1250. This wave was attenuated by a factor of 100 in the Solartron® 1286 to yield a signal of 20 mV (RMS). In this way better accuracy was obtained than if an unattenuated 20 mV signal from the Solartron® 1250 was directly utilised. The maximum number of integration cycles on the transfer function analyzer was set to 20 cycles of the fundamental frequency in order to strike a balance between accuracy
and a reasonable integration time. The relatively large excitation amplitude was necessary in order to obtain a signal of a large enough magnitude to analyse, since the current changes very little as a function of the potential in the passive regime.

After the cathodic pre-treatment, the electrode was polarised to a potential at the beginning of the passive regime. The electrode was allowed to stabilize for 3600 s, after which the data were collected at this potential. The film formation time of 3600 s was chosen on the basis of trial experiments that showed that this was a good compromise between a reasonable experimental time, while still approaching steady state conditions at every potential. At the end of 10800 s (starting the time measurement at the instant of polarisation to the potential considered), the potential was stepped in the anodic direction, and the procedure described above (stabilization followed by data collection) was repeated. This cycle was repeated until transpassivity was reached. In this way all the passive films examined had the same ‘history’. This was seen as a necessary requirement, because preliminary work showed that the environmental ‘history’ often had an important effect on the impedance results.

The Solartron® 1286 electrochemical interface uses a voltage drop technique to determine the magnitude of the current passed. This technique necessitates the use of a different resistor as the current changes. The current is a function of the impedance of the specimen, since the applied excitation is always the same, and the current and voltage applied is related through the law \( E = I \times Z \). As the impedance of the specimen changes with frequency, a different resistor may be required due to the change in current. Because the impedance of the electrode at each potential (as a function of frequency) varied over several orders of magnitude during any particular frequency sweep, it was necessary to typically employ a series of four standard resistors to measure the impedance. This changing of resistors resulted in four data sets at each frequency, which were then treated by the procedure in §[6.5.1.] to consolidate the data into a single data set.
6.4.2. Potential sweep experiments

Single frequency capacitance measurements were carried out during a potential sweep after pre-forming the passive film at different potentials and formation times. All runs were conducted with the electrolyte deaerated/aerated for at least 30 minutes before the start of the experiment. The deaerating gas was pre-purified grade Airco® H₂. In some cases Airco® N₂ was used in place of H₂. A check for deaeration was carried out by monitoring the potential of the platinum electrode against the reference electrode in the cases that H₂ was used as deaerating gas. No differences in the electrochemical behaviour could be observed in experiments in which the only variable was the deaerating gas used. The electrodes, prepared as described in §[6.1.], were polished to a 0.3 μm finish using alumina paste and Microcloth® just before the start of each experiment. Cathodic reduction of the specimen at a current density of 10 μA was carried out for a period of 1800 seconds in order to reduce the air formed film on the surface.

The excitation wave form for the impedance measurements was a sine wave of 1 V (RMS) generated by the Solartron® 1250. This wave was attenuated by a factor of 100 in the Solartron® 1286 to yield a signal of 10 mV (RMS). In this way better accuracy was obtained than if an unattenuated 10 mV signal from the Solartron® 1250 was directly utilised. The maximum number of integration cycles on the transfer function analyzer was set to 50 cycles of the fundamental frequency in order to strike a balance between accuracy and a reasonable integration time. The excitation frequency was 100 Hz in all cases because at this frequency (i) induction effects due to the cell geometry were not present, and (ii) the electrode was in the capacitive regime. Effects that may lead to a deviation from pure capacitive behaviour at high frequency are also discussed in §[6.5.1.]. Figure [6.10.2.] shows that the electrode is in the capacitive regime at 100 Hz.

After the cathodic pre-treatment, the electrode was polarised to the specified film formation potential for 300 s. At the end of this period, the potential was stepped to a potential of -0.6 V versus SCE. From this point a potential sweep at 10 mV/s was immediately initiated. The terminal potential was 0.9 V. These two potentials correspond to a potential regime where the currents for all the alloys were low enough to make the
photoelectrochemical measurements without a serious degradation in the sensitivity. During the sweep the capacity was measured every 2 s, corresponding to one measurement every 20 mV. After reaching the terminal potential, the electrode was returned to the formation potential, and kept there until 3600 s had elapsed (t=0 taken as the time at the end of the cathodic pre-treatment). At the end of this period, the potential was again stepped to a potential of -0.6 V versus SCE, and the sweep and acquisition cycle described above repeated. In this way all the passive films examined had the same 'history'. Similar 'histories' was seen as a necessary requirement, because preliminary work showed that the environmental 'history' often had an important effect on the impedance results. The relatively fast scan rate was utilised in order to prevent, as far as possible, changes in the passive film while the measurement was being carried out, while giving sufficient time to detect the impedance response via the FRA technique.

6.5. Data treatment and presentation

6.5.1. Frequency sweep experiments

Because several standard resistors were used in the course of a measurement at a single potential (see also discussion in §6.4.1.), it was necessary to combine these measurements into a single data set. Consolidation of the data sets obtained with the various resistors was done by inspecting the data visually, and selecting only the data values that fell on the continuous curve. All other values were discarded. An example of a phase angle plot of an untreated data set, consisting of the measurements as obtained by four different resistors, is shown in figure 6.10.4. This illustrates how each resistor is only accurate over a specific frequency range.

The measured impedance spectra exhibited a resistive component at high frequency. This component was attributed to the solution resistance between the Luggin capillary and the working electrode. The solution resistance was subtracted from the resistive parts of all the measurements. All subsequent treatments were conducted with this modified data set. Because the solution resistance was relatively large, due to the relatively dilute electrolyte employed, it was very difficult to correct the data values with the exact value of the solution
resistance. For this reason the best possible estimate of the solution resistance was made and the data set corrected by this value. In figure [6.10.3.] it is shown that, at high frequency, the phase angle \( \theta \) bends downwards to smaller values. This is due to the imperfectly compensated solution resistance. This effect was normally not serious and did not detract from the ability to analyse the data. The effects of imperfect solution resistance compensation are further discussed in §[6.6.1.].

Frequency sweep curves exhibited a capacitive range that typically extended over several orders of magnitude. This capacitive behaviour resulted in a series of lines that were almost parallel when presented in the conventional Bode format. Presentation of such a large amount of data (17 curves for each alloy) resulted in visual clutter, so that the individual data sets can not be discerned. As an example consider figure [6.10.2.] and [6.10.3.]. Presentation of the data on separate graphs has two drawbacks, namely: (i) A very large number of graphs are necessary (17 for each alloy tested) and (ii) The trends as a function of potential are not visible when the data are presented on separate graphs. In order to make the data presentable, and also to show the pertinent trends in the impedance behaviour as a function of potential and frequency, the reduction procedure described below was adopted. Information loss when using this procedure was minimal, and all aspects relevant to the analysis as presented in §[6.6.1.] were retained. In addition to the reduced data sets, that was used for all analyses, three dimensional representations of log\((Z)\) and phase angle as functions of the excitation frequency and electrode potential were also constructed, and are given as figures [6.10.5.] to [6.10.14.].

The Bode and phase angle plots at any specific potential in the passive regime, for the alloy system investigated, had the characteristics of the schematic diagrams shown in figures [6.10.15.] and [6.10.16.] respectively. When the Bode plot is examined, is evident that it consists of a linear, pseudo capacitive response region at high and intermediate frequencies. At lower frequencies, a deviation from linear response is observed in some cases. The corresponding phase angle plot confirms that the response at high and intermediate frequencies are pseudo capacitive, and that a resistive component which appears at low frequencies is responsible for the deviation from linear behaviour of the Bode plot.
It is well known that any straight line may be fully described by the slope and intercept of the line. To describe the linear portion of the Bode plot, only the slope and intercept of the linear portion needs to be calculated. In order to then fully characterize the complete impedance response at every frequency value in the regime where the Bode plot is linear, it is necessary to also specify the value of the phase angle, $\theta$. Because the value of the phase angle is also constant (neglecting the small distortion introduced by imperfect solution resistance compensation which, as will be shown in §[6.6.1.], is only an artifact) only this constant value of the phase angle, $\theta$, for the linear is needed in order to exactly describe the impedance behaviour in the pseudo capacitive regime.

The phase angle plot is more sensitive to the appearance of the resistive component, and will show a decreasing phase angle, indicative of the appearance of a resistive component, even when the contribution is still too small to cause visible deviation from linear behaviour of the Bode plot. It is not easy to reduce the impedance results in the regime where the response deviates from linear response in a manner analogous to the process carried out in the pseudo capacitive regime. In order to get an idea of the extent to which a resistive component is present at the lower frequencies, it is useful to plot the value of the phase angle at the low end of the frequency range employed. It will be shown that this parameter is very useful in describing the impedance behaviour. To eliminate the detrimental effect of a possible single erroneous value at the very low frequency, the parameter that was actually plotted is the average of the phase angle for the lowest five frequency values employed. The complete data treatment procedure is summarised in §[12.1.2.].

6.5.2. Potential sweep experiments

The capacitance data presented are corrected for the double layer capacitance, $C_d$, as well as the surface roughness factor, $R$. Estimates of the surface roughness factor, $R$, range between 1.6 [Stimming 1976] and 1.8 [Moshtev 1968]. A surface roughness factor of $R = 1.6$ was utilised for all capacitance data represented. Studies on platinum electrodes indicated $C_d$ to be between 25 $\mu$F/cm$^2$ [Bai 1987], and 50 $\mu$F/cm$^2$ [Glarum 1979]. Capacitance measurements on iron at the corrosion potential indicated a value of 36 $\mu$F/cm$^2$ [Denholm 1964] and 38 $\mu$F/cm$^2$ [Moshtev 1968]. Lossev [Lossev 1953] determined the
double layer capacitance as 35 μF/cm². In the experiments conducted in the present study, the value appeared to be slightly higher than this, and a value of 45 μF/cm² was assumed for the double layer capacitance, $C_{dl}$, for all subsequent calculations. The completed procedure for calculating the capacitance values is given as part of §[12.1.3].

6.6. Results

6.6.1. Frequency sweep experiments

For the potentials in the passive regime of all the alloys investigated, a pseudo capacitive response was measured over a wide frequency range. This linear region on the bode plot could be characterized by the slope, intercept and phase angle as described in §[6.5.1]. In order to characterize the resistive component that is present, the phase angles at the low frequency regime are useful. The difference in the magnitude of the phase angle in the pseudo capacitive regime and at the lowest excitation frequencies, $\Delta \theta$, is useful to illustrate the appearance of an additional resistive element in the equivalent circuit. Because the pseudocapacitive regime is not a perfect capacitor with a phase angle of 90°, and a slope of -1, the exact impedance response measured cannot be represented in terms of simple electric elements. Such an approximation can at best serve only as an approximation. In the absence of this resistive component, the electrified interface may be approximated by the equivalent circuit as shown in figure [6.10.17], while appearance of a second resistive component indicates an equivalent circuit of the form as shown in figure [6.10.18].

The slope of the plot of log(Z) versus log(ω) is very important in deciding what type of electrical elements are present. A slope of 0 indicates purely resistive response, while a slope of -1 indicates purely capacitive response. Figure [6.10.19] shows the slopes for the alloys investigated. For the pure Fe the slope decreases from -0.82 at -0.7 V, to -0.90 at 0.3 V, indicating more perfect capacitive behaviour. Between 0.3 and 0.7 V the slope is relatively constant, ranging between -0.90 and -0.91. Above 0.7 V, the slope increases rapidly to -0.80 at 0.9 V. In contrast, the slope for the pure Cr is already very close to unity (-0.91) at -0.7 V, the potential at which this investigation was started. As the potential is increased, the slope decreases slightly, to -0.95 at -0.1 V. From -0.1 V it
decreases initially slowly to 0.94 at 0.0 V, and then subsequently exhibits a rapid decrease. The alloys show behaviour between that of the pure elements, as is expected. In the low potential regime, the slopes are almost identical to that of pure Fe. In the intermediate potential regime from -0.3 V to 0.1 V, the slope increases monotonically to between -0.95 and -0.96, almost exactly the same value as the pure Cr. Above 0.1 V where, as discussed, the slope of the Cr rapidly increases, the slope of the graph of the impedance response of the alloys also show an increase, followed by a subsequent decrease. This behaviour is very interesting since this is also the regime in which the alloys show a secondary breakdown and repassivation regime.

The intercept of the plot of log(Z) versus log(ω) provides a complement to the slope in specifying the linear portion of the Bode plot. It is expected that, because the lines are straight, and originate from at points very close to one another, that the intercept should increase as the slope of the line decreases. Figure [6.10.20.] shows the intercepts for all the alloys studied. The intercept for Fe, corresponding to the absolute impedance of Fe at ω=1 rad/s, decreases from log(Z) = 3.76 at -0.7 V to log(Z) = 3.37 at -0.5 V. After this, log(Z) increases to 4.52 at 0.7 V. The latter increase is initially rapid, and subsequently slows down at the higher potentials. At even higher potentials, the intercept rapidly decreases to 3.88 at 0.9 V. For the Cr, the intercept increases at a more moderate rate from 4.58 at -0.7 V to 4.77 at 0.0 V and then rapidly decreases to 3.87 at 0.4 V.

For the alloys the behaviour is a little more complex. Between -0.7 and -0.5 V the intercept decreases. The alloys show, in the potential regime between -0.5 and 0.1 V, monotonically increasing values of the intercept. At the lower end of this potential regime, the values of the intercepts increase with an increase in the Cr concentration, but at the higher potential regime, the values for the different alloys do not differ appreciably for Cr concentrations ranging between 5 and 30 wt%, although the log(Z) values tended to increase marginally with increase in the wt% Cr in the alloy. Log(Z) ranged from ~ 4 at -0.5 V to 4.7 at 0.1 V. At 0.1 V, corresponding to the potential at which the log(Z) value for Cr starts to decrease rapidly, the log(Z) values of the alloys also start to decrease. The values of log(Z) subsequently exhibit a minimum, followed by an increase to another maximum at 0.7 V. Over this potential range of 0.1 to 0.7 V the behaviour of the alloys
depend on the Cr concentration. The greater the wt% Cr, the greater the decrease in the log(Z) value, and also the lower the value of the final maximum. At potentials greater than 0.7 V the log(Z) values for all the alloys decreases rapidly.

The only remaining parameter needed, in order to fully specify the impedance characteristics of the alloy over the linear pseudo capacitive regime, is the phase angle. The values for the phase angle over this regime are shown in figure [6.10.21.]. As can be seen in figure [6.10.3.] the phase angle varied slightly over this potential regime, due to imperfect solution resistance compensation. For Fe the phase angle increases rapidly with the onset of passivity and then remains fairly constant at 82 - 83° over the potential regime of -0.4 to 0.7 V. With the onset of transpassivity, the phase angle decreases rapidly. For the Cr, the phase angle is already very close to 90°, the value expected for a pure capacitor at the start of the measurement, with a phase angle of 84.72° at -0.7 V. The phase angle for Cr is relatively constant over the passive regime, increasing to 86.48° as the potential is increased. Above 0.1 V, where Cr dissolves as Cr⁶⁺, the phase angle decreases rapidly.

The Fe-Cr alloys are unusual in that the higher wt% Cr alloys show, at the lower potentials in the passive potential regime, a phase angle lower than that of both the Fe and the Cr. The phase angle, however, increases rapidly with an increase in potential. The phase angle exceeds that of Fe, and increases to a value of 86-87°, the same as pure Cr, at a potential of 0.1 V. Between 0.1 and 0.7 V, the phase angle shows a decrease, followed by a subsequent increase. The magnitude of this local minima is a function of the Cr content of the alloy, with the phase angle being suppressed to lower values with an increase in the Cr content of the alloy. At the onset of transpassivity above 0.7 V, the phase angle decreases rapidly.

Some authors, for example Cahan [Cahan (1982) (b)] have attributed the downwards bending of the phase angle at very high frequencies to a resistive process (as also noted in the above discussion), especially in the cases where the value of the constant phase element is significantly less than 90°. Cahan’s results are shown in figure [6.10.22.], and the decreasing phase angle can clearly be seen at high frequency and high potential values. A similar decrease in the phase angle is also shown in figure [6.10.3.], for the results
obtained in this current investigation. Experimentation with various values for the solution resistance indicated that the variation in the phase angle from a constant value at high frequencies actually occurs because of imperfect compensation of the contribution of the solution resistance. The next discussion will show that instead of a decreasing phase angle due to a resistive process, the phase angle in the pseudo capacitive regime is most likely a constant phase element (CPE) coupled with imperfect solution resistance compensation. It is postulated that CPE behaviour is present even at the high potentials investigated by Cahan. It will be shown that the downwards sloping of the phase angle plot as shown in figure [6.10.22.], taken from the results of Cahan [Cahan (1982) (b)], can be explained by imperfect solution resistance compensation.

The reason why a small error in compensation can significantly affect the constancy of the phase angle at high frequency and high potential values is very important, and thus merits a more detailed discussion. The phase angle is defined as $\tan(\theta)$. At very high frequency values the imaginary component $\text{Im}$, due to the capacitive nature of the passive film is very small (remember that $C = \frac{1}{2\pi f \text{Im}}$ for a parallel plate capacitor). When an impedance measurement is carried out, there is, for corroding systems, a small uncompensated solution resistance $R_s$. The total resistance measured equals the real part of the impedance response, and, $\text{Re} = R_s + R_f$. If this value $\text{Re}$ is now used in the uncorrected form, to calculate the phase angle, the phase angle calculated will decrease in the high frequency regime. The decrease indicates the presence of a resistive component. This resistive component is the solution resistance. The phase angle at high frequencies will therefore be lower than the phase angle in the pseudo capacitive regime, due to this effect. An example of such behaviour can be seen in the raw data set presented in figure [6.10.4.]. Since investigators are aware of this factor $R_s$ is normally subtracted out of any data. This correction for the solution resistance was also carried out for the data in the present investigation, as has been pointed out in §[6.5.1.]. The value of $R_s$, is usually determined by extrapolating the value of the real component $\text{Re}$, as a function of $\omega$ to infinite frequency. This process is, however, always an approximation, and can give rise to faulty interpretation of the data, such as that of Cahan [Cahan (1982) (b)], as is discussed in §[12.2.1.].
The present data obtained for the passive film on iron correspond closely to that found in the literature [Cahan 1982 (a), Azumi 1986 (a), Azumi 1987]. Cahan, however, interpreted the decrease of the phase angle at high frequencies to a second resistive component. Azumi, in turn postulated the existence of a second relaxation process due to adsorption at the passive film/electrolyte interface [Azumi 1986 (a)]. Both these investigators therefore propose an equivalent circuit for the electrified interface as shown in figure [6.10.23.]. As has been shown above, the additional component observed most likely corresponds to an imperfectly compensated solution resistance as well as dispersive effects due to low solution resistance and finite cell geometry. In the present investigation, extremely linear behaviour was observed in the Bode plots as long as the potential remained in the passive regime, and a second relaxation process was never observed.

The role of Cr on the impedance behaviour of the Fe-Cr alloys is to increase the overall impedance of the passive film. The addition of the Cr, also makes the passive film behave more like a perfect capacitor (ie. increases the phase angle to a value closer to 90°, which indicates pure capacitive behaviour). Addition of Cr, however, has the effect of decreasing the phase angle at potentials above which the pure Cr is thermodynamically unstable, as can be seen in figures [6.10.24.] and [6.10.25.]. The latter figure plots $\Delta \theta = \theta_{\text{pcap}} - \theta$ a measure of the deviation of the phase angle at low frequencies from the phase angle in the pseudocapacitive region. Lastly the addition of Cr, results in the appearance of a resistive component at low frequencies in the high potential regime where Cr dissolves transpassively. Tables [6.9.1.] to [6.9.5.] summarise the parameters for the impedance experiments.

6.6.2. Potential sweep experiments

The potential sweep experiments were designed in order to examine the behaviour of a passive film formed at a specific potential, as a function of potential. The capacity versus electrode potential curves at various film formation potentials are given in figures [6.10.26.] to [6.10.28.]. The experiments were thus designed so that the film properties were relatively unchanged while the capacitance as a function of the electrode potential was determined.
Capacitance values decrease rapidly with an increase in potential at the onset of passivity, then decrease more slowly in the passive regime. Capacitance values are, for a wide potential regime, fairly constant. At the onset of transpassivity, the capacitance values again increase rapidly. In the potential range of 0.2 to 0.7 V, the higher Cr content alloys show more complex behaviour, and exhibit a region of capacitance increase followed by a capacitance decrease. For the potential regime below the transpassive reaction of Cr (Cr$^{3+}$ to Cr$^{6+}$), the measured capacitance values decrease as the Cr concentration is increased. It can be seen from figures [6.10.26.] to [6.10.28.] that the absolute differences in the measured capacitance response are small. Very accurate measurements are therefore required and very little data scatter in the capacitance values can be tolerated in order to still be able to carry out meaningful analysis.

6.7. Discussion

In contrast to the photoelectrochemical results which probe only the surface layers of the passive film, as will be discussed in §[7.7.], the impedance measurements determine the response of the entire passive film. A change in the composition, and consequently in the properties of the passive film as a function of depth will therefore be 'seen' by the impedance method as a change in the 'average' value of the parameter of the passive film; this must be kept in mind when the results from impedance measurements are analysed.

6.7.1. Frequency sweep experiments

The results from the impedance experiments indicate that the passive film on Fe-Cr alloys behaves like an imperfect capacitive element. The capacitive nature of the passive film is increased by the addition of Cr to the alloy. This increase in capacitive nature can be seen in the increase of the phase angle of the pseudocapacitive regime. The passive film is inhomogeneous, as can be seen from the dispersion in the impedance results.

The transition of the Cr$^{3+}$ oxidation state to the Cr$^{6+}$ state results in increased dispersion. The influence of this oxidation state change is clearly visible in the decrease in the phase
angle, \( \theta \), in the regime in which this takes place as can be seen in figure [6.10.24.]. The subsequent increase in \( \theta \) is postulated to be related to the removal of the Cr from the passive film, so that the passive film in this secondary passive regime is most likely more enriched in Fe. As has been discussed in §[3.1.], this removal of Cr is as is expected from thermodynamic considerations.

6.7.2. Potential sweep experiments

A great many experiments of the capacitive behaviour of Fe may be found in the literature. The impedance results presented in this study will be analysed with the intention of gaining a better understanding of the role of the addition of Cr to the alloy. The capacitive behaviour of pure Fe will, however, be briefly analysed with a view towards consolidating the current models in the literature that describe the behaviour of the passive film on iron. This will be used as a starting point to describe the behaviour of the Fe-Cr alloys. In analysing the passive film on iron, the results of the current investigation, will be compared to the 'semiconductor' or 'band' model of the passive film [Stimming 1976] and the 'chemi-conductor' model of the passive film [Chen 1982, Cahan 1982 (a), Cahan 1982 (b)]. A summary of the 'band' and 'chemi-conductor' models can be found in §[3.4.3.] and §[3.5.].

6.7.2.1. Semiconductor or dielectric?

One of the most interesting questions that can be investigated by means of capacity measurements in the pseudo capacitive regime, is whether the passive film behaves like a semiconductor or whether it acts as a dielectric. Evidence for both types of behaviour exist in the literature. As discussed in §[3.5.], Stimming [Stimming 1976] divided the typical capacitance as a function of voltage behaviour for the passive film on iron into three regions. In the first low potential region, Mott-Schottky behaviour was assumed (ie. capacitance control by growth of a space charge layer as a function of potential) In the intermediate potential regime Stimming postulates an exhaustion of donors while at even higher potentials an increase in the capacitance is observed which Stimming explains this by an increase in the hole concentration in the valence band, yielding a dominating space
charge concentration at the surface. The three regions are shown in figure [6.10.29.]. Cahan and Chen on the other hand [Chen (1982), Cahan (1982) (a), Cahan (1982) (b)] model the passive films as a dielectric of which the dielectric constant is a function of the formation potential (see also summary of Cahan's model in §[3.4.3.]).

The band model of the passive film has, in addition to the limitations in the analysis as described in §[3.5.], some features that have not yet been adequately addressed. Measurement of the electrode capacitance as a function of the electrode potential can supply very useful information. Dielectric behaviour should result in $1/C$ versus $E$ showing straight line behaviour, if the passive film can be assumed to thicken linearly with an increase in the potential. Semiconductive behaviour should show straight line behaviour for a plot of $1/C^2$ versus $E$ (see also discussion following). In practice, however, it is often very difficult to tell whether $1/C$ or $1/C^2$ versus $E$ gives a better fit. As an illustration of how difficult it is to determine whether $1/C$ or $1/C^2$ gives a better linear fit, consider figure [6.10.33.], taken from Cahan [Cahan 1982 (a)], which shows that both plots seem linear, albeit over different potential ranges.

Consider the expected behaviour of the passive film if it behaves like a dielectric on a conductive substrate. The combination substrate/passive film/electrolyte is then anticipated to be electrically equivalent to a parallel plate capacitor, as is shown in figure [6.10.34.]. The thickness of the passive film thus functions as the dielectric in this capacitive element. The thickness of the dielectric controlling the capacitance is therefore only a function of the thickness of the passive film and, provided that the thickness of the passive film stays constant, is not a function of the electrode potential. The relationship between the film thickness and the capacitance is then given by [Halliday 1978]:

$$ C = \frac{\varepsilon \varepsilon_0 A}{D_{pf}} $$

[6.7.]

For this type of element the capacitance characteristics are expected to show a linear $1/C$ versus $E$ relationship if the passive film is expected to thicken linearly with potential, as is often the case for Fe-Cr passive films. Another important aspect to consider is the potential
drop over a passive film of this type. For argumentative purposes a homogeneous film will be assumed. As illustrated in figure [6.10.35.], an increase in the electrode potential is then simply manifested as an increase in the electric field in the passive film. Note that the potential drop still takes place over the same thickness, in this case the thickness of the passive film.

Results from the investigation by Azumi [Azumi 1986 (a), Azumi 1987] have shown that the passive film contains an inner region in which no electric field is supported. This lack of an electric field in the inner part of the passive film indicates that at least the inner portion of the passive film is electronically conductive. Azumi’s results, however, are such that no conclusions about the outer portion can be made - ie. it could be dielectric or semiconductive. Consider for the purposes of the current argument that the outer portion of the passive film is dielectric. If a potential is applied over a hypothetical passive film consisting of an inner conductive and an outer dielectric film, the potential drop will be over the outer dielectric layer, while no potential gradient in the inner conductive layer will exist. If the potential applied over this film is now increased, the potential drop will still be over the dielectric portion. The electric field in this part of the passive film will increase with an increase in the potential. This hypothetical situation is illustrated in figure [6.10.36.].

Consider now the case where the passive film consists of a thin semiconductive layer on a conductive metal substrate. Imagine now that the passive film is an n-type semiconductor and that the electrode is polarised to a potential more anodic than the flat band potential. In this case a depletion layer forms at the film/electrolyte interface. The thickness of this depletion layer is a function of the potential to which the electrode is polarised. The thickness and consequently the capacitance of the electrode will therefore vary as the electrode potential is changed. In this case the electrode capacitance will be given by the Mott-Schottky equation [see for example Bard 1980]:

\[
\frac{1}{C_z^2} = \left( \frac{1.41 \times 10^{20}}{\varepsilon N_d} \right) \cdot [\Delta E - 0.0261]
\]

[6.8.]
In equation [6.8.], written for $T=300\, \text{K}$ and for an area of $1\, \text{cm}^2$, $N_d$ is in $\#.\text{cm}^{-3}$, $\Delta E$ in $\text{V}$, and $C_{sc}$ in $\mu\text{F.cm}^2$. If space charge layer formation is controlling the capacitance of the electrode, a plot of $1/C^2$ versus $E$ should exhibit straight line behaviour. Manipulation of this equation can therefore yield, via measurement of the slope of a $1/C^2$ versus $E$ plot, the donor density $N_d$, of the passive film, as well as the flat band potential, $E_{fb}$, as the intercept with the $E$ axis of such a plot. Note that the conditions as set out in §[3.5.] must be met for this equation to be applicable.

Consider now the potential drop over a film of this type. The thickness of the layer over which the potential drop takes place is the thickness of the depletion layer which, as described above, is a function of the electrode potential. At low overpotentials, the thickness of the depletion layer is small, therefore, the distance over which the potential drop takes place is also small. As the electrode potential is increased, the thickness of the space charge layer increases, and consequently the thickness over which the potential drop takes place is also increased. The potential distribution over the space charge layer is complex. Analytically solving for the potential gradient in such a film under depletion layer conditions is theoretically possible though convoluted [McKelvey 1986 p. 488]. In practice solving for the potential gradient, however, is often impossible because of the effects of perturbations. One such a perturbation is, for example, surface states.

Because the passive film on Fe-Cr alloys is thin, at high potentials the thickness of the space charge layer may approach the thickness of the passive film. In this case the potential drop takes place over the entire thickness of the passive film. At potentials even higher than this, the passive film is expected to be exhausted of carriers. Under these conditions the passive film is expected to behave exactly as if the passive film in it's entity is dielectric. This sequence of behaviour as a function of the electrode potential is illustrated in figure [6.10.37.]. Note that for ease of illustration only one of the bands are shown.

The case of an exhausted semiconductor can be distinguished from that of a dielectric with thickness equivalent to the thickness of the whole passive film, because the latter situation is not physically realisable since the inner layer of the passive film has been shown to be semiconductive [Azumi 1986]. If it can, therefore, be proven that the entire passive film
behaves like an exhausted semiconductor, it can be concluded that a space charge layer mechanism is operative, and that the whole passive film is semiconductive.

From a comparison of the thickness of the passive film, \( d \), the thickness of the layer in the passive film that would give the observed capacitive behaviour if the passive film is considered as a dielectric, \( D_{ls} \), and the thickness of the space charge layer, \( D_{sc} \), some conclusions as to which model is more applicable can be made. In our case the thickness of the passive film may be determined by optical techniques such as ellipsometry or reflectometry. From a plot of \( 1/C \) versus the electrode potential \( E \), the maximum value for \( 1/C \) may be determined. At this value it is known that the film thickness that acts as a dielectric may be determined from [Azumi 1987]:

\[
D_{ls} = \frac{\varepsilon \varepsilon_0}{C_{\text{max}}} \tag{6.9}
\]

The thickness of the passive film, assuming that it exhibits dielectric behaviour can be calculated via equation [6.9.], and the value of the maximum capacitance. The maximum capacitance may be obtained via a measurement of the capacitance as a function of the electrode potential. In the same manner, from the Mott-Schottky equation follows:

\[
D_{sc} = \left[ \frac{2e \varepsilon_0 A E_{sc}}{\varepsilon N_d} \right]^{1/2} \tag{6.10}
\]

From equation [6.10.], the thickness of the depletion layer may be determined assuming that the passive film behaves like a semiconductor, and using the value for \( N_d \) calculated from a Mott-Schottky plot. \( D_{ls} \) is not dependent on the electrode potential, while \( D_{sc} \) shows an inverse parabolic dependence on the electrode potential. The lines giving \( D_{sc} \) and \( D_{ls} \) as a function of the electrode potential will thus, because they are not both straight and parallel, show an intersection at some potential. Below this potential value at which the intersection takes place, the thickness of the dielectric layer will be greater than the space charge layer thickness, while above this potential the thickness of the dielectric layer will be smaller than the thickness of the space charge layer.
Initially the frequency sweep experiments as described in §[6.4.1.] were carried out. When the values obtained in this manner were analysed and plotted in the Mott-Schottky format described above, it became clear that the film thickness and composition were functions of both the formation potential and time. Due to the change in the film characteristics while the measurements were carried out, the Mott-Schottky analyses were, therefore, not valid for the results obtained from frequency sweep experiments. The results of these investigations, however, are very useful to show that frequency dispersion of the Mott-Schottky behaviour exists for all the alloys investigated.

The non-linearity of the results in the current investigation can clearly be seen in figure [6.10.38.] which shows the Mott-Schottky plots for the 10 wt% Cr, Fe-Cr alloy investigated at frequency values of 1030, 103, 10.3 and 1.03 Hz. Note that dimensionless capacities are plotted. The actual magnitudes of the capacitances differed from the capacitances as determined by the sweep measurements due to roughening of the electrode surface in the later experiments, caused by the long immersion time. This roughening causes a resultant increase in the effective surface area which in turn causes an increase in capacitance. The other alloys investigated showed similar frequency dispersion. As a result of this observation, the experimental procedure as described in §[6.4.2.] were designed and carried out. The latter experimental procedure minimised the change in the passive film while the measurement was carried out.

Figures [6.10.39.] to [6.10.41.] compare the thickness of the space charge region, $D_{sc}$ as calculated from equation [6.10], the thickness of the isolator, $D_{is}$ as calculated by equation [6.9.], and the thickness of the passive film, $d^\dagger$, on iron at various film formation

$^\dagger$ Little data of film thickness as a function of potential for Fe-Cr alloys in neutral electrolytes exist in the literature. Apart from potential the main variable affecting film thickness is the pH of the electrolyte. For the 10 and 30 wt% Cr, Fe-Cr alloys, no thickness data as a function of potential could be found for a borate electrolyte such as the one employed in the capacitance measurements. For pH values close to neutral, Seo [Seo 1980] showed that the film thickness as a function of the electrode potential vs hydrogen electrode in same solution ($E_{he,H2}$) is relatively independent of pH. This experimental observation enables us to use the

(footnote continued on bottom of next page)
potentials for this new type of experiment. It can be seen that the thickness of the space charge layer or the thickness of the material functioning as a dielectric is in all cases lower than the thickness of the passive film. Throughout the passive regime there, therefore, must be a regime in the passive film where no electric field exists, regardless of whether semiconductive or dielectric behaviour is exhibited, in accord with the data of Azumi [Azumi 1986 (a)]. It may, therefore, be concluded that at least the inner layer of the passive film sustains no electric field, and that the inner layer of the passive film cannot be a dielectric material.

No prediction of the properties of the outer portion of the passive film can be made at this stage. It is impossible to tell whether the outer layer that supports an electric field, does so because a depletion layer exists, or whether it does so because it behaves like a dielectric material.

From the conclusion made earlier, that if the outer layer acts like a dielectric, the entire film can never be entirely exhausted, it may be determined which situation holds for the passive films on Fe-Cr. Consider the case of the 10 wt% Cr and 30 wt%, Fe-Cr alloys. Figures [6.10.42.] to [6.10.47.] compare, as before, the thickness of the space charge region, $D_{sc}$ calculated from equation [6.10.], the thickness of the isolator, $D_{is}$ calculated from equation [6.9.], and the thickness of the passive film, $d$. Consider figures [6.10.42.] and

thickness values for the passive film on Fe-Cr alloys as determined by Sugimoto [Sugimoto 1980] in a pH 6 acidified sulphate solution as the thicknesses in the pH 8.6 solution used in this investigation by manipulation as follows:

1. Replot Sugimoto's data as a function of $E_{hess}$ for a pH 6 solution.

2. Convert the $E_{hess}$ values to potentials via $E_{sce}$ for a pH 8.6 solution.

The data obtained in this fashion will give a very good estimation of the film thicknesses in the Borate buffer solution, and was used for the discussion that follows. For Fe in a borate buffer, substantial film thickness data exists in the literature, and for the purposes of this discussion, the data of Szklarska-Smialowska for Fe in a pH 8.45 borate buffer (prepared by mixing 0.15 M $H_3BO_4$ and 0.0375 M $Na_2B_4O_7$) was used [Szklarska-Smialowska 1984].
In these cases the thickness of the space charge layer as predicted from equation [6.10.], exceeds the thickness of the passive film at high potentials. This scenario is not physically possible, thus, it is concluded that the entire thickness of the passive film behaves like an electronically exhausted layer at the higher potentials. If the entire passive film is exhausted, the thickness of the passive film and the thickness of the equivalent dielectric layer should be the same. At this stage it will then have been proved that the whole passive film is semiconductive.

Figure [6.10.42.] shows that the thickness of the calculated dielectric layer and the thickness of the passive film are the same in the cases of passive films formed at 0.1 V on a 10 wt% alloy, while figures [6.10.45.] to [6.10.47.] show that also the passive film on a 30 wt% Cr, Fe-Cr alloy at 0.1, 0.5 and 0.8 V has the thickness of the calculated dielectric layer and the thickness of the passive film the same. For the passive film formed on the 10 wt% Cr, Fe-Cr alloy at 0.5 and 0.8 V, the film thickness is comparable to the space charge layer thickness. In the latter cases the situation is somewhere in between the situation on Fe, where the thickness of the predicted space charge layer is smaller than the passive film thickness, and the situation described above where the thickness of the predicted space charge layer exceeds the passive film thickness.

A comparison of the thickness of the dielectric layer with the passive film thickness above, has thus shown that in some cases they closely correspond. Figures [6.10.48.] to [6.10.50.] show a summary of the comparison of $D_{sc}$, $D_{is}$ and $d$, at the film formation potentials. It is therefore concluded that the outer material is indeed semiconductive and not dielectric, as the physically observed phenomenon is incompatible with a dielectric outer layer of the passive film.

One question that remains to be clarified is why, for the cases where the film thickness exceeds the space charge layer thickness, the capacitance, $C$, reaches a minimum, before the space charge layer has reached the maximum thickness (ie. the capacitance starts increasing before the potentials reach the value at which the thickness of the space charge layer is a maximum). The phenomenon responsible for this behaviour is dielectric
breakdown of the passive film material. To illustrate that dielectric behaviour is responsible for the increase in capacitance at higher potentials, consider the potential drop in a semiconductive layer on top of a metal. Analytically solving for the potential gradient in such a film under depletion layer conditions is theoretically possible, though convoluted [McKelvey 1986 p. 488]. An analytical solution, however, is in practice often impossible because of the effects of perturbations such as surface states. A simplified view which illustrates the mechanism is, however, possible. Consider equation [6.10.] which gives the dependence of the space charge layer thickness $D_{sc}$ on the polarisation away from flat band conditions. From equation [6.10.] it is clear that:

$$ D_{sc} \propto \Delta E_{sc}^{1/2} $$  \hspace{1cm} [6.11.]

If the distribution of the potential in the passive film is ignored, but instead only the average electric field is considered:

$$ E_{field} \propto \frac{\Delta E_{sc}}{D_{sc}} $$  \hspace{1cm} [6.12.]

Combining equations [6.11.] and [6.12.] it is concluded that:

$$ E_{field} \propto \Delta E_{sc}^{1/2} $$  \hspace{1cm} [6.13.]

From equation [6.13.] it is evident that the average electric field strength in the space charge layer increases as the potential bias is increased. Consider now what will happen if the electric field strength at any point in the space charge layer exceeds the dielectric constant of the passive film material. Dielectric breakdown will occur at that point, potential redistribution will follow over a smaller effective thickness, resulting in even higher field strengths. Ultimately this higher field will result in total dielectric breakdown.

Knowledge of the potential at which the dielectric breakdown occurs, can give us an idea of what the dielectric field strength of the passive film material is. Note that only an estimate can be calculated, since the actual potential distribution (which is non-linear) in the passive
film in the cases where the passive film is not completely depleted cannot be calculated; this has been pointed out previously. Table [6.9.6.] summarises the dielectric strength of the passive films calculated in the following manner. The maximum potential drop in the passive film was taken as the value of the potential at the lowest capacitance minus the flat band potential [Stimming 1979]:

\[ \Delta E_{sc}^{\text{max}} = E_{\text{peak}} - E_{fb} \]  \[6.14.\]

The thickness over which the potential drop takes place was taken as the minimum of the film thickness and the space charge layer thickness as predicted by equation [6.10.]. This choice is justified, because it has been shown that the space charge layer will increase with an increase in potential until it takes up the whole passive film thickness, after which, with an additional increase in potential, it will begin exhausting the passive film of donors. At potentials below the point where \( D_{sc} = d \), the potential drop will thus be over the space charge layer thickness, while at potentials above this, the potential drop will be over the entire passive film thickness.

As is shown in Table [6.9.6.], the dielectric strength of the passive film decreases with an increase in the film formation potential, and with an increase in the wt% Cr in the alloy, although all values are of the same order of magnitude. The values for the dielectric strength correspond closely to the value of \( 1.11 \times 10^8 \) V/m estimated by Macdonald and Chao [Chao 1982] from the data by Goswami [Goswami 1971] for the passive film on Fe in a pH 8.4 borate solution.

**6.7.2.2. Donor densities and flat band potentials**

The two most important parameters that may be calculated from the capacitance plots are the flat band potential \( E_{fb} \), and the donor density \( N_d \). These parameters may be calculated from equation [6.8.], in the case that Mott-Schottky behaviour is assumed. As has been pointed out in §[6.7.2.1.], measurement of the slope of a \( 1/C^2 \) versus \( E \) plot gives, via equation [6.8.], the donor density \( N_d \) of the passive film, while the flat band potential, \( E_{fb} \), may be determined as the intercept with the \( E \) axis of such a plot.
This value for the flat band potential for the pure iron corresponds well with the value of the flat band potential documented in the literature for similar pH solutions as summarised by Simoes [Simoes 1990]. Table [6.9.7.] shows a comparison of the flat band potential data $E_{fb}$ for Fe obtained in this study as compared to that documented in the literature, while tables [6.9.8.] and [6.9.9.] summarise the values for $N_d$ and $E_{fb}$ respectively for all the alloys investigated as a function of the film formation potential, $E_{form}$, and the wt% Cr in the alloy.

Three trends are immediately visible from tables [6.9.8.] and [6.9.9.]: (i) the donor density decreases as the film formation potential is increased (ii) the donor density decreases as the %Cr in the alloy is increased (iii) the $E_{fb}$ values are not significantly affected by either the Cr concentration or the film formation potential $E_{form}$. The above trends indicate that the amount of structural and electronic defects in the passive film decreases as the film thickness increases, in accord with the results from Azumi [Azumi 1987]. The constant flat band potential will be important in analysing the structure of the passive film via photoelectrochemical measurements in §[7.].

6.8. Conclusions

It is concluded that the entire passive film is electronically conductive. Progressive formation of a depletion layer with increasing potential is responsible for the observed capacitance behaviour. It is therefore concluded that the outer layer is indeed a semiconductor, and not a ‘chemi-conductor’ such as Cahan proposed [Cahan 1982 (b)] or a dielectric such as proposed by Moshtev [Moshtev 1968]. The evidence from this study therefore supports the semiconductor model of Stimming and Schultze [Stimming 1976, Stimming 1979].

The results from this study can therefore, in summary be said to closely correspond to the results in the literature, namely that (i) the passive film behaves like a highly doped, n-type semiconductor (ii) the capacitance response cannot be fully analysed in terms of the Mott-Schottky treatment, as frequency dispersion is present. It is also noted that the Mott-
Schottky layer is, even neglecting frequency dispersion, only applicable over a limited potential range, as the film thickness and the space charge layer thickness are of comparable thickness.

The behaviour of the Fe passive films may be compared with the description given by Stimming [Stimming 1976, Stimming 1979] and by the theoretical calculations of Khan [Khan 1980]. For the film formation time of 3600 s examined in this study, it was shown that for Fe, the second stage of band bending in the entire thickness of the passive film with subsequent depletion never occurs because of the comparatively great thickness of the passive film. For the alloys containing 10 and 30 wt% Cr, this depletion does, however occur in some cases.
6.9. Tables - Impedance measurements
Table [6.9.1.] Parameters of the results of the frequency sweep impedance experiments as a function of the film formation potential. Fe in a 0.1 M borate buffer.

<table>
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<tr>
<th>E</th>
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Table [6.9.2.] Parameters of the results of the frequency sweep impedance experiments as a function of the film formation potential. 5 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer.

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Table [6.9.3.] Parameters of the results of the frequency sweep impedance experiments as a function of the formation potential. 15 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer.

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<td>85.57</td>
<td>80.41</td>
<td>5.16</td>
</tr>
<tr>
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<td>84.43</td>
<td>78.93</td>
<td>5.50</td>
</tr>
<tr>
<td>0.5</td>
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<td>83.67</td>
<td>58.87</td>
<td>24.80</td>
</tr>
<tr>
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<td>26.76</td>
</tr>
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<td>85.20</td>
<td>67.94</td>
<td>17.26</td>
</tr>
<tr>
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<td>84.89</td>
<td>77.34</td>
<td>7.55</td>
</tr>
<tr>
<td>0.9</td>
<td>-0.88</td>
<td>4.21</td>
<td>81.88</td>
<td>63.41</td>
<td>18.47</td>
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### Table [6.9.4.]

Parameters of the results of the frequency sweep impedance experiments as a function of the film formation potential. 30 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer.

<table>
<thead>
<tr>
<th>$E$</th>
<th>Slope</th>
<th>Intercept</th>
<th>$\theta$ max</th>
<th>$\theta$ min</th>
<th>$\Delta\theta$</th>
</tr>
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<tbody>
<tr>
<td>-0.7</td>
<td>-0.86</td>
<td>4.17</td>
<td>79.40</td>
<td>68.60</td>
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</tr>
<tr>
<td>-0.6</td>
<td>-0.85</td>
<td>4.13</td>
<td>79.07</td>
<td>75.48</td>
<td>3.59</td>
</tr>
<tr>
<td>-0.5</td>
<td>-0.84</td>
<td>4.09</td>
<td>78.42</td>
<td>75.64</td>
<td>2.78</td>
</tr>
<tr>
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<td>-0.86</td>
<td>4.15</td>
<td>79.28</td>
<td>75.49</td>
<td>3.79</td>
</tr>
<tr>
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<td>-0.88</td>
<td>4.29</td>
<td>80.95</td>
<td>75.76</td>
<td>5.19</td>
</tr>
<tr>
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<td>83.72</td>
<td>79.46</td>
<td>4.26</td>
</tr>
<tr>
<td>-0.1</td>
<td>-0.93</td>
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<td>85.42</td>
<td>81.33</td>
<td>4.09</td>
</tr>
<tr>
<td>0.0</td>
<td>-0.94</td>
<td>4.66</td>
<td>86.34</td>
<td>82.22</td>
<td>4.12</td>
</tr>
<tr>
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<td>86.37</td>
<td>82.41</td>
<td>3.96</td>
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<td>81.14</td>
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<td>78.18</td>
<td>5.02</td>
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<tr>
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<td>80.38</td>
<td>74.14</td>
<td>6.24</td>
</tr>
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<td>80.88</td>
<td>66.50</td>
<td>14.38</td>
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<td>81.80</td>
<td>58.71</td>
<td>23.09</td>
</tr>
<tr>
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<td>83.38</td>
<td>71.27</td>
<td>12.11</td>
</tr>
<tr>
<td>0.8</td>
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<td>4.52</td>
<td>83.71</td>
<td>75.94</td>
<td>7.77</td>
</tr>
<tr>
<td>0.9</td>
<td>-0.87</td>
<td>4.21</td>
<td>80.70</td>
<td>63.67</td>
<td>17.03</td>
</tr>
<tr>
<td>E</td>
<td>Slope</td>
<td>Intercept</td>
<td>θ max</td>
<td>θ min</td>
<td>Δθ</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>-----------</td>
<td>-------</td>
<td>-------</td>
<td>-----</td>
</tr>
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<td>73.75</td>
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<tr>
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<td>84.96</td>
<td>78.38</td>
<td>6.58</td>
</tr>
<tr>
<td>-0.5</td>
<td>-0.93</td>
<td>4.64</td>
<td>85.31</td>
<td>79.41</td>
<td>5.90</td>
</tr>
<tr>
<td>-0.4</td>
<td>-0.93</td>
<td>4.66</td>
<td>85.28</td>
<td>80.13</td>
<td>5.15</td>
</tr>
<tr>
<td>-0.3</td>
<td>-0.94</td>
<td>4.70</td>
<td>85.52</td>
<td>79.81</td>
<td>5.71</td>
</tr>
<tr>
<td>-0.2</td>
<td>-0.95</td>
<td>4.76</td>
<td>86.43</td>
<td>81.30</td>
<td>5.13</td>
</tr>
<tr>
<td>-0.1</td>
<td>-0.95</td>
<td>4.78</td>
<td>86.48</td>
<td>80.90</td>
<td>5.58</td>
</tr>
<tr>
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<td>-0.94</td>
<td>4.77</td>
<td>85.89</td>
<td>81.36</td>
<td>4.53</td>
</tr>
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<td>80.77</td>
<td>3.84</td>
</tr>
<tr>
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<td>4.52</td>
<td>81.54</td>
<td>78.04</td>
<td>3.50</td>
</tr>
<tr>
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<td>77.80</td>
<td>73.25</td>
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<tr>
<td>0.4</td>
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<td>3.87</td>
<td>71.42</td>
<td>48.76</td>
<td>22.66</td>
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</table>

Table [6.9.5.] Parameters of the results of the frequency sweep impedance experiments as a function of the formation potential. Cr in a 0.1 M borate buffer.
Table [6.9.6.] Values for the dielectric field strength of the passive film as a function of the Cr content and the film formation potential.

<table>
<thead>
<tr>
<th>$E_{\text{form}}$ (V)</th>
<th>ε 0% (V/m)</th>
<th>ε 10% (V/m)</th>
<th>ε 30% (V/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>5.19×10^8</td>
<td>3.74×10^8</td>
<td>2.53×10^8</td>
</tr>
<tr>
<td>0.5</td>
<td>3.12×10^8</td>
<td>2.29×10^8</td>
<td>1.79×10^8</td>
</tr>
<tr>
<td>0.8</td>
<td>2.58×10^8</td>
<td>2.11×10^8</td>
<td>1.48×10^8</td>
</tr>
</tbody>
</table>

Table [6.9.7.] Values for the flat band potentials for passive iron and iron oxide from the literature compared with the results from this study.

<table>
<thead>
<tr>
<th>Substance</th>
<th>pH</th>
<th>$E_{\text{fb}}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycr.line α-Fe$_2$O$_3$</td>
<td>8.9</td>
<td>-0.340</td>
<td>[Wilhelm 1979]</td>
</tr>
<tr>
<td>Polycr.line α-Fe$_2$O$_3$</td>
<td>8.9</td>
<td>-0.340</td>
<td>[Okamoto 1973]</td>
</tr>
<tr>
<td>Polycr.line α-Fe$_2$O$_3$</td>
<td>9.0</td>
<td>-0.317</td>
<td>[Wilhelm 1981]</td>
</tr>
<tr>
<td>Passive iron</td>
<td>8.4</td>
<td>-0.260</td>
<td>[Wilhelm 1979]</td>
</tr>
<tr>
<td>Passive iron</td>
<td>8.4</td>
<td>-0.340</td>
<td>[Simoes 1990]</td>
</tr>
<tr>
<td>Passive iron</td>
<td>8.6</td>
<td>-0.220</td>
<td>[Current study]</td>
</tr>
<tr>
<td>Passive iron</td>
<td>9.0</td>
<td>-0.317</td>
<td>[Wilhelm 1981]</td>
</tr>
<tr>
<td>Passive iron</td>
<td>9.2</td>
<td>-0.380</td>
<td>[Gillot 1981]</td>
</tr>
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</table>
Table [6.9.8.] Donor densities in a 0.1 M borate solution at 100 Hz at various Cr concentration and film formation potentials. \( R=1.6, C_{dl}=45 \mu F, t_{form}=3600 \) s.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( N_d ) (0.1 V)</th>
<th>( N_d ) (0.5 V)</th>
<th>( N_d ) (0.8 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>( 2.14 \times 10^{20} )</td>
<td>( 1.71 \times 10^{20} )</td>
<td>( 1.63 \times 10^{20} )</td>
</tr>
<tr>
<td>10%</td>
<td>( 1.49 \times 10^{20} )</td>
<td>( 1.20 \times 10^{20} )</td>
<td>( 1.30 \times 10^{20} )</td>
</tr>
<tr>
<td>30%</td>
<td>( 1.14 \times 10^{20} )</td>
<td>( 1.08 \times 10^{20} )</td>
<td>( 9.30 \times 10^{19} )</td>
</tr>
</tbody>
</table>

Table [6.9.9.] Flat band potentials in a 0.1 M borate solution at 100 Hz at various Cr concentration and film formation potentials. \( R=1.6, C_{dl}=45 \mu F, t_{form}=3600 \) s.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( E_{fb} ) (0.1 V)</th>
<th>( E_{fb} ) (0.5 V)</th>
<th>( E_{fb} ) (0.8 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>-0.226</td>
<td>-0.218</td>
<td>-0.222</td>
</tr>
<tr>
<td>10%</td>
<td>-0.227</td>
<td>-0.229</td>
<td>-0.226</td>
</tr>
<tr>
<td>30%</td>
<td>-0.247</td>
<td>-0.246</td>
<td>-0.234</td>
</tr>
</tbody>
</table>
6.10. Figures - Impedance measurements
Evacuate with syringe to fill

Calomel or sulphate reference electrode

Agar/K$_2$SO$_4$ salt bridge

Luggin probe filled with electrolyte

K$_2$SO$_4$ soln Electrolyte

Electrolyte

Figure [6.10.1.] Schematic diagram of the salt bridge arrangement used to prevent the intrusion of Cl$^-$. 
Figure [6.10.2.] Bode plot (log(Z) versus log(ω)) of the impedance response of a 15 wt% Cr, Fe-Cr alloy in a 0.1 M borate solution.
Figure [6.10.3.]  Phase angle plot (Tan⁻¹(Im/Re) versus log(ω)) of the impedance response of a 15 wt% Cr, Fe-Cr alloy in a 0.1 M borate solution.
Figure [6.10.4.] Phase angle plot ($\tan^{-1}(\text{Im}/\text{Re})$ versus $\log(\omega)$) of an untreated data set showing how each resistor is only accurate over a specific frequency regime.
Figure [6.10.5.] Bode plot (log(Z) vs log(ω)) of the impedance response of Fe in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.6.] Phase angle plot ($\tan^{-1}(\text{Im}/\text{Re})$ vs $\log(\omega)$) of the impedance response of Fe in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.7.] Bode plot (log(Z) vs log(ω)) of the impedance response of a 5 wt% Cr, Fe-Cr alloy in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.8.] Phase angle plot (Tan⁻¹(Im/Re) vs log(ω)) of the impedance response of a 5 wt% Cr, Fe-Cr alloy in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.9.] Bode plot (log(Z) vs log(ω)) of the impedance response of a 15 wt% Cr, Fe-Cr alloy in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.10.] Phase angle plot \((\tan^{-1}(\text{Im}/\text{Re}) \text{ vs } \log(\omega))\) of the impedance response of a 15 wt\% Cr, Fe-Cr alloy in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.11.] Bode plot (log(Z) vs log(ω)) of the impedance response of a 30 wt% Cr, Fe-Cr alloy in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.12.] Phase angle plot \( (\tan^{-1}(\text{Im}/\text{Re}) \ vs \ \log(\omega)) \) of the impedance response of a 30 wt\% Cr, Fe-Cr alloy in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.13.] Bode plot (log(Z) vs log(ω)) of the impedance response of Cr in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.14.] Phase angle plot (Tan⁻¹(Im/Re) vs log(ω)) of the impedance response of Cr in a 0.1 M borate solution as a function of electrode potential.
Figure [6.10.15.] Schematic diagram of Bode plot (log(Z) vs log(ω)) for the data. The resistive component shown at low frequency was only present in some cases.
Figure [6.10.16.] Schematic diagram of phase angle plot ($\tan^{-1}(\text{Im}/\text{Re})$ vs $\log(\omega)$) for the data. The resistive component shown at low frequency was only present in some cases.
Figure [6.10.17.] Equivalent circuit for the electrified interface in the absence of a resistive component at low frequency.
Figure [6.10.18.] Equivalent circuit for the electrified interface in the presence of a resistive component at low frequency.
Figure [6.10.19.] Slope of the capacitive portion of a Bode plot (log(Z) versus log(ω)) for Fe, Cr as well as 5 wt%, 15 wt% and 30 wt% Cr, Fe-Cr alloys in 0.1 M borate solution.
Figure [6.10.20.] Intercept at log(ω)=0 of the capacitive portion of a Bode plot (log(Z) versus log(ω)) for Fe, Cr as well as 5 wt%, 15 wt% and 30 wt% Cr, Fe-Cr alloys in 0.1 M borate solution.
Figure [6.10.21.] θ of the capacitive portion of a phase angle plot (Tan⁻¹(Im/Re) versus log(ω)) for Fe, Cr as well as 5 wt%, 15 wt% and 30 wt% Cr, Fe-Cr alloys in 0.1 M borate solution.
Figure [6.10.22.] Impedance results of the passive film on Fe showing downwards bending of the $\theta$ at high frequencies and high potentials [Cahan 1982 (a)].
Figure [6.10.23.] Proposed equivalent circuit at high potential [Cahan 1982 (a)].
Figure [6.10.24.] θ for the low frequency regime of a phase angle plot (Tan⁻¹(Im/Re) versus log(ω)) for Fe, Cr as well as 5 wt%, 15 wt% and 30 wt% Cr, Fe-Cr alloys in a 0.1 M borate solution.
Figure [6.10.25.] $\Delta \theta$ for Fe, Cr as well as 5 wt%, 15 wt% and 30 wt% Cr, Fe-Cr alloys in 0.1 M borate solution.
Figure [6.10.26.] C versus E behaviour for 0 wt%, 10 wt% and 30 wt% Fe-Cr alloys in a 0.1 M borate solution at 100 Hz. $R=1.6$, $C_{di}=45 \mu F$, $t_{form}=3600$ s, $E_{form}=0.1$ V.
Figure [6.10.27.] C versus E behaviour for 0 wt%, 10 wt% and 30 wt% Fe-Cr alloys in a 0.1 M borate solution at 100 Hz. R=1.6, C_{dl}=45 \mu F, t_{form}=3600 s, E_{form}=0.5 V.
Figure [6.10.28.] C versus E behaviour for 0 wt%, 10 wt% and 30 wt% Fe-Cr alloys in a 0.1 M borate solution at 100 Hz. $R=1.6$, $C_{dl}=45 \mu F$, $t_{form}=3600$ s, $E_{form}=0.8$ V.
Figure [6.10.29.] C vs E behaviour for Fe [Stimming 1976].
Mott-Schottky plots for Fe in a 0.1 M borate buffer. Mott-Schottky plots obtained at 100 Hz. $R=1.6$, $C_{dl}=45 \mu F$, $t_{form}=3600 s$, $E_{form}=0.1, 0.5$ and $0.8 \text{ V}$.

Figure [6.10.30.]
Figure [6.10.31.] Mott-Schottky plots for a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. Mott-Schottky plots obtained at 100 Hz. R=1.6, $C_{dl}=45 \ \mu F$, $t_{form}=3600 \ s$, $E_{form}=0.1$, 0.5 and 0.8 V.
Mott-Schottky plots for a 30 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. Mott-Schottky plots obtained at 100 Hz. $R=1.6$, $C_{dl}=45 \mu$F, $t_{form}=3600$ s, $E_{form}=0.1$, 0.5 and 0.8 V.
Figure [6.10.33.] 1/C and 1/C^2 vs E [Cahan 1982 (a)].
Figure [6.10.34.] Equivalent circuit for a dielectric film on a metal substrate.
Figure [6.10.35.] Potential drop over a dielectric film on a metal substrate.
Figure [6.10.36.] Potential drop over a film on a metal substrate, consisting of a conductive inner layer and a dielectric outer layer.
Figure [6.10.37.] Exhaustion of a semiconductive film on a metal substrate by space charge layer formation.
Figure [6.10.38.] Capacitance versus potential behaviour for 10 wt% Cr, Fe-Cr alloy in a pH 8.6 borate buffer at 1030, 103, 10.3 and 1.03 Hz, showing dispersion with variation in frequency.
Figure [6.10.39.] Comparison of $D_{sc}$ and $D_{is}$ with $d$ for Fe in a 0.1 M borate buffer. $R=1.6$, $C_{dl}=45$ μF, $t_{form}=3600$ s, $E_{form}=0.1$ V.
Figure [6.10.40.] Comparison of $D_{sc}$ and $D_{is}$ with $d$ for Fe in a 0.1 M borate buffer. $R=1.6$, $C_{dl}=45 \, \mu F$, $t_{form}=3600 \, s$, $E_{form}=0.5 \, V$. 
Figure [6.10.41.] Comparison of $D_{sc}$ and $D_{ls}$ with $d$ for Fe in a 0.1 M borate buffer. 
$R=1.6$, $C_{dl}=45 \mu F$, $t_{form}=3600$ s, $E_{form}=0.8$ V.
Figure [6.10.42.] Comparison of $D_{sc}$ and $D_{is}$ with $d$ for a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. $R=1.6$, $C_{dl}=45 \mu F$, $t_{form}=3600 \text{ s}$, $E_{form}=0.1 \text{ V}$. 

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Figure [6.10.43.] Comparison of $D_{sc}$ and $D_{is}$ with $d$ for a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. $R=1.6$, $C_{dl}=45 \mu F$, $t_{form}=3600$ s, $E_{form}=0.5$ V.
Figure [6.10.44.] Comparison of $D_{sc}$ and $D_{is}$ with $d$ for a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. $R=1.6$, $C_{dl}=45 \, \mu F$, $t_{form}=3600 \, s$, $E_{form}=0.8 \, V$. 
Figure [6.10.45.] Comparison of $D_{sc}$ and $D_{is}$ with $d$ for a 30 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. $R=1.6$, $C_{dl}=45 \mu F$, $t_{form}=3600$ s, $E_{form}=0.1$ V.
Figure [6.10.46.] Comparison of $D_{sc}$ and $D_{is}$ with $d$ for a 30 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. $R=1.6$, $C_{dl}=45 \mu F$, $t_{form}=3600$ s, $E_{form}=0.5$ V.
Figure 6.10.47. Comparison of $D_{sc}$ and $D_{is}$ with $d$ for a 30 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. $R=1.6$, $C_{dl}=45 \ \mu F$, $t_{form}=3600 \ \text{s}$, $E_{form}=0.8 \ \text{V}$. 
Comparison of $D_{sc}$ and $D_{is}$ with $d$ as a function of the film formation potential $E_{form}$, for Fe in a 0.1 M borate buffer.
Figure [6.10.49.] Comparison of $D_{sc}$ and $D_{is}$ with $d$ as a function of the film formation potential $E_{form}$, for a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer.
Figure [6.10.50.] Comparison of $D_{sc}$ and $D_{ls}$ with $d$ as a function of the film formation potential $E_{form}$, for a 30 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer.
7. PHOTOELECTROCHEMISTRY

7.1. Materials

The materials utilized for the impedance experiments were the same as those described in §[5.1.]. The electrodes were prepared in the same way as described in §[5.1.], with the exception that the glass tube as shown in figure [5.10.2.] was replaced with a combination of glass and heat shrinkable flexible Teflon® tubes in order to facilitate easy insertion into the photoelectrochemical cell described in the equipment section below. The modified electrode is shown in figure [7.10.1].

7.2. Electrolytes

The testing was conducted in the 0.5 M H₂SO₄ solution and the 0.1 M borate buffer, prepared as described in §[5.2.]. For the purposes of this chapter, these solutions will be referred to as ‘acid’ and ‘borate’ respectively.

7.3. Equipment

The cell was an airtight unit, based on a modified 75 mm nominal diameter Pyrex® O-ring joint. The front and rear faces of the cell were machined out of Teflon®, while the front face was equipped with a 38.1 mm diameter × 10 mm thick fused silica Oriel # 44970 beam splitter substrate. Fused silica was used in order to limit absorption in the UV spectrum. The cell was constructed in such a way that the specimen could be oriented perpendicular to the light source. Seven ports were provided. The cell is shown in figure [7.10.2].

A saturated mercury/mercury sulphate electrode equipped with a Vycor® tip, supplied by Princeton Applied Research was used for all experiments. For consistence with the experiments in §[5.] and §[6.], all potentials were translated to potentials versus the saturated calomel electrode. Use of the sulphate electrode was necessary because a typical experiment lasted 48 hours, and Cl⁻ intrusion from the reference electrode proved to be a
problem if a saturated calomel electrode were used. The salt bridge arrangement used in the AC experiments (see §[6.]) could not be used due to the geometric constraints of the experimental arrangement. The counter electrode consisted of a 80 mesh platinum grid of 13 cm². The temperature controlling system was similar to that described in §[5.3.1]

The illumination system for generation of the photocurrents consisted of a Photon Technologies LPS 200 power supply, in conjunction with a Photon Technologies LPS 02-A1000 arc lamp housing with quartz window. The arc lamp used was a Hanovia 901-B1 200 W Hg (Xe) lamp. The irradiation curve for this model is given in figure [7.10.3.]. The output from the arc lamp was monochromated by a Zeiss model M4 QIII monochromator, focused to an area of ~ 15 x 15 mm by means of an Oriel model 41570 2.54 cm diameter fused silica 150 mm focal length lens which was situated 13 cm from the front face of the monochromator.

Because the photoelectric current was very small (10⁻⁹ - 10⁻¹² A/cm²), a lock-in technique was used to detect the photocurrent. An Ithaco/HMS model 320 light beam chopper with the chopping wheel situated 2 cm from the front face of the monochromator was used to modulate the light output from the monochromator. The chopper provided a reference signal which was, together with the output from the potentiostat (see below) fed into a Stanford Research Systems Model SR530 dual phase lock-in amplifier.

The electrode was controlled at the chosen potential by a PAR 173 potentiostat equipped with a PAR 376 linear/logarithmic converter, in combination with a PAR 175 universal programmer. The input filter of the potentiostat was switched out of line, so that the modulation of the current would not be filtered out. The accuracy of the current metering system of the potentiostat was checked by the procedure described in §[5.3.]. The linear output of the PAR 376 linear/logarithmic converter was used in all cases and was, together with the reference signal from the chopper (see above), fed into a Stanford Research Systems Model SR530 dual phase lock-in amplifier. The combination of the two signals made possible lock-in detection of the photocurrent.
The analog voltage output of the lock-in amplifier was recorded using an Apple Macintosh® II microcomputer equipped with a National Instruments™ NuBus® NB-M1016 analog to digital converter. Two software programs for data acquisition of the two different kinds of experiments described in §[7.4.] were developed, using LabDriver® and Microsoft QuickBasic®. The listings for these programs are given in §[12.3.4.] and §[12.3.5.]. A Fisher Omniscribe® X-T recorder was used as a secondary means of recording data.

The non-linear light throughput of the system was determined by means of a Oriel model 7070 photomultiplier read out / high voltage source, a model 7078 photomultiplier head, and a 7733-41 UV-extended visible photomultiplier tube. The latter was calibrated by Optronic Laboratories, so that the absolute throughput of the optical system could be determined at 10 nm intervals over the range 250 to 700 nm. This optical throughput curve was then used to normalise the acquired data for the system throughput. A schematic diagram of the complete experimental set up is shown in figure [7.10.4.]

7.4. Experimental procedures

7.4.1. Pseudo steady state photocurrent measurements

All runs were conducted with the electrolyte deaerated/aerated for at least 30 minutes before the start of the experiment. The deaerating gas was pre-purified grade Airco® H₂. In some cases Airco® N₂ was used in place of H₂. A check for deaeration was carried out by monitoring the potential of the platinum electrode against the reference electrode in the cases that H₂ was used as deaerating gas. No differences in the behaviour could be observed in experiments in which the only variable was the deaerating gas used. Before each run the specimen prepared as described in §[7.1.] was polished to a 600 grit finish using Carbimet® disks. Cathodic reduction of the specimen at a current density of 10 μA was then carried out for a period of 1800 seconds in order to reduce the air formed film on the surface.

The passive film was formed on the specimen at the desired potential by stepping to the potential to be investigated and subsequently allowing the passive film to stabilize for a
period of 24 hours. The photoresponse of the passive film was then taken as a function of wavelength. The wavelength of the monochromated light was stepped with intervals of 10 nm, starting at 250 nm and ending at 700 nm. The photoresponse of the film was determined at each of these points. This wavelength range represent the limits between which the photoresponse was large enough to be detected. As can be seen in figure [12.4.1.], below 250 nm the system throughput became too low to detect the photocurrent. At wavelengths above 700 nm the quantum efficiency of the film became so low that the photocurrent signal dropped below detection limits, even though the light throughput of the system was still substantial.

The chopping frequency was 20 Hz in all cases. The analog output of the lock-in amplifier was sampled through the analog to digital circuitry as described in §[7.3.]. At the end of the measurement, the passive film was allowed to stabilize for an additional period of 24 hours; the response was again measured at the end of this period to check for any time dependent behaviour.

The sensitivity and time constant of the lock-in amplifier, and the sample time at each wavelength was varied as a function of signal intensity, because the throughput of the system and the response of the specimen was not linear. With lower signal intensities, such as were observed at the ultraviolet end of the spectrum (light throughput of the system limiting detection) and the infrared end of the spectrum (photoresponse of the film limiting detection), sampling times of up to 5 minutes had to be used in order to get acceptable accuracy. The slit width of the monochromator was set at the maximum possible value in order to ensure maximum throughput, except in cases where the linearity of the film photocurrent response with increasing illumination was tested.

7.4.2. Cyclic voltammetry photocurrent measurements

All runs were conducted with the electrolyte deaerated/aerated for at least 30 minutes before the start of the experiment. The deaerating gas was pre-purified grade Airco® H₂. In some cases Airco® N₂ was used in place of H₂. A check for deaeration was carried out by monitoring the potential of the platinum electrode against the reference electrode. Before
each run the specimen prepared as described in §[7.1.] was polished to a 600 grit finish using Carbimet® disks. Cathodic reduction of the specimen at a current density of 10 μA was carried out for a period of 1800 seconds in order to reduce the air formed film on the surface.

Immediately after reduction, the specimen was stepped to the beginning of the passive regime as determined from the anodic polarisation diagrams given in figures [5.10.5] and [5.10.8]; cyclic voltammetry was immediately started between this potential and a vertex potential just below the onset of transpassivity. The scan rate was 10 mV/s in all cases. The cyclic voltammetry was continued until pseudo-steady state behaviour was achieved. At that time the photocurrent measurements were started.

The chopping frequency was 20 Hz in all cases. The analog output of the lock-in amplifier was sampled through the analog to digital circuitry as described in §[7.3.]. Because the measured signal was small, the photocurrent as a function of potential was measured for 10 - 15 voltammetric cycles at each wavelength to ensure that a reliable average photocurrent value could be calculated at each potential. These measurements were carried out at wavelength increments of 50 nm in the range 300 to 700 nm. The slit width of the monochromator was set to its maximum value in order to ensure maximum light throughput and, therefore, maximum photoresponse.

7.5. Data treatment and presentation

7.5.1. Pseudo steady state photocurrent measurements

The complete data treatment and presentation is given in §[12.1.4.]. All reported results are corrected for the throughput efficiency of the illumination system. The normalization with respect to the throughput efficiency can be carried out because the photoresponse of the film is linear with respect to the light intensity at the light intensities used in the experiments. Figure [7.10.5.] shows that the response is a linear function of the light intensity over the entire spectral range and light intensities investigated.
7.5.2. Cyclic voltammetry photocurrent measurements

The data acquired by the procedure described in §[7.4.2.] was modified by the procedure given in §[12.1.5.] and then plotted. As in the case of the pseudo steady state measurements, all reported results were corrected for the throughput efficiency of the illumination system.

7.6. Results

7.6.1. Pseudo steady state photocurrent measurements

As can be seen in figure [7.10.6.], widely differing quantum efficiencies for the films on the different alloys were obtained. The magnitude of the photoresponse decreases as the Cr content of the alloy is increased. Despite determined efforts, no photocurrent could be measured on a pure Cr electrode. This latter observation is in agreement with the lack of a measurable photocurrent noted by some investigators [Burleigh 1989], but in contrast to the results of Sunseri and co-workers who report measurements of the photoresponse of the passive film formed on a pure Cr electrode in an acidic solution [Sunseri 1987, Sunseri 1990], as well as recent studies by Searson [Searson 1990] on both air formed as well as electrochemically formed films. Sunseri and co-workers report a band gap of \(-2.5\) eV for the passive film on Cr, while Searson [Searson 1990] reports a value of \(-2\) eV.

When the results are examined, a first look at figure [7.10.6.] leaves the impression that the passive film on the different alloys have different characteristic photoresponse. Normalization of the results, however, shows that the characteristic response for all the alloys is exactly the same, differing only in magnitude. This similar characteristic response is most easily seen by examining figure [7.10.7], in which the same data as in figure [7.10.6.] is replotted on normalized coordinates. The slight scattering of results at the higher photon energies are the results of the low throughput of the illumination system, as is shown in figure [12.4.1.]. The low light throughput leads to a drastic amplification of any measurement error in the photocurrent when the results are normalised with respect to light intensity.
If a comparison of the photoresponse as a function of the formation potential of the passive film is made, a response differing only in magnitude is found; this is the case for pure Fe, as is shown in figure [7.10.8.], as well as for the alloys. An example is shown in figure [7.10.9]. When the photoresponse of the passive film in neutral borate electrolytes is compared with the response in the acid electrolyte, the normalised photoresponse is also found to be the same; this is true for pure Fe, as is shown in figure [7.10.10.], as well as for the alloys. Representative examples are shown in figures [7.10.11.] and [7.10.12.]. Several explanations are possible for the observation that the photocurrent does not exhibit a change in characteristic with film formation potential (provided that one remains in the passive regime) and/or pH of the solution. The discussion that follows will focus on showing that the measured results are accurate, and not merely artifacts.

The first and most obvious possible cause for the observed behaviour is that the base alloy consists of two phases, of which one is Fe rich. Formation of two different passive films over the two phases, of which one is 'Cr like' and having no measurable response, the other 'Fe like' and having response similar to that of the passive film on Fe, would give the characteristics seen. X-Ray diffraction, however, indicated that the alloys consisted of a homogeneous solid solution, with a small amount of the retained δ phase, which is Cr rich, for the higher wt% Cr alloys. The δ phase is expected from the Fe-Cr phase diagram, which is shown in figure [5.10.1.]. The second phase was also visible under the electron microscope, and EDAX analysis confirmed that the observed second phase was the high Cr phase expected. No depletion of the matrix within the detection limits of the EDAX apparatus could be found around such second phase inclusions, where present. Exactly the same photoresponse characteristics were measured for alloys given a homogenising heat treatment of 5 days at 1100 °C.

The second possible explanation for the invariant photocurrent characteristics is that a secondary iron oxide film is deposited over the surface of the specimen. The existence of such an oxide film would be in agreement with the XPS and ISS measurements of Calinski and Strehblow [Calinski 1989]. A time dependant measurement was carried out in order to investigate the possibility that this film is not present immediately after passivation, but
only forms at longer polarisation times. According to Calinski and Strehblow, the Fe over layer is expected to be displaced by the Cr at longer polarisation times, due to the greater dissolution rate of the Fe; however, the results from the current study indicate that the measured characteristics do not differ in nature for the various film formation/oxidation times. In figures [7.10.13.] and [7.10.14.], it is shown that, with the exception that the magnitude of the photocurrent increased with increasing time, the measured photoresponse characteristics are time invariant. A significant change in the photocurrent only took place in the first 24 hours. The photoresponse at 21 and 45 hours was nearly identical, as can be seen in figure [7.10.13.]. Dissolution of the over layer at long polarisation times as postulated by Calinski does therefore not take place. The results also show that the Fe oxide over layer is present even at short times, thus, a precipitation mechanism following prolonged immersion is not likely. Because the complete wavelength scan in these experiments takes approximately four hours to complete, the characteristics of the film at very short immersion times was not accessible by this type of experiment. In order to provide further information at short times, the photoelectrochemical cyclic voltammetry, was carried out. In this experiment the passive film is repeatedly formed and reduced, so that the photoresponse characteristics at very short formation times are able to be determined. Results from the photoelectrochemical cyclic voltammetry experiments are discussed in §[7.6.2.].

The measured increase in magnitude of photoresponse with time corresponds to greater amounts of Fe in the film. It is postulated that this increase in magnitude corresponds to the increase of the linear dimension of the film with increasing time. The increase in the quantum efficiency with time is in correspondence with the results of Sunseri and co-workers who investigated a series of ferritic stainless steels [Sunseri 1987], and who found that long polarisation times (up to 24 hr) had to be used in order to obtain photocurrents of an accurately measurable magnitude. Simoes and co-workers [Simoes 1990], however, found the magnitude of the photocurrent not to be a function of the polarisation time. The results of Simoes are in contrast to both the results of this study and the results of Sunseri.

A third possible explanation for the similar observed response on all the alloys is that the response of the passive film is not linear over the range of light intensities investigated, and
that the observed response is therefore an artifact. In order to evaluate this possibility, an experiment measuring the photocurrent as a function of the light intensity for various intensities in the wavelength range 250 - 700 nm was conducted. The results are shown in figure [7.10.5.], showing that the passive film response is absolutely linear with light intensity, and that a nonlinear effect is not responsible for the observed behaviour. The linear response of the electrode with increase in the light intensity also indicates that the decisive role in the phenomenon is played by the photoelectric processes in the semiconductor interior, rather than by surface processes, and that the processes which are present are single photon processes [Pleskov 1986 p. 192]. An interior process is also indicated by the data in figure [7.10.13.], that shows the magnitude of the response of the film to be a function of the formation time. At longer times the film thickness is greater, and thus a greater response is observed. The linear response also indicates that the rate determining step in the process is the generation of carriers, and not the charge transfer process to the electrolyte [Butler 1977]. Results from the time dependent studies also indicate that the species that is responsible for the photoresponse is present both at short and long polarisation times.

From the experimental evidence obtained, it is therefore concluded that the measured invariant response is not an artifact. A model that accounts for the observed invariant behaviour will be presented in the discussion in §[7.7.].

### 7.6.2. Cyclic voltammetry photocurrent measurements

It was originally decided to do cyclic voltammetry, with simultaneous acquisition of the photoresponse, in order to investigate the possibility that the observed photoresponse in the pseudo steady state measurements due to an over film of iron(III) oxide. Such an film, if present, would be in agreement with the surface analytical results of Calinski [Calinski 1989].

The photoresponse of Fe, as well as for 10 wt% Cr and 15 wt% Cr, Fe-Cr alloys are shown in figures [7.10.15] to [7.10.20.] as a function of the electrode potential at a variety of wavelengths. Using this set of data (one parameter as a function of two other parameters),
it is possible to do the transformation schematically shown in figure [7.10.21.], in order to change the independent coordinate from one variable to another. In this way the data from the cyclic voltammetry photocurrent measurements can be transformed to the same format as the data from the pseudo steady state photocurrent measurements. The data for the cyclic voltammetry photocurrent measurements transformed in this manner, overlayed on the pseudo steady state response characteristic for the passive film on Fe, are presented in figures [7.10.22.] to [7.10.25.], and are shown to correspond closely to the results obtained in the pseudo steady state experiments. Some scattering at high photon energies is present, especially in the case of the 10 wt% alloy. This latter scattering is due to inaccuracies in the measurement of the photocurrent since the magnitude of the photocurrent was approaching the detection limit of the experimental apparatus. The photocurrents generated for the higher wt% Cr alloys are small due to the thinness of the passive film formed on these alloys during cycling experiments.

From the cyclic voltammetry photocurrent measurements, it is therefore concluded that the Fe-like phase that is probed in the photoelectrochemical measurements, is formed from the onset of formation of the passive film. The Fe oxide is, therefore, not deposited only later, at long polarisation times. In conjunction with the time dependent measurements described in the previous paragraph, it is also concluded that the Fe layer is not depleted from the passive film over the time scale of the longest polarisation experiments performed (48 h).

From an examination of the transformation procedure illustrated in figure [7.10.21.], it is clear that normalization of the photocurrent as a function of potential should give a single coincident curve. In figures [7.10.26.] to [7.10.33.] the normalised response for each wavelength is shown to coincide, both for the pure Fe as well as the 10, 15 and 30 wt% Cr, Fe-Cr alloys. These results indicates that the photocurrent measurement is probing only one specie. These data are thus consistent with the results from the pseudo steady state measurements, and indicate that the measured results are real.
7.7. Discussion

When the response of the passive film as a function of formation potential is examined, it has been shown in §[7.6.1.], that within the passive range, the characteristic response remains the same, although the magnitude of the response differs. It has also been shown that if the effect of the electrolyte is examined, an invariant response characteristic is obtained (invariant means that the shape of the $i_{ph}$ versus $h\nu$ curve is the same). The magnitude of the response in the acidic media, however, was slightly smaller than the magnitude of the response in the borate buffer. This decrease in response with decrease in $pH$, may be due to the decrease in film thickness with an increase in acidity, which is documented for this class of alloys [Sugimoto 1980, Seo 1980], or may be due to the increased solubility of Fe in the acidic media. The rest of this discussion will now centre around finding an explanation for the observed invariant behaviour, and is aimed at formulating a suitable model.

7.7.1. Optical characteristics of passive films

7.7.1.1. Band gap values for passive films

Optical transitions of crystalline semiconductors can be deduced from the variation in the adsorption coefficient near the band edge. In §[12.2.3.] it is shown that the following equation which relates the photocurrent to photon energy is applicable near the band edge:

\begin{equation}
\frac{d\eta A(h\nu-E_g)^n}{h\nu}
\end{equation}

Direct transitions are characterized by $n=\frac{1}{2}$ and indirect transitions by $n=2$. The minimum energy required for indirect transitions can be evaluated by plotting $(i_{ph} \times h\nu)^{1/2}$ versus $h\nu$, while the energy for direct transitions may be evaluated by plotting $(i_{ph} \times h\nu)^2$ versus $h\nu$.

In figure [7.10.34.] it can be seen that there is a linear relationship between $(i_{ph} \times h\nu)^{1/2}$ and $h\nu$ in the low photon energy regime. This result indicates an indirect transition in the lower
photon energy regime. The same data can also be used to estimate the band gap of the material, by calculating the intercept where $(i_{ph} \times h\nu)^{1/2} = 0$. Analysis of the characteristics of the response as a function of exciting energy of the photons indicate that the band gap of the passive film material is 1.9 eV for all the materials studied. The same band gap is found for the passive films formed in the acid electrolyte. Exact values for the band gaps of the passive film formed on the alloys as well as on Fe, are summarised in table [7.9.1]. Comparison of the results obtained in all cases indicates a response very similar to that of the passive film iron.

The pH independent band gap, corresponds well to the potential-modulated reflectance results of Larramona [Larramona 1989]. Larramona concluded that a single phase comprised the primary constituent of the passive film in the passive region, for electrolytes ranging in pH from 1 to 14. A pH independent band gap for the passive film on iron was also reported by Abrantes [Abrantes 1983] for photocurrent spectra. Abrantes calculated the band gap as being 1.95 eV. The results from the present study also correspond to the differential reflectance measurements by Azumi [Azumi 1986 (b)], who found a pH independent band gap of 2.6 eV. Searson, however [Searson 1988], showed that the high value of the band gap found by Azumi, is due to a faulty assumption. He replotted Azumi’s data, and found a band-gap of 1.75 eV, which corresponds closely to the photocurrent measurements of his, as well as the present study. Searson [Searson 1988] determined a value of 1.9 eV for the band gap of the passive film material on iron in a borate buffer.

Froehlicher [Froehlicher 1983] compared the response of the passive film on Fe, at various film formation potentials, with that of bulk oxide electrodes. He concluded that Fe(II) is present in the film, and that ‘Fe$_3$O$_4$ like’ behaviour is produced by the passive film. Froehlicher’s results are in contrast to the other data cited here, which indicated Fe(III) to be the main component of the passive film. When the value of the band gap as determined above is compared with that of various Fe oxides and oxyhydroxides, it is found that it most closely corresponds to α-Fe$_2$O$_3$ (hematite), a rhombohedral material, with all the Fe(III) ions octahedrally coordinated. This material is an n-type semiconductor and has an optical edge at 2.2 eV (570 nm). It is therefore concluded that in the passive film of all
the alloys under interest, an ‘α-Fe₂O₃-like’ phase is present in the passive regime. Larramona [Larramona 1989], who examined the passive film on Fe, also concluded that an ‘α-Fe₂O₃-like’ phase constitutes the predominant species in the passive film in acid, neutral and basic electrolytes.

One component of the passive film is therefore the same for all the alloys investigated. The bulk oxide/hydroxide that this component corresponds most closely to is α-Fe₂O₃. The fact that no measurable photoresponse could be measured on pure Cr, indicates that at present the experimental set up employed is not sensitive enough to probe the photoresponse of the Cr contribution in the passive film. The observation that the photocurrent on Cr must be very small is also reinforced by figure [7.10.6.], where it is shown that a very small response for Cr is to be expected if the magnitude of the photocurrent trend for the other alloys are extrapolated.

Because a well developed band structure is necessary in order to exhibit a photo effect, it is concluded that the Fe-oxide layer must be spatially distributed in either (i) a layer of sufficient thickness, or, (ii) clusters large enough for the development of a band structure. The spatial distribution of the Fe-oxide is further discussed in §[7.7.1.2.], §[7.7.1.3.], as well as §[7.7.2.], after further experimental evidence is introduced.

### 7.7.1.2. Flat band potentials of passive films

Theoretically it can be derived that the flat band potential $E_{fb}$ is directly proportional to the square of the photocurrent [Pleskov 1986 p. 193]. The final relationship is:

$$E - E_{fb} = \left( \frac{N_D}{2\varepsilon \varepsilon_0 \alpha J_0} \right) \left( \frac{i_{ph}}{\alpha J_0} \right)^2$$

[7.2.]

Using equation [7.2.] and plotting $i_{ph}^2$ versus $E$, it is possible to extract the flat band potential of the material considered as the point at which $i_{ph} = 0$. Figures [7.10.35.] to [7.10.38.] show this construct for the 10, 15 and 30 wt% Cr Fe-Cr alloys, as well as for pure Fe. The two data sets shown on each graph represent the results from the ‘up’ and
'down' scans respectively. The values of the flat band potentials are summarised in table [7.9.2.], while figure [7.10.39.] shows a comparison of the flat band potentials as determined by the photoelectrochemical technique with that as determined by the impedance measurements as described in §[6.7.2.]. As revealed in this figure, the flat band potentials as determined by the photoelectrochemical technique decrease with an increase in the Cr content, while the values of $E_{fb}$, as determined by the impedance technique, show only a slight dependence on Cr content.

To understand the differences in the $E_{fb}$ values as determined by the two techniques the differences between the two methods of determining $E_{fb}$ must be analysed. Factors that may contribute to the value of $E_{fb}$ which was determined from the photoresponse being greater than the value as determined from capacity measurements are documented in the literature. Stimming [Stimming 1986] notes that this discrepancy may also be accounted for by surface states or electron - hole recombination. A discrepancy between the two methods for single phase systems has also been noted by Andermann [Andermann 1984], by Hirano [Hirano 1980], as well as by Wilhelm [Wilhelm 1981]. These results, however, cannot explain why a clear dependence of $E_{fb}$ on wt% Cr is shown to exist in the case of the photoelectrochemical measurements, while the results from the impedance measurements do not show such a dependence.

For the photoelectrochemical technique, it has been shown in §[7.7.1.1.] that only one specie in the passive film is probed. This phase corresponds most closely to $\alpha$-Fe$_2$O$_3$. The flat band potential as probed will therefore represent the flat band potential of this species only. The impedance technique, on the other hand, measures the response of the entire passive film, determining the average property for the whole film. The proposed model to explain the former dependence, is a passive film which consists of an Fe oxide over layer with a Cr oxide enriched inner layer. The $E_{fb}$ value for the Fe oxide over layer is shifted by n-type doping by higher oxidised Cr species. The lattice of the outer part, thus, remains characteristic of $\alpha$-Fe$_2$O$_3$, though the $E_F$ and $E_{fb}$ for the material are shifted. Such a structure would display both (i) the Fe oxide like photoresponse, if the photoelectrochemical technique only probes the surface layer, as well as (ii) the $E_{fb}$ value shift indicated by the photoelectrochemical technique, but not by the results from the
impedance spectroscopy. The $E_{fb}$ shift, if due to this mechanism, will exhibit a dependence on the Cr concentration as is shown in the data. From a comparison of the $E_{fb}$ values, as determined by the photoelectrochemical technique, to the value of $E_{fb}$ as determined by the impedance technique, a non-homogeneous passive layer is once again indicated. This result is in accord with the conclusion reached in §7.7.1.1. The doping of the outer part of the passive film is also discussed in §8.2.

7.7.1.3. Poole-Frenkel behaviour

An indication of the mechanism of excitation may be obtained by investigating the potential dependence of the photocurrent. If the photo excitation process involves localised states, the electron must be removed from these traps in order for the photocurrent to occur. Several researchers have discussed this type of investigation when applied to the photoelectrochemical characterization of a passive metal [Searson 1988, Stimming 1986, Newmark 1987]. For a zero field, the escape probability is very low. Recombination is expected in this case. When the field strength is increased ($F > 0$), the ionization energy of the electron in the direction of the field, and that of the hole in the opposite direction is decreased [Mott 1971]. A schematic diagram of the coulombic well that surrounds a trap is shown in figure [7.10.40]. The magnitude of the lowering is $\beta F^{1/2}$, where $\beta = (\epsilon^3/\pi \varepsilon_0)^{1/2}$ [Frenkel 1938]. As a result of the lowering, $i_{ph}$ depends exponentially on the square root of the electric field:

$$i_{ph} \propto \exp \left[ \frac{\beta F^{1/2}}{kT} \right]$$

[7.3.]

Straight lines in a plot of log($i_{ph}$) versus $F^{1/2}$, therefore, indicates Poole-Frenkel behaviour. As the field strength in the passive film is assumed to be,

$$F = \frac{E - E_{fb}}{d}$$

[7.4.]

it can be concluded that, if Poole-Frenkel behaviour is responsible for the sub-band gap response of the passive film, a plot of log($i_{ph}$) versus $(E-E_{fb})^{1/2}$ should give straight line...
behaviour. Figure [7.10.41.] shows such a plot for the alloys investigated in this study. This plot was constructed using the values for $E_{fb}$ as summarised in table [7.9.2.]. These values were determined from the $i_{ph}^2$ versus $E$ plots as described previously. The data taken in the ‘up’ part of the scan was used for determination of $E_{fb}$. The same trends hold for the data from the ‘down’ scan, but the absolute values differ slightly due to the offset between the ‘up’ and ‘down’ scans.

In figure [7.10.41.] the characteristic linear relationship between $\log(i_{ph})$ and $(E-E_{fb})^{1/2}$, indicating Poole-Frenkel behaviour, is shown. Poole-Frenkel behaviour indicates that localised states take part in the excitation process at low polarisation away from the flat band potentials. Figure [7.10.41.] also shows that the slope of the Poole-Frenkel plot is the same for all the alloys investigated. The slope is a function of the temperature and dielectric constant only [Newmark 1987]. As all the runs were carried out at constant temperature, it is concluded that the dielectric constant of the probed part of the film is the same for all the alloys investigated. At higher polarisation potentials, a deviation from the linear behaviour is apparent. This behaviour is similar to that documented by Searson for the passive film on iron [Searson 1988]. This effect at higher potentials can be ascribed to tunnelling processes becoming significant, at the higher field strengths. Tunnelling effects will be discussed in more detail in §[7.7.1.4.].

### 7.7.1.4. Tunnelling through passive films

An explanation for the peak that exists in the photocurrent response of the passive film on iron has never been explained in the literature. As can be seen from a comparison of the polarisation behaviour, and the photoresponse curves for the alloys, shown in figures [7.10.42.] to [7.10.45.], the peak in the photocurrent response does not coincide with the potential at which the Fe-oxide species becomes unstable kinetically and dissolves. The peak can therefore not be ascribed to the disappearance of the Fe oxide species at potentials greater than the peak potential. An explanation will be forwarded by making use of the Poole-Frenkel model described in §[7.7.1.3.].
Table [7.9.3.] shows the potential difference between the flat band potentials, $E_{fb}$, and the potential at which the peak is observed, $E_{peak}$. As can be seen, this potential difference is constant within the limits of the experimental data. It is therefore concluded that the ‘peak’ is observed for all the alloys investigated at exactly the same band bending. As has been shown above, all the films exhibit Poole-Frenkel behaviour at low band bending, followed by a deviation from this behaviour that was ascribed to tunnelling processes becoming significant. It is, therefore, concluded that the photocurrent starts to decrease as soon as the tunnelling processes become significant. As the passive films on all the alloys exhibit exactly the same band bending before tunnelling commences, it is again concluded that the part of the passive film that is probed must, in all cases, be very similar to the passive film on pure Fe. A bi-layer structure for the passive film on the Fe-Cr alloys as described previously in §[7.7.1.1.] and §[7.7.1.2.], is therefore indicated.

7.7.1.5. Urbach tail behaviour

At low photon energies, the passive films examined exhibit so called ‘Urbach’ behaviour. Urbach behaviour is an experimentally observed logarithmic dependence of the magnitude of the photocurrent on the photon energy. In this phenomenon, first described by Urbach [Urbach 1953], the absorption coefficient, $\alpha$, is therefore dependent on the photon energy as follows:

$$\alpha = \alpha_0 \exp \left[ \frac{\chi(h\nu - E_0)}{kT} \right]$$  [7.5.]

No single explanation exists for this behaviour, although several models exist in the literature, for instance Mott’s model [Mott 1971]. A plot of $\log(i_{ph})$, which is proportional to $\alpha$, versus the photon energy would therefore yield a straight line if Urbach behaviour is present. This behaviour is typically observed for highly disordered or amorphous films. In figure [7.10.46.], an Urbach plot is shown for the alloys investigated. Straight line behaviour at low photon energies, corresponding to the Urbach behaviour is present at photon energies smaller that 1.9 eV. The presence of the Urbach tail indicates that the passive films investigated are most likely amorphous, and that there is sub band gap response.
7.7.2. Comparison of results with existing models

In §[7.7.1.], it was shown that the passive film on Fe-Cr alloys must consist of two distinct parts, only one of which can be distinguished by measurement of the photoelectrochemical response. The question that must now be addressed is how this phase is distributed on the surface of the specimen. It has been concluded in §[7.7.1.1.] and §[7.7.1.2.] that, because the photoelectrochemical technique can only probe a structure with a well developed band structure, the probed ‘Fe oxide like’ component must exist in the passive film either as clusters large enough to develop a band structure, or as a layer of sufficient thickness to constitute a separate phase. Because the magnitude of the photoresponse decreases as the amount of Cr in the base alloy is increased, either the number of these clusters, or the thickness of the over layer decreases as the Cr content is increased. It must, therefore, be determined if the Cr is present as ‘cluster like’ areas of enrichment, or as an over layer over a Cr enriched film.

Calinski and Strehblow [Calinski 1989] indicate the existence of an Fe rich layer over a Cr enriched inner layer, while Sieradzki and Newman favour a passive film in which areas of Cr enrichment coexist with areas where Fe is enriched [Sieradzki 1986, Newman 1988]. Evidence has already been given in §[7.7.1.2.] for a over-layer type structure, but the two possibilities will now be investigated more thoroughly.

Dispersed clusters are predicted by the percolation model of Sieradzki [Sieradzki 1986]. (See also the discussion of the percolation model in §[3.3.2.], as well as the mathematical basis of percolation in §[12.2.2.]) Consider the Cr atoms displacing the Fe on the BCC Fe lattice. As the amount of Cr in the lattice is increased, the probability that the Cr atom on any arbitrary site is situated next to another Cr atom increases. Tamman showed that the ‘critical’ amount of Cr is lower than the amount where Cr atoms have to touch [Tamman 1928]. Consider now that all the Cr atoms that are closer to each other than a chosen distance \( l_p \) have to be mapped. As the Cr concentration is increased, the average ‘cluster’ size of Cr atoms that are closer to one another than \( l_p \) increases. At a certain point \( p_c \) the network of Cr in the Fe matrix becomes continuous, and it is possible to transverse the
lattice from one side to the other, taking steps of no longer than \( l_p \), and to always 'step' on Cr atoms along any part of the way. One of the clusters in the matrix thus spans the entire matrix. This cluster is called the unbounded cluster or percolation path. This situation is schematically shown in figure [12.4.2.]. The point at which this becomes possible is called the percolation threshold \( p_c \) for the geometry under consideration.

At the percolation threshold \( p_c \), the percolation probability, \( P(p) \), departs from zero. The percolation probability, \( P(p) \), can be visualized physically as the fraction of the atoms in the entire matrix that belongs to the unbounded cluster. Since no unbounded cluster exists below \( p_c \), \( P(p) = 0 \) for all \( p < p_c \). At \( p = p_c \), unconnected loose clusters of the Cr still exist in the matrix. Increasing the Cr concentration above \( p_c \), results in a rise in the average cluster size \( s_{av} \), and also a rise in the unbounded cluster size, and consequently in \( P(p) \). When the concentration of 100 at\% Cr is reached, the percolation probability, \( P(p) \), becomes equal to unity. Physically this means that every Cr atom is a part of the unbounded cluster. For the enrichment of Cr in the passive film, three-dimensional site percolation is of interest. The critical volume fraction for percolation in the BCC matrix if second nearest neighbour interactions are considered, \( p_c(1,2) \), is 17.5 at\%, while that for third nearest neighbour interactions \( p_c(1,2,3) \) is 9.5 at\%. [Newman 1988]. For second neighbour interactions, \( l_p \) is no longer than \( \sqrt{2} a \), for third nearest neighbour interactions, \( l_p \) is no longer than \( \sqrt{3} a \).

Newman postulates that the critical percentage of Cr required to ensure passivity is the \( \%Cr \) where the Cr matrix extends through the entire film. When the percolation model is examined, it is evident that even at low Cr content, finite clusters exist. It could be expected that the Cr would enrich in these parts of the film, just as it would enrich over the area spanned by the unbound cluster. An enrichment in Cr even at Cr concentrations lower than the percolation threshold is also expected. Newman, however, postulates that these clusters do not act protectively, since they do not form part of the infinite cluster and dissolution can, therefore, occur around them.

The variation of the cluster size near the percolation threshold can be obtained by considering the critical exponent. Near the percolation threshold, in the critical regime, the
percolation function is known to obey a power law dependence on the parameter \((p-p_c)\). These power law dependences have values for each parameter that do not depend on the type of lattice, but only on the dimensionality of the lattice. For the three dimensional case the relationship is [Zallen 1983]:

\[
s_{av}(p) \sim (p-p_c)^{-1.7}
\]  

[7.6.]

Figure [7.10.47.] shows the variation in the value of the average cluster size on the Cr atom fraction in the matrix, assuming third nearest neighbour percolation. For third nearest neighbour percolation, \(p_c(1,2,3)\) is 9.5 at% in the BCC lattice [Newman 1988]. As can be seen from figure [7.10.47.] Cr clusters of considerable size can be expected even below the percolation threshold. Newman reports the removal of 100 nm ferromagnetic particles from a corroded 11.6 atom % Cr Fe-Cr alloy [Newman 1988]. This size of particle corresponds to a cluster of \(~3 \times 10^8\) atoms. If the actual percolation threshold is 9.5 % Cr as Newman postulates, the measured particle size value is approximately \(10^5\) greater than expected from the critical exponent calculation. If all other conditions are kept constant, the relative magnitude of the photocurrent under conditions of equal band bending is directly proportional to the amount of Fe oxide phase in the passive film. According to the percolation model described above, a very sudden enrichment in Cr occurs at the percolation threshold. This enrichment in turn, should, if the percolation model is correct, be visible as a drastic decrease in the photocurrent at the percolation threshold, because the amount of Fe oxide phases on the surface exposed to the electrolyte suddenly decreases.

Any threshold will be manifested as a change in slope of the plot of relative magnitude of the photoresponse versus the % Cr in the alloy, assuming that a ‘cluster’ mechanism on the surface is operative. Figure [7.10.48.] shows a plot of the relative magnitude of the photoresponse under conditions of constant band bending versus the amount of Cr in the base alloy. As can be seen, straight line behaviour is exhibited, so that any drastic change in the amount of Fe in the passive film is ruled out. The evidence, therefore, is not in support of the percolation model for the conditions investigated. The data supports that of Calinski [Calinski 1989] who concluded (by means of ion scattering spectroscopy (ISS) surface analysis in combination with sputtering), that the amount of the Cr in the passive
film is proportional to the amount of Cr in the base alloy. The only model that predicts cluster like distribution of α-Fe₂O₃ is the percolation model. The results from the photoelectrochemical behaviour contradict the expected behaviour from a percolation mechanism and a layer model is, therefore, more applicable.

7.8. Conclusions

The similar photocurrent spectra measured for the passive films on the Fe-Cr alloys and the Fe, indicate that the same Fe-rich phase exists in the passive film on all the alloys. The quantity of this phase decreases as the amount of Cr in the base alloy increases. The photoresponse of the passive film on pure Cr was below the detection limits of the experimental set-up employed, indicating that the amount of this phase goes to zero as the Fe in the base alloy goes to zero. The lack of a measurable result on pure Cr also indicates that the photoeffect of the passive film is very small, and thus the photoeffect for passive films highly enriched in Cr is also expected to be small.

Analysis of the photocurrent spectra of the Fe rich phase indicate a band gap of ~1.9 eV. This Eg is in very good correspondence to the value for the passive film on Fe reported in the literature. The bulk oxide to which this value most closely corresponds is α-Fe₂O₃. Existence of an ‘α-Fe₂O₃-like’ phase is therefore indicated in the passive films of all the Fe-Cr alloys investigated. The existence of a well developed band structure for the ‘α-Fe₂O₃-like’ phase indicates that this phase occurs in volumes large enough for development of a characteristic band structure. No sudden decrease in the amount of Fe was found near the 12 wt% limit often described as ‘critical’ in the literature, and which is predicted to be a threshold by the percolation model. The experimental data therefore rule out cluster formation by the percolation model. The Fe film is thought to exist as an outer ‘α-Fe₂O₃-like’ layer on top of an inner Cr enriched film, as postulated by Calinski and Strehblow [Calinski 1989]. This outer layer, however, is present even a very long polarisation times, and does not dissolve due to the greater mobility of Fe as compared with Cr, as postulated by Calinski.
The measurement of the flat band potentials as a function of the Cr content indicated that for the Fe-like phase, the flat band potential decreased monotonically with an increase in the amount of Cr in the alloy. This result indicates that the Fe-rich phase in the passive film is doped more highly n-type, thus decreasing $E_{fb}$. The n-type doping results in upwards band bending of the Fe-rich phase in the alloy at higher potentials in the passive regime, as is schematically illustrated in figure [7.10.49]. It has been postulated that upwards band bending can be beneficial to aiding passivity [Burleigh 1985]. According to Burleigh, the electric field in the Schottky barrier, will induce an equal and opposite image field in the solution. This image field is most likely formed by adsorption of hydroxyls in aqueous solution [Morrisson 1980]. The twin electric fields has the effect of (i) preventing metal cations from escaping into the solution, and (ii) favouring the adsorption of anions onto the surface, thus possibly blocking active sites. An alternate view of the mechanism of protection of the n-type doping is proposed in §[8.2].

Whether the junction in the passive film is n-p is not clear because the photoresponse of the passive films on Cr could not be determined, and it is therefore not clear if the Cr passive film is n or p-type. It is, however, more likely that the Cr passive film is p-type than n-type (see also discussion in §[3.5]), and an n-p heterojunction is, therefore, expected in the passive films on Fe-Cr alloys with high Cr concentration. A factor to bear in mind, however, is that the effective oxygen concentration decreases from the passive film/electrolyte interface to the passive film/metal interface. If the oxygen concentration in the inner layer on the passive film (where the Cr is found) is very small, the low oxygen partial pressure regime where Cr$_2$O$_3$ has been shown in §[3.5] to be n-type may be entered, so that the inner layer could also exhibit a p-type conduction mechanism.

Both the presence of Poole-Frenkel behaviour and the occurrence of a peak in the photoresponse of the passive films at exactly the same bend bending indicate that the material probed is the same in all cases. The presence of the Urbach behaviour indicates that the passive film is highly doped and probably amorphous.

In summary, therefore, passivity in the Fe-Cr alloy system is due to a compact passive film. This passive film consists of an inner Cr oxide layer, on which an outer Fe oxide
layer is found as is schematically illustrated in figure [7.10.50.] The outer Fe oxide layer is present even in very acidic solutions, where the dissolution rate of the pure elemental iron is much greater than that of the Cr. The bulk oxide to which the outer layer most closely corresponds to is $\alpha$-Fe$_2$O$_3$. Doping of the Fe oxide over layer by Cr ions gives rise to increased band bending in the passive regime as the Cr concentration in the alloy is increased. The increased band bending sets up an electric field that has been postulated by other investigators to inhibit the further dissolution of metal cations [Burleigh 1985]. The latter may explain the presence of the Fe oxide over layer in very acidic solutions, where iron oxide is thermodynamically unstable, and is expected to dissolve.
7.9. Tables - Photoelectrochemical measurements
Table [7.9.1.] $E_g$ for 5-30 wt% Cr, Fe-Cr alloys and Fe in a 0.1 M borate buffer. Film formation potential 0.75 V versus SCE.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.89</td>
</tr>
<tr>
<td>5</td>
<td>1.89</td>
</tr>
<tr>
<td>7.5</td>
<td>1.94</td>
</tr>
<tr>
<td>10</td>
<td>1.85</td>
</tr>
<tr>
<td>12.5</td>
<td>1.89</td>
</tr>
<tr>
<td>15</td>
<td>1.89</td>
</tr>
<tr>
<td>30</td>
<td>1.90</td>
</tr>
</tbody>
</table>

Table [7.9.2.] $E_{fb}$ values for 10-30 wt% Cr, Fe-Cr alloys and Fe in a 0.1 M borate buffer.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$E_{fb}$ (up)</th>
<th>$E_{fb}$ (do)</th>
<th>$E_{fb}$ (avg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.49</td>
<td>0.43</td>
<td>0.46</td>
</tr>
<tr>
<td>10</td>
<td>0.36</td>
<td>0.19</td>
<td>0.29</td>
</tr>
<tr>
<td>15</td>
<td>0.27</td>
<td>0.10</td>
<td>0.19</td>
</tr>
<tr>
<td>30</td>
<td>0.01</td>
<td>-0.05</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

Table [7.9.3.] Potential difference between $E_{fb}$ and $E_{peak}$, for 10-30 wt% Cr, Fe-Cr alloys and Fe in a 0.1 M borate buffer.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$E_{fb}$ (up)</th>
<th>$E_{peak}$ (up)</th>
<th>$E_{fb}$-$E_{peak}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.49</td>
<td>0.70</td>
<td>0.21</td>
</tr>
<tr>
<td>10</td>
<td>0.36</td>
<td>0.65</td>
<td>0.29</td>
</tr>
<tr>
<td>15</td>
<td>0.27</td>
<td>0.50</td>
<td>0.23</td>
</tr>
<tr>
<td>30</td>
<td>0.01</td>
<td>0.30</td>
<td>0.29</td>
</tr>
</tbody>
</table>
7.10. Figures - Photoelectrochemical measurements
Figure [7.10.1.] Electrode design for photoelectrochemical measurements.
Figure [7.10.2.] Schematic diagram of the electrochemical cell used for the photoelectrochemical measurements.
Figure [7.10.3.] Irradiance curve for the Hanovia 901-B1 200 W Hg(Xe) lamp, used for photoelectrochemical experiments.
Figure [7.10.4.] Schematic diagram of the photoelectrochemical experimental set up.
Figure [7.10.5.] Plot of photocurrent versus light intensity for Fe in a 0.1 M borate buffer. Film formation potential 0.75 V versus SCE.
Figure [7.10.6.] Plot of normalized $i_{ph}$ versus photon energy for 5-30 wt% Cr, Fe-Cr alloys and Fe in a 0.1 M borate buffer. Film formation potential 0.75 V versus SCE.
Figure [7.10.7.]  Plot of dimensionless $i_{ph}$ versus photon energy for 5-30 wt% Cr, Fe-Cr alloys and Fe in a 0.1 M borate buffer. Film formation potential 0.75 V versus SCE.
Figure [7.10.8.] Plots of dimensionless $i_{ph}$ versus photon energy for Fe in a 0.1 M borate buffer at various film formation potentials.
Figure [7.10.9.] Plots of dimensionless $i_{ph}$ versus photon energy for 5 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer at various film formation potentials.
Figure [7.10.10.]  Plots of dimensionless \( i_{ph} \) versus photon energy for Fe in a 0.1 M borate buffer and in 0.5 M \( \text{H}_2\text{SO}_4 \).
Figure [7.10.11.] Plots of dimensionless $i_{ph}$ versus photon energy for a 5 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer and in 0.5 M $H_2SO_4$. 

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Figure [7.10.12.] Plots of dimensionless $i_{ph}$ versus photon energy for a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer and in 0.5 M H$_2$SO$_4$. 
Figure [7.10.13.] Plots of normalized $i_{ph}$ versus photon energy for 5 wt% Cr alloy in a 0.1 M borate buffer at various film formation times.
Figure [7.10.14.] Plots of dimensionless $i_{ph}$ versus photon energy for 5 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer at various film formation times.
Figure [7.10.15.] Plots of normalized $i_{ph}$ versus $E$ for Fe in a 0.1 M borate buffer. Data for the 'up' scan of cyclic voltammetry at 10 mV/s between -0.35 and 0.95 V versus SCE.
Figure [7.10.16.] Plots of normalized $i_{ph}$ versus $E$ for Fe in a 0.1 M borate buffer. Data for the 'down' scan of cyclic voltammetry at 10 mV/s between -0.35 and 0.95 V versus SCE.
Figure [7.10.17.] Plots of normalized $i_{ph}$ versus $E$ for a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. Data for the ‘up’ scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.18.] Plots of normalized $i_{ph}$ versus $E$ for a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. Data for the ‘down’ scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.19.] Plots of normalized $i_{ph}$ versus $E$ for a 15 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. Data for the ‘up’ scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.20.] Plots of normalized $i_{ph}$ versus $E$ for a 15 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. Data for the 'down' scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.21.] Data transformation to present data from the cyclic voltammetry photocurrent measurements on the same coordinates as the results from the pseudo steady state measurements.
Figure [7.10.22.] Comparison of dimensionless $i_{ph}$ for Fe by PSS method (line) and for Fe during the 'up' scan of cyclic voltammetry (dots).
Figure [7.10.23.] Comparison of dimensionless $i_{ph}$ for Fe by PSS method (line) and for Fe during the ‘down’ scan of cyclic voltammetry (dots).
Figure [7.10.24.] Comparison of dimensionless $i_{ph}$ for Fe by PSS method (line) and for a 10 wt% Cr, Fe-Cr alloy during the ‘up’ scan of cyclic voltammetry (dots).
Figure [7.10.25.]  Comparison of dimensionless $i_{ph}$ for Fe by PSS method (line) and for a 10 wt% Cr, Fe-Cr alloy during the ‘down’ scan of cyclic voltammetry (dots).
Figure [7.10.26.] Plots of dimensionless \( i_{ph} \) versus \( E \) for Fe in a 0.1 M borate buffer. Data acquired during the 'up' scan of cyclic voltammetry at 10 mV/s between -0.35 and 0.95 V versus SCE.
Figure [7.10.27.] Plots of dimensionless $i_{ph}$ versus $E$ for Fe in a 0.1 M borate buffer. Data acquired during the ‘down’ scan of cyclic voltammetry at 10 mV/s between -0.35 and 0.95 V versus SCE.
Figure [7.10.28.] Plots of dimensionless $i_{ph}$ versus $E$ for a 10 wt% Cr, Fe–Cr alloy in a 0.1 M borate buffer. Data acquired during the 'up' scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.29.] Plots of dimensionless $i_{ph}$ versus $E$ for a 10 wt% Cr, Fe–Cr alloy in a 0.1 M borate buffer. Data acquired during the 'down' scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.30.]  Plots of dimensionless \( i_{ph} \) versus \( E \) for a 15 wt% Cr, Fe–Cr alloy in a 0.1 M borate buffer. Data acquired during the ‘up’ scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.31.] Plots of dimensionless $i_{ph}$ versus $E$ for a 15 wt% Cr, Fe–Cr alloy in a 0.1 M borate buffer. Data acquired during the 'down' scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.32.] Plots of dimensionless $i_{\text{ph}}$ versus $E$ for a 30 wt% Cr, Fe–Cr alloy in a 0.1 M borate buffer. Data acquired during the ‘up’ scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.33.] Plots of dimensionless $i_{ph}$ versus $E$ for a 30 wt% Cr, Fe–Cr alloy in a 0.1 M borate buffer. Data acquired during the ‘down’ scan of cyclic voltammetry at 10 mV/s between -0.45 and 0.95 V versus SCE.
Figure [7.10.34.] Plot of \((i_{ph} \times h\nu)^{1/2}\) versus photon energy for 5-30 wt% Cr, Fe-Cr alloys and Fe in a 0.1 M borate buffer. Film formation potential 0.75 V versus SCE.
Figure [7.10.35.] $i_{ph}^2$ versus E for Fe in a 0.1 M borate buffer. Cyclic voltammetry was at 10 mV/s between -0.35 and 0.95 V versus SCE. Average value for all the wavelengths investigated shown.
Figure [7.10.36.]  $i_{ph}^2$ versus $E$ for a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. Cyclic voltammetry was at 10 mV/s between -0.45 and 0.95 V versus SCE. Average value for all the wavelengths investigated shown.
Figure [7.10.37.] $i_{ph}^2$ versus $E$ for a 15 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. Cyclic voltammetry was at 10 mV/s between -0.45 and 0.95 V versus SCE. Average value for all the wavelengths investigated shown.
Figure [7.10.38.] $i_{ph}^2$ versus $E$ for a 30 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer. Cyclic voltammetry was at 10 mV/s between -0.45 and 0.95 V versus SCE. Average value for all the wavelengths investigated shown.
Figure [7.10.39.] $E_{fb}$ for Fe, 5-30 wt% Cr, Fe-Cr alloys as well as Cr in a 0.1 M borate buffer from impedance measurements at 100 Hz (filled circles) and from photoelectrochemistry (open circles).
Figure [7.10.40.] Schematic diagram of the coulombic well that surrounds the localised state, showed with and without an applied field F [Mott 1971].
Figure [7.10.41.] Plot of log(i_{ph}) versus (E - E_{fb})^{1/2} as a function of wavelength for Fe, 10, 15 and 30 wt% Cr, Fe-Cr alloys, showing Poole-Frenkel behaviour.
Figure [7.10.42.] Comparison of the polarisation characteristics of Fe in a 0.1 M borate buffer, with $i_{ph}$ from the ‘up’ scan at 10 mV/s between -0.35 and 0.95 V versus SCE. $\lambda = 350$ nm.
Figure [7.10.43.] Comparison of the polarisation characteristics of a 10 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer, with $i_{ph}$ from the 'up' scan at 10 mV/s between -0.45 and 0.95 V versus SCE. $\lambda = 350$ nm.
Figure [7.10.44.] Comparison of the polarisation characteristics of a 15 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer, with $i_{ph}$ from the ‘up’ scan at 10 mV/s between -0.45 and 0.95 V versus SCE. $\lambda = 350$ nm.
Figure [7.10.45.] Comparison of the polarisation characteristics of a 30 wt% Cr, Fe-Cr alloy in a 0.1 M borate buffer, with $i_{ph}$ from the ‘up’ scan at 10 mV/s between -0.45 and 0.95 V versus SCE. $\lambda = 350$ nm.
Figure [7.10.46.] Plot of $\log(i_{ph})$ versus photon energy for 5-30 wt% Cr, Fe-Cr alloys and Fe in a 0.1 M borate buffer. Film formation potential 0.75 V versus SCE.
Figure [7.10.47.] Variation in the average cluster size $s_{av}$ with variation in the fraction Cr in the matrix, near the percolation threshold. Percolation threshold of 9.5 at% Cr assumed.
Variation in the magnitude of the photoresponse as a function of the Cr content in the alloy, showing that no sudden discontinuity occurs at the 12.5% level.
Downwards band bending

Upwards band bending

Figure [7.10.49.] Schematic diagram of the band bending and flat band potentials $E_{fb}$, for Fe, 5-30 wt% Cr, Fe-Cr alloys in a 0.1 M borate buffer.
Figure [7.10.50.] Schematic diagram of the bi-layer structure of the passive film formed on Fe-Cr alloys.
8. A model for passivity in the Fe-Cr system

8.1. Existence of an outer Fe enriched layer

In the preceding discussions it has been shown that the passive film on Fe-Cr alloys consist of a bi-layer structure, consisting of an outer Fe enriched ‘α-Fe₂O₃ like’ phase, and an inner Cr enriched, most likely ‘Cr₂O₃ like’ phase. As has been shown, this bi-layer structure is present, even under conditions where the outer ‘α-Fe₂O₃ like’ phase is kinetically unstable, and is not expected to be present. Chao and Macdonald [Chao 1981] have postulated that such a film might be formed by re-precipitation from the solution. Chao reasoned that, because the passive film oxide is much more defected than the pure crystalline oxide, the free energy of the passive film is correspondingly higher than the free energy of the perfect crystal. Parallel to the higher free energy of the passive film, the equilibrium ionic concentration in the solution at such a passive film interface, will be at higher concentrations than for a perfect crystal. Chao therefore postulates that the ions will tend to re-precipitate to form a highly crystalline (low defect) over film. In the present investigation, however, it has been shown that the over films, as detected by the photoelectrochemical measurements, are highly doped, and therefore most likely highly defective. In addition, it has been demonstrated in §[7.7.1.5.] that the over film shows distinct Urbach tail behaviour. Urbach behaviour is normally associated with amorphous or highly defected semiconductors, and therefore it would seem that the suggestion that the over film is highly crystalline is not supported.

8.2. Protective characteristics of the passive film

8.2.1. Electronic properties

It has been indicated in §[7.] that the passive film on Fe-Cr alloys consists of a bi-layer structure, with the top layer being ‘α-Fe₂O₃’ like, and exhibiting an n-type conduction mechanism. It has also been shown in §[3.5.] that the inner layer of the passive film on alloys containing high amounts of Cr is most likely a semiconducting phase with a p-type conduction mechanism. The passive film on Fe-Cr therefore most likely contains a diffuse...
p-n semiconductor heterojunction. The band structure of such a p-n heterojunction is shown in figure [8.4.1].

It can be illustrated by the oxidation/reduction of single electron transfer redox couples at the passive film/electrolyte interface that the transfer of electrons through the passive film is not the rate limiting step, but that electrons can be transferred through the oxide film to/from the redox couple at rates greatly exceeding the electron flux at steady state passive conditions. Investigations of redox couples on Fe, Fe-Cr and Cr have shown that electron transfer through these passive films can be driven at rates exceeding the rate of electron transfer at steady state passive conditions [Prazak 1976, Schultze 1978]. Despite the interesting current-voltage characteristics of such heterojunctions, the transport of electrons and/or holes across the semiconductor passive film is, therefore, considered to be rapid. It is consequently concluded that ionic transport properties of the passive film has to be investigated in order to determine the rate limiting steps for the formation and dissolution of the passive film.

8.2.2. Oxygen vacancies and film growth

The following discussion will aim at linking the electronic structure of the passive film, as determined by the photoelectrochemical and impedance measurements, with the ionic defect structure of the passive film. It is hoped that by considering these two aspects of the passive film in tandem, instead of separately, as has been the case in investigations up to now, an enhanced understanding of the nature of protection by passive films will ensue so that, by reasoning in this manner, a model that both accounts for the existence of the bi-layer structure, as well as the increased corrosion resistance of alloys containing increased amounts of Cr can be formulated.

The electronic structure of the passive film should firstly be considered, particularly the concentration of holes and electrons in the semiconductor at a specific temperature. The creation of an electron-hole pair may be treated as an ionization reaction:

\[
\text{Lattice} \leftrightarrow \text{e}^- + \text{h}^+ \quad [8.1.]
\]
The quantity $n$, denotes the electron concentration in the semiconductor, while $p$ denotes the hole concentration. The product of the $n$ and $p$ depends on the value of $E_g$, and for each material has a specific value, $K_{sc}$ at constant temperature, $T$. $K_{sc}$ is therefore a material property.

$$np = K_{sc}$$ [8.2.]

If the semiconductor is an intrinsic one, the concentration of the holes and the electrons are equal:

$$n = p = K_{sc}^{1/2}$$ [8.3.]

If an electron donor is now added to the intrinsic semiconductor, we may get a release of electrons into the system. As an example consider:

$$\text{Cr}^{3+} \leftrightarrow \text{Cr}^{4+} + \epsilon$$ [8.4.]

The $K_{sc}$ value is still unchanged (because the temperature is constant), thus the product $np$ stays fixed. The concentration of holes in the system is thus decreased by the addition of an electron donor. If the addition of the ionization compound controls the electron concentration, the number of holes are then given by:

$$h = K_{sc}/[\text{Cr}^{4+}]$$ [8.5.]

In an analogous manner, the addition of an electron acceptor will increase the hole population, with a corresponding decrease in the electron population. The changes in the relative numbers of holes and electrons with addition of an electron donor or electron acceptor are illustrated in figure [8.4.2.]. Note that the areas indicating the concentration of holes and electrons in this figure are not to scale. Typically the concentrations of holes and electrons in a doped semiconductor differ by several orders of magnitude from each other, with the result that it is difficult to visually represent. If drawn to scale, the ratio of the
areas would, therefore, be much greater. The condition for charge neutrality in such a doped system changes from that described by equation [8.1.] to:

\[ n + N_a = p + N_d \]  \[8.6.\]

Consider the addition of an electron donor such as described by equation [8.4.], to an intrinsic semiconductor. Doping in the above manner, will result in the introduction of donor states near the conduction band edge. As a result of this change in the average state of the electrons, the Fermi level, which is midway in the gap for an undoped semiconductor, is moved closer to the conduction band edge. The Fermi level directly influences the work function of the semiconductor \( E_w \), which is just the difference between the initial position of the Fermi level and the height of the surface potential barrier. It is consequently concluded that if the Fermi level is moved towards the conduction band, the effective work function of the material is lowered.

The process that occurs when a semiconductor is contacted with an electrolyte must be examined. Because the Fermi level is analogous to a chemical potential, it is known that, after contacting, the Fermi levels of the electrolyte and the Fermi level of the semiconductor must line up. This equilibration of the Fermi levels is accomplished by electron transfer from the phase with the lower work function to the material with the higher work function. The amount of charge transferred depends on the difference between the work functions of the two phases. The charge transfer process in turn sets up a space charge layer at the interface, the magnitude of which depends on the difference between the work functions of the two contacted phases.

It has been shown above that the work function depends on the Fermi level, therefore, it follows that (for the case where the work function of the electrolyte is greater than the work function of the semiconductor), the more n-type the semiconductor is doped, the greater the electron transfer from the semiconductor to the electrolyte. Greater electron transfer in turn implies a greater space charge layer that forms at the interface semiconductor/electrolyte. This process is schematically illustrated in figure [8.4.3.].
The flat band potential, $E_{fb}$, is the potential at which the bands are bent completely flat, and where the depletion layer described above ceases to exist. The greater the depletion layer that is formed upon contact (due to the differences in the work functions between the contacted phases), the more negative the potential that has to be externally applied to bend the bands flat ie. the lower $E_{fb}$. It follows that the more n-type the semiconductor is doped, the lower (ie. more negative on the SCE scale) the flat band potential for the semiconductor under otherwise identical conditions.

The above discussion must now be considered in terms of the data acquired for the passive films on Fe-Cr alloys. It has been shown in §[7.] that the outer part of the passive film consists of an ‘α-Fe$_2$O$_3$ like’ phase, and that this phase is present in both acidic (where pure Fe oxides are expected to be thermodynamically unstable) and basic electrolytes. In figure [7.10.39.], however, it was shown that the $E_{fb}$ of the passive film on these alloys are shifted downwards as a function of the wt% Cr in the base alloy. As indicated in the above discussion, the latter shift is due to increasingly n-type doping of the outer part of the passive film by an ionic species with a higher valence state than the 3+ valence state of the Fe ions in the matrix of the ‘α-Fe$_2$O$_3$ like’ phase. Since the amount of doping is a function of the Cr concentration in the alloy, the doping must be by (a) Cr oxide specie(s), most likely by a reaction analogous to equation [8.4.]. It can, therefore, be concluded that the outer part of the passive film is doped increasingly n-type as the Cr concentration in the alloy is increased. The doping is by a Cr oxide species in which the Cr has a valence state higher than 3+.

The mechanism by which n-type doping may increase the corrosion resistance of the outer part of the passive film has to be investigated. Existing evidence in the literature indicates that α-Fe$_2$O$_3$ may be doped both n and p type [Morin 1954, Tannhauser 1962, Acket 1966, Van Daal 1967, Benjelloun 1984], so that the observed n-type behaviour is not out of line with what is expected. In the following discussion, the species Cr$^{4+}$ will be assumed as the dopant, because the potential regime in which the n-type doping is observed is well below the potential regime in which Cr$^{6+}$ is thermodynamically expected to be present in the passive film. It must be kept in mind, however, that the bulk thermodynamics do not always hold well for high surface area to volume ratios such as
typically encountered in the study of passive films, so that Cr\textsuperscript{6+} may be present in the passive films in the potential regimes investigated. Evidence of Cr\textsuperscript{4+} species has also been observed to be present in the passive film on pure Cr at intermediate potentials in the passive regime by Moffat [Moffat 1989], who examined the passive film on Cr by means of angular resolved XPS. Halada [Halada 1988] indicated that the Cr\textsuperscript{4+} species may be due to the photoreduction of Cr\textsuperscript{6+} species during the XPS measurement. Photoreduction may lead to an under-determination of the Cr\textsuperscript{6+} species. The nett effect of the higher valence state species in the lower valence state matrix, however, remains the same, so that the derivation that follows is equally applicable if an oxide in which the oxidation state is Cr\textsuperscript{6+} instead of Cr\textsuperscript{4+} is assumed as the dopant.

The relationship between the electron and the point defect densities is an important aspect of semiconductor electrochemistry. Consider as an example the doping of Fe\textsubscript{2}O\textsubscript{3} by CrO\textsubscript{2}. Fe\textsubscript{2}O\textsubscript{3} is an oxygen deficient material [Gardner 1963]. The dominant defect concentration is, thus, expected to be doubly charged oxygen vacancies. Addition of an oxide with the metal cation oxidized to a higher valence state to an oxygen deficient oxide such as above, will decrease the concentration of doubly charged oxygen vacancies (see for example Kofstad [Kofstad 1988] p. 51). It is expected that, if a high enough concentration of this n-type dopant is added to the matrix, the electron density will be controlled by the addition of this dopant, according to reaction [8.4.] above. The equality \( n = \text{Cr}\textsuperscript{4+} \) will therefore hold. At the same time the oxygen vacancy concentration is controlled by:

\[
2 \text{CrO}_2 + \text{Fe}_2\text{O}_3 \rightarrow 2 \text{Cr}_\text{Fe} + 3 \text{O}_0 + \frac{1}{2} \text{O}_2 + 2\, \varepsilon
\]

and

\[
\text{O}_0 \rightarrow \frac{1}{2} \text{O}_2 + \text{V}_0^\text{\textsuperscript{\textcircled{\textbullet}}} + 2\, \varepsilon
\] \[8.7.\]

From the Schottky equilibrium:

\[
\text{null} \leftrightarrow 2\, \text{V}_{\text{Fe}}^\text{\textsuperscript{\textcircled{\textbullet}}} + 3\, \text{V}_0^\text{\textsuperscript{\textcircled{\textbullet}}}
\] \[8.8.\]
For equation [8.8.] the equilibrium constant, $K_{\text{Schottky}}$ can be written:

$$K_{\text{Schottky}} = \left[ \frac{V_O}{V_{Fe}} \right]^2$$

[8.9.]

If the concentration of $V_O^{..}$ is controlled by reaction [8.7.], then, according to reaction [8.9.], in which $K_{\text{Schottky}}$ has to remain constant, the concentration of $V_{Fe}'$ will go up. The above discussion shows that the concentration of the oxygen anion vacancies decrease when the ‘$\alpha$-Fe$_2$O$_3$ like’ outer part of the passive film is doped to a more n-type state. The point defect concentration change, in turn could have important effects on the passive film formation and breakdown kinetics.

Very little data on the transport properties of anodically formed passive films exist. Experiments at the Chalk River Nuclear Nuclear Laboratories have shown that for all the metals investigated (Al, Hf, Nb, Si, Ta, U, W, Zr), anodic film growth is largely due to anion transport [Davis 1965, Whitton 1968, Brown 1973, Mackintosh 1976, Mackintosh 1977]. No similar data could, however, be found for the transport mechanism in Fe and Fe-Cr based anodically formed films. High temperature investigations of $\alpha$-Fe$_2$O$_3$ have indicated that the oxygen and iron self diffusion coefficients in this material are approximately the same [Reddy 1983]. The latter result can not, however, be expected to extrapolate to room temperature.

Goetz [Goetz 1987] investigated the film growth kinetics of pure iron in borate buffers by $^{18}$O SIMS (secondary ion mass spectroscopy), and concluded that film growth occurs primarily by inward diffusion of oxygen anions. Film growth, thus, occurs at the metal/film interface. If the assumption is made that oxygen anion migration (or equivalently migration of oxygen vacancies in the opposite direction) is responsible for the film growth at the metal/passive film interface, it is expected that the film thickness and film growth kinetics should be a function of the Cr concentration in the base alloy, since the oxygen vacancy concentration in the passive films depends on the amount of Cr in the base alloy. Film growth rate and film thickness should decrease with a reduction in oxygen vacancy concentration. Thinner films are therefore expected on alloys with more Cr.
Figure [8.4.4.], modelled after the work of Chao and Macdonald [Chao 1981, Macdonald 1990], shows the reactions that are expected to give rise to the film growth. The reactions as written assume that (i) the growth of the passive film takes place at the metal/film interface and (ii) ignore passive film dissolution (which will be treated in a subsequent paragraph). Figure [8.4.4.] indicates that the relevant reactions at the metal/film interface are:

\[
\text{Fe} + V_{\text{Fe}}^{	ext{iv}} \rightarrow \text{Fe}_{\text{Fe}} + 3\epsilon \tag{8.10.}
\]

and

\[
\text{Fe} \leftrightarrow \text{Fe}_{\text{Fe}} + \frac{3}{2} V_{\text{O}}^{	ext{v}} + 3\epsilon \tag{8.11.}
\]

The reactions at the passive film/electrolyte interface is:

\[
\text{Fe}_{\text{Fe}} \leftrightarrow \text{Fe}_{\text{aq}}^{3+} + V_{\text{Fe}}^{	ext{iv}} \tag{8.12.}
\]

and

\[
V_{\text{O}}^{\text{v}} + \text{H}_2\text{O} \leftrightarrow \text{O}_2 + 2\text{H}^+ \tag{8.13.}
\]

With the exception of reaction [8.11], all the reactions are conservative, i.e. conserves the lattice, while [8.11.] represents the film formation, and is non-conservative.† Examination of the reactions show that cation vacancies are produced at the film/solution interface, and

† Goetz' experimental evidence presented previously indicates that the passive film is formed primarily at the metal/film interface. It is assumed that the reactions representing film formation at the film/solution interface by diffusion of metal vacancies into the passive film, namely \( \frac{3}{2} \text{O}_2 + 6 \epsilon \leftrightarrow 3 \text{O}_2 + 2 V_{\text{Fe}}^{\text{iv}} \) taking place at the film/solution interface, and \( V_{\text{Fe}}^{\text{iv}} + \text{Fe} \leftrightarrow \text{Fe}_{\text{Fe}} + 3 \epsilon \) taking place at the metal/film interface, occur at very slow rates. The latter two reactions are, therefore, ignored in the analysis.
are consumed at the metal/film interface. At the same time, anion vacancies are produced at the metal/film interface, and are consumed at the film/solution interface. Reaction [8.11.], therefore, describes injection of anion vacancies into the matrix at the metal/film interface, while reaction [8.13.] describes consumption of oxygen anion vacancies at the film/electrolyte interface. Reactions [8.10.] and [8.12.] represent metal vacancy generation and diffusion connected with cation emission from the passive film at the film/electrolyte interface.

The effect of the decreased concentration of oxygen vacancies, such as is the case when the film is doped more n-type has to be considered. Since the film growth is primarily due to the diffusion of oxygen vacancies, it follows that if the concentration of this diffusing species is decreased, the flux will accordingly be smaller, and thus the growth rate of the film will also be reduced. Figure [8.4.5.], taken from the work of Kirchheim [Kirchheim 1989] shows that the film growth rates, as measured by the current passed when a specimen is polarised to a specific point in the passive regime, become lower as the Cr concentration in the base alloy is increased. It is also reported that the thickness of the passive film decreases as the Cr concentration is increased [Sugimoto 1980]. The above observations support the evidence that the concentration of anion vacancies in the passive film control the growth of the passive film, and the postulate that when the concentration of these defects are decreased, the film growth kinetics are slowed down. It can, therefore be reasoned that the lowering of the equilibrium number of oxygen vacancies by n-type doping has the effect of decreasing the passive film growth rate. Note that the data presented do not take into account the dissolution of the passive film, but assume that the majority of the charge passed is stored in the passive film.

8.2.3. Dissolution of the passive film

When analysing the role of the point defects in the passive film, it is important not only to consider the growth of the passive film, but also the dissolution of the passive film. Any model that attempts to explain the protective properties of the passive film, not only has to explain the thin spatial dimension of the passive film (as has been done above), but also has to take into account that the passive film, in order to be protective against corrosion, has to
exhibit a low dissolution rate and low transmission of cations. The latter two characteristics are required in order that the base metal is not consumed.

When the mechanism of dissolution of the passive film metal oxide is investigated, reducing and non-reducing conditions of film dissolution has to be considered. For the material/electrolyte combinations studied, non-reducing conditions are of interest. Zinder [Zinder 1986], examined the dissolution of α-Fe₂O₃ particles in aqueous electrolytes. Under non-reducing conditions, a detachment of a surface metal species can occur subsequent to the polarisation and weakening of the metal-oxygen bonds at the hydrous oxide surface. The weakening can be caused either by protons which are bound to the oxide ions, or by ligands bound to the metal ions. According to Zinder, in the absence of ligands that may bind to the metal oxide centre, the general rate law for proton promoted dissolution is:

\[ R_H = k_H C_H^n \]  

[8.14.]

Where \( R_H \) is the rate of proton-promoted dissolution (moles m\(^{-2}\) h\(^{-1}\)), \( k_H \) is the reaction constant, \( C_H \) the surface concentration of protons (moles m\(^{-2}\)), and \( n \) the number of protons per metal centre required for weakening of the metal-oxygen bonds. The surface protonation reaction is fast [Vetter 1954, Weil 1955, Zinder 1986], so that for the dissolution reaction, it is (one of) the removal step(s) that is rate limiting. The slow step is likely the removal of the metal centre from the surface after protonation. In the present case, under non-reducing conditions, the overall reaction for passive film dissolution is:

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

[8.15.]

The reaction thus consists of the concerted removal of both the oxygen and adjacent metal ions [Macdonald 1990], and is therefore not lattice conservative.

Reactions [8.10.] and [8.12.] which describes metal cation transport through the passive film, followed by ejection at the film/electrolyte interface, and reaction [8.15.] which details removal of the oxide passive film, describe the total metal loss, and thus the corrosion rate.
of the alloy under interest. At steady state, the thickness of the passive film is expected to be constant, and the rate of oxide loss due to dissolution balances film growth. Reactions [8.11.] and [8.13.] describe film growth, and the rate at which these reactions proceed at steady state, therefore describes one component of the passive current density, namely the amount of oxide dissolved.

Transmission of cations through the metal film is the other component of the passive current density. As can be seen from reactions [8.10.] and [8.12.], the transmission of cations through the passive film is not expected to be pH dependent, since H⁺ or OH⁻ is not among the reacting species. As has been shown in §[5.], the measured passive current density is strongly dependent on the pH. The passive density greatly increases as the pH of the solution is decreased. The component of the passive current measured that is expected to be strongly pH dependent is the dissolution of the metal oxide. The effect of a pH change can be seen in reaction [8.15.], where it can be seen that the dissolution of the metal oxide is favoured with an increase in the H⁺ concentration (reaction shifted right). The latter result indicates that the majority of the measured passive current is not due to cation transmission, but rather to oxide dissolution, controlled by a pH dependent rate law such as [8.14.].

Additional supporting evidence for the hypothesis that the greater part of the passive current density at steady state is due to oxide dissolution also comes from considering reactions [8.10.] and [8.12.]. It has been shown earlier that the concentration of oxide vacancies decrease as the passive film is doped more n-type. Due to the equilibrium constant given in [8.9.], this implies that the metal vacancy concentration is increased. An increase in the equilibrium metal vacancy concentration suggest, that for the diffusionally controlled reactions [8.10.] and [8.12.], the rates of reaction will increase. An increase in the rates of reactions of [8.10.] and [8.12.] in turn will be measurable as an increase in the passive current density with an increase in the n-type character of the passive film. Experimentally, however, it has been shown that the passive current density does not increase as the film is doped more n-type, indicating that the metal vacancy diffusion rate is slow compared to the oxygen vacancy diffusion rate. Cation transmission through the passive film is, therefore, not an important contribution to the passive current density, and the bulk of the passive
current density is thus due to the chemical dissolution of the oxide film by a pH dependent rate law. Only under conditions where the dissolution of the passive oxide film is very slow, is cation transmission expected to contribute a significant portion of the passive current density.

The question as to why addition of Cr to the passive film results in slower chemical dissolution kinetics of the passive film oxide phase, in addition to influencing the growth kinetics, as has been described above, becomes the final point for consideration. A possible hypothesis follows. The neutral media $K_{sp}$ values of the relevant bulk oxides are: $K_{sp}(Fe_2O_3) < K_{sp}(Cr_2O_3) << K_{sp}(Fe_3O_4)$. It has also been indicated in §[3.4.3.] that the bulk oxide $Fe_2O_3$ cannot exist in equilibrium with the Fe metal substrate, so that a gradient of $Fe_3O_4$ must be present in the passive film on pure iron. The stoichiometry of the phase in contact is a function of the temperature [Vetter 1962]. The $Fe_3O_4$ is, as has been indicated above, much more soluble than the $Fe_2O_3$, so that the passive film is expected to be much less resistant to dissolution than would be the case if a pure $Fe_2O_3$ film is considered.

Consider now the case when Cr is added to the metal. Addition of this Cr species makes possible the elimination of $Fe_3O_4$ by $Cr_2O_3$ that is much less soluble than the $Fe_3O_4$. The addition of $Cr_2O_3$ to the passive film, thus, has the effect of making it more resistant to corrosion by eliminating the lower oxidised Fe species from the passive film, so that the addition of Cr in the alloy is expected to decrease the corrosion rate. The slightly greater solubility of $Cr_2O_3$ as compared to $Fe_2O_3$ can explain why the Cr is found to be depleted in the outermost layer of the passive film. The $Cr_2O_3$, while much more resistant against dissolution than the $Fe_3O_4$, is still more soluble than the pure $Fe_2O_3$, so that it is depleted in the very outermost layer by dissolution. The bi-layer structure observed experimentally results, so that the passive film consists of an inner Cr enriched, and an outer Fe enriched layer.

It must be kept in mind, however, that the properties of the bulk oxides cannot easily be extended to the complex situation that exists in the passive film, so that further investigation of the passive film is needed, to determine the change in the amount of $Fe_3O_4$, and
consequent change in solubility with the addition of increasing amounts of Cr to the alloy. It is also not possible at this time to explain why the outer layer is enriched in Fe even in acidic solutions where Fe$_2$O$_3$ is unstable.

8.3. Final observations

The results from this investigation have shown that an intimate relationship exists between the structural, electronic and transport properties of passive films. The main limitation in the analysis of the acquired data is the availability in transport data for passive films. The acquisition of such data is difficult because of the small spatial dimension of passive films, and of the relatively low temperatures at which the transport data are required. It is hoped that the relationships between chemistry, electronic and transport parameters illustrated in this thesis will encourage other investigators to examine transport properties of passive films.
8.4 Figures - Conclusions
Figure [8.4.1.] Schematic illustration of the p-n heterojunction likely present in the passive film on Fe-Cr alloys.
Figure [8.4.2.] Changes in the hole and electron population with n-type doping of the passive film. From Sze [Sze 1980].
Figure [8.4.3.] Changes in $E_F$ and $D_{se}$ with n-type doping of the passive film. (a) $E_F$ before contacting. (b) $E_F$ and bending for undoped semiconductor. (c) $E_F$ and bending for n-type doped semiconductor.
Figure [8.4.4.] Schematic diagram of the physico-chemical processes that occur within a passive film. After Macdonald [Macdonald 1990].
Current transients for a potential step from the active regime to midway in the passive regime, showing that the current density decreases as the Cr concentration of the alloy increases. From Kirchheim [Kirchheim 1989].
9. CONCLUSIONS

9.1. DC and open circuit experiments

1. The Uhlig explanation of a critical transition is by electronic theory of the catalysing surface. The d-orbital model relates the electronic structure of the catalysing surface to a hydrodynamically controlled parameter, namely the diffusion limited oxygen reduction reaction current density, and is therefore not believed to be an accurate description.

2. No transition of the type as predicted by the percolation model occurs for alloys with the amounts of Cr under the conditions investigated, and the percolation model is therefore not thought to be operative.

3. Spontaneous passivity of the alloys in the Fe-Cr system is usually associated with the diffusionally limited oxygen cathodic reduction reaction. The limiting current density of this reaction normally places the limitation on which alloys will passivate and which will not. Under natural convection the latter observation implies that only if \( i_{\text{crit}} < i_{\text{oxidiff}} = 2.4 \times 10^{-4} \text{ A/cm}^2 \), can the alloy passivate spontaneously.

4. Under different hydrodynamic conditions, the magnitude of the diffusion limited current density will be different, and consequently the wt% Cr at which spontaneous passivity will vary.

9.2. Impedance measurements

1. The entire passive film is electronically conductive and behaves like a highly doped semiconductor. Progressive formation of a growing depletion layer with increases in potential is responsible for the observed capacitance behaviour.

2. The semiconductor model for the passive film on Fe is applicable also to Fe-Cr alloys. The passive films behave like highly doped, n-type semiconductors.

3. The passive film on Fe-Cr alloys comprises an inner Cr enriched layer and an outer Fe enriched layer.
9.3. Photoelectrochemistry

1. The same ‘α-Fe₂O₃-like’ phase exists in the passive film on all the alloys, however, the quantity of this phase decreases as the amount of Cr in the base alloy increases.
2. The amount of the ‘α-Fe₂O₃-like’ phase varied linearly with the amount of Cr in the alloy, ruling out establishment of passivity by the percolation model.
3. The photoresponse of the passive film on pure Cr was below the detection limits of the experimental set-up employed.
4. The ‘α-Fe₂O₃-like’ outer layer is present even at very long polarisation times, and does not dissolve due to the greater mobility of Fe as compared with Cr.
5. Comparison of the capacitance and photoelectrochemical data indicates that the passive films consist of an outer α-Fe₂O₃ like layer on top of an inner Cr enriched film.
6. The presence of the Urbach behaviour indicates that the passive film is highly doped and probably amorphous.

9.4. A model for passivity Fe-Cr system

1. The electronic and structural properties of the passive films were shown to be intimately related.
2. The outer part of the passive film is progressively doped more n-type by Cr⁴⁺ or Cr⁶⁺ species as the [Cr] in the base alloy is increased.
3. Increased n-type doping decreases the number of oxygen vacancies, which in turn decreases the film growth rate and steady state film thicknesses.
4. The passive current density was shown to consist of two parts (i) a part associated with cation transmission through the passive film, and (ii) a portion associated with dissolution of the oxide passive film.
5. The passive current density is largely due to the dissolution of the oxide based passive film.
10. RECOMMENDATIONS FOR FUTURE WORK

10.1. Modifications in experimental technique and equipment

10.1.1. Experimental method

If the data treatment procedure for the photoelectrochemical spectroscopy given in §[12.1.4.] is considered, it is immediately obvious that the sensitivity of the experimental set up is affected by the magnitude of $I_{\text{max}}$, the full scale range setting on the potentiostat. The current density can be fairly high in the prepassive, secondary passive, or transpassive regimes. In practice, the sensitivity of the photoelectrochemical set-up is degraded so much that an accurate measurement of the photocurrent becomes impossible for systems in which the photon efficiency is low. As a consequence of this low sensitivity, this method can usually only access information in the passive regime itself for systems that have low photon efficiencies.

Another method of accessing electronic characteristics of passive films in situ is by measuring the reflected portion of an incident light beam. As indicated in §[7.7.], Searson [Searson 1988] replotted Azumi’s [Azumi 1986] modulation spectroscopy results, and found that the light reflection, which is the complement to the light absorption, is proportional to the photocurrent. The reflectance measurement, therefore, provides the same type of information as the photocurrent measurement. The same result from the two kinds of experiments is expected from the theoretical derivation given in §[12.2.3.], provided that the film is thin and the absorption coefficient, $\alpha$, is not too high.

Modulation reflectance spectroscopy [Hara 1979, Azumi 1986, Simoes 1990] is not limited to accessing information on the band structure of the passive film solely when the Faradayic currents are very low. The measured signal is not carried in the current signal, but rather in the light reflected, so that an increase in the current does not automatically mean a decrease in the sensitivity of the experimental set up. The drawback of this method, however, is that the experiment must be carried out in a dark box. There is also an increased sensitivity to the specimen surface condition. It is likely, however, that the
advantages of a proper reflectance set up would outweigh the disadvantages. It is suggested that future experimental work include investigation of this technique, as the experimental apparatus consists of the same main components employed in the photoelectrochemical set up. Modulation reflectance experiments would therefore not imply additional equipment expenses, making this technique very attractive.

10.1.2. Experimental apparatus

From the determination of the light throughput of the experimental system given in §[12.1.4.], it is clear that the light throughput of the current experimental system is severely limited in the UV regime. The main factor contributing to this cut off is the monochromator used in this study, which was an old prism type. From the results of Hara [Hara 1979], it is clear that many interesting features, including strong absorption peaks, exist for both Fe, Cr and their alloys at photon energies in the UV range. Replacement of the prism monochromator with a modern grating monochromator would greatly increase the usability of the system, with a view towards exploring the photoresponse features at higher photon energies. The addition of a drive unit to allow computer control of the monochromator would enable automated wavelength scanning, and would greatly facilitate the implementation of wavelength dependent measurements.

10.2. Future work on passive films in the Fe-Cr system

10.2.1. Transport properties of passive films

As indicated in §[8.2.], the absence of data on the relative mobility of Fe and O species in the passive film limits the analysis of the experimental data. It is proposed that studies similar to that carried out by Mackintosh and Plattner [Mackintosh 1977] is carried out to determine the mobile species during anodic film formation. Identification of the mobile species can be accomplished by implanting markers of inert noble gas ions by low energy ion implantation. The marker locations is then precisely determined by a technique such as Rutherford backscattering. The metallic specimen is then anodically oxidized to the desired film thickness in the electrolyte under interest, and the position of the markers may then be
again determined. In this manner it may be determined if the film growth occurs at the film/electrolyte interface, or at the metal/film interface. By the above discussed technique, it may be assured that the assumption that was made, namely that the film growth occurs at the metal/film interface in the Fe-Cr alloy system is in fact correct. A very powerful supporting technique to determine the mobile species during oxide growth is to carry out oxygen isotope studies coupled with SIMS analysis to determine the distribution of tagged oxygen atoms in the passive film, similar to the work of Goetz [Goetz 1987]. By a comparison of the two techniques as a function of the Cr concentration of the alloy, a good idea of the mobilities of Fe and O in the passive film can be obtained.

10.2.2. Photoelectrochemical / Reflectance spectroscopy

As indicated in §[10.1.], technique and equipment limitations have restricted the current investigation to films within the passive regime, and to low photon energies. It is proposed that with the modification to the technique and the experimental apparatus proposed above, the potential regimes and photon energies not accessible in the current examination could be studied. Modification of the experimental technique, as described, will also enable study of the passive films under conditions of film breakdown, where the current densities are normally higher, and the currently used technique consequently suffers from reduced sensitivity.

10.2.3. Investigation by means of redox couples

As is evident from the work presented in this thesis, it is not yet clear whether the passive film on Cr is an n-type or p-type semiconductor, or whether it is an insulator. It is clear from the literature [Metikos-Hukovic 1987, Sunseri 1987, Burleigh 1989, Searson 1990], that due to the thinness of the passive film on Cr, the photocurrent is extremely small. It is, therefore, very difficult to measure the conduction mechanism by means of a photoelectrochemical measurement. Another way to determine the type of semiconductive behaviour is by measuring the kinetics of electron transfer of a well characterized redox couple on the passive film surface. This technique has been applied with success to characterize the passive film on iron [Delnick 1978, Stimming 1979], and a modification of
this technique has been used to characterize the Cr passive film [Moffat 1990]. It is proposed that this technique be used to study the change in behaviour of the passive film as a function of the Cr concentration.

10.3. Related materials - Fe$_2$O$_3$/Cr$_2$O$_3$ oxide electrodes

Preliminary work has shown that the results from pressed and sintered Fe$_2$O$_3$-Cr$_2$O$_3$ electrodes are not reproducible enough to make any conclusions about the type of conduction mechanism which is operating in these materials. A more precise method of making ceramic specimens, as used by Sugimoto [Sugimoto 1985], employs chemical vapour deposition (CVD). It is possible to deposit thin oxide layers on a conducting substrate by the CVD technique. An investigation of a series of Fe$_2$O$_3$-Cr$_2$O$_3$ specimens prepared by CVD under precisely controlled conditions, would be valuable in providing insight into the conduction mechanism of the oxides. These results in turn could be compared to the experimental results obtained in this thesis, and to the results from the experiments as proposed in §[10.2.2].

10.4. Dissolution kinetics of oxide passive films

The work conducted in this thesis showed that the rate limiting step for metal loss from an Fe-Cr alloy, except in cases where the solution is very non-aggressive, is dissolution of the metal oxide at the film/solution interface, and not the transport of metal cations across the passive film. This finding indicates that a large part of future research efforts have to be directed at determining the dissolution kinetics of thin Fe-Cr oxide films and Fe-Cr bulk oxides. Of particular value should be determination of the rate limiting step for oxide dissolution. Experiments that can help in the latter quest include investigation of the effects of attached ligands to the metal centres of the passive film, similar to the work by Zinder [Zinder 1986] on small Fe$_2$O$_3$ particles, but applied to the dissolution kinetics of the passive films.
11. BIBLIOGRAPHY

43. Flade, F., Z. Phys. Chem. 76, 513 (1911).
12.1. Data treatment procedures
12.1.1. Polarisation data treatment

Treatment by the data acquisition program

1. Mains electrical noise elimination

It was determined by use of a Phillips model [PM 3305] oscilloscope that the output of the potentiostat unit had noise pick-up from the electrical mains that manifested itself as a noise source of ~ 20 mV rms at 60 Hz. This noise was not visible when a chart recorder was used to record data, because of the relatively long time constant (response time) of the recorder. Because the NB-MIO 16 data acquisition board typically completes an acquisition in 15 μS, the data values taken were in error. The magnitude of the error depended on where on the noise sine wave (superimposed on the real data) the measurement was taken. To eliminate this source of error the NB-MIO 16 data acquisition board was programmed to take 167 samples at intervals of 100 μs, thus sampling the signal over one complete noise cycle of 0.0167 s. The average of the 167 samples was taken, so that because the noise source was sinusoidal, averaging the sample with the noise over one noise cycle cancelled this error entirely, while making available one data point. Mathematically the cancellation of the error follows because:

\[ \int_0^{2\pi} \sin(x) \, dx = 0 \]

[12.1.]

2. Conversion to true voltage and current values

The potential value read in this way directly evaluated to the voltage of the specimen. Because the transfer function of the PAR 376 log conversion unit was 1 V/current decade, the value of the current per unit surface area was determined by the relationship:

\[ \log(i) = \log\left[10^{\log(I_{\max}) - E_{\text{read}}}/A\right] \]

[12.2.]
3. Storage of current/potential pairs

Unless otherwise noted, the scan rate of the 175 universal programmer was 1 mV/s. Data was acquired every 10 seconds. The acquisition cycle (of 167 points) described above (yielding a single data value) was thus carried out every 10 seconds, and the average value was saved to disk. Both the log current output and the potential monitor of the PAR 173/376 potentiostat were saved in this way. At a scan speed of 1 mV/s, a 10 second sample interval corresponds to one reading every 10 mV. The data was saved as ASCII data potential/log current density pairs.

Treatment of data saved by the data acquisition program

1. Adding of range offset and smoothing

The potentiostat that was used in most of the potentiodynamic runs had a log current output which was only accurate to about 0.1% of the full scale. In many typical potentiodynamic scans however, the current varied by more than 6 orders of magnitude during the run. It was therefore necessary to switch the current range on the potentiostat during the course of a run, in order to maintain sufficient accuracy at all current values. Doing this introduced an offset into the data that was saved by the data acquisition procedure described above. This offset was added by using a custom written spreadsheet in Microsoft Excel®. During this process a three point moving average smoothing was also applied to the data.

2. Interpolation to the same potential values

Because the data acquisition was started at the beginning of the potential scan, and taken thereafter with 10 second intervals, it follows that the data from one run to the next were not taken at exactly the same potential values. For averaging the current densities of successive runs, it is important to have the data available at exactly the same set of potentials. The data was therefore interpolated by the Quickbasic® program given in §[12.3.2.]. A second order Lagrangian interpolation was used.
3. **Averaging of identical runs**

Because three identical runs were carried out, the current value at each potential for the three runs were averaged, except where otherwise noted. This operation was carried out using Microsoft Excel®.
12.1.2. Frequency sweep data treatment

Treatment by the H. P. data acquisition program

The data from the Solartron® 1250 FRA were accumulated in memory until the lowest frequency specified for the resistor was reached. The data were, after compensating for the surface area and resistor used for the measurement, subsequently saved to disk as a continuous ASCII file. The lines in the afore-mentioned file consisted of the following information: (i) Filename (ii) Version number of acquisition program (iii) Revision number of the acquisition program (iv) Number of data pairs acquired, N (v) N × 5 lines of data consisting of (a) Frequency (b) Real part (c) Imaginary part (c) Error code (d) Resistor used for measurement. One such file was thus saved for each frequency sweep carried out.

Transfer of the data from the H. P. 9816 microcomputer to the Macintosh II computer

The data as acquired above, was transferred via the serial ports of the two computers and was stored as an ASCII file on the Macintosh®. Typically many of the files as produced by the Hewlett-Packard computer were transferred together, so that the structure of the raw data file on the Macintosh® was in the form of (i) Filename (ii) Version number of acquisition program (iii) Revision number of the acquisition program (iv) Number of data pairs acquired, N (v) N lines of data consisting of (a) Frequency (b) Real part (c) Imaginary part (c) Error code (d) Resistor used for measurement, with a chr$(9) character between these parameters. This format of file is compatible with Microsoft Excel®, so that the files could be read by the latter program.

Treatment on the Macintosh computer

1. Consolidation of data from different resistors

The data file as produced above, was separated into the data at each potential; the data were then plotted in order to examine the data visually. By visually examining the data, the frequency range over which each resistor was most accurate could be determined. The data
were consolidated in Excel® by manually cutting and pasting the data from the various resistors to produce a single continuous data series containing all the points that lie on the continuous curve.

2. Subtraction of the solution resistance

The single data curve produced showed a resistive component at high frequencies due to the solution resistance between the Luggin probe and the face of the electrode. Subtraction of this component was necessary in order to isolate the contribution of the electrode only. The value of the resistance at 6500 Hz was therefore subtracted from each resistive component in Excel® in order to eliminate the contribution of the solution resistance. Perfect compensation of the solution resistance in this manner is not possible, and some distortion of the impedance curve remained. This solution resistance correction procedure is also discussed in §[6.6.1].

3. Presentation of data

The data as corrected for the solution resistance were then used to calculate the parameters \( \theta \) and \( \log(Z) \), as well as the intercepts and slopes of the Bode plots. The phase angle in the pseudocapacitive regime was also calculated. These parameters were plotted in Cricket Graph® as a function of the potential. The parameters \( \theta \) and \( \log(Z) \) were consolidated into a single data file by cutting and pasting, and subsequently saved in Excel® as an ASCII file. This file was exported to Wings®. Each of the variables \( \theta \) and \( \log(Z) \), was plotted in 3-D format as a function of the frequency and the potential by means of Wings®.
12.1.3. Potential sweep data treatment

Treatment by the H. P. data acquisition program

The data from the Solartron® 1250 FRA were accumulated in memory until the lowest frequency specified for the resistor was reached. The data was, after compensating for the surface area and resistor used for the measurement, subsequently saved to disk as a continuous ASCII file, with the lines in the file consisting of the following information: (i) Filename (ii) Version number of acquisition program (iii) Revision number of the acquisition program (iv) Number of data pairs acquired, \( N \) (v) \( N \times 5 \) lines of data consisting of (a) Frequency (b) Real part (c) Imaginary part (c) Potential (d) Current used for measurement. In this way one such file was saved for each sweep carried out.

Transfer of the data from the H. P. 9816 microcomputer to the Macintosh® II computer

The data as acquired above were transferred via the serial ports of the two computers and was stored as an ASCII file on the Macintosh®. Typically many of the files as produced by the Hewlett-Packard computer were transferred together, so that the structure of the raw data file on the Macintosh® was in the form of (i) Filename (ii) Version number of acquisition program (iii) Revision number of the acquisition program (iv) Number of data pairs acquired, \( N \) (v) \( N \) lines of data consisting of (a) Frequency (b) Real part (c) Imaginary part (c) Potential (d) Current, with a chr$(9)$ character between these parameters. This format of file is compatible with Microsoft Excel®, so that the files could be read by the latter program.

Treatment on the Macintosh computer

The imaginary portion of the data as acquired above was utilized to calculate the capacitance of the electrode. The total capacitance of a passive electrode may be calculated as:

\[
C_t = \frac{\text{Im}}{2\pi f} \tag{12.3.}\]
This capacitance is the series combination of the double layer capacitance $C_{dl}$, and the space charge layer capacitance $C_{sc}$. Therefore, in order to plot the $C_{sc}$:

$$\frac{1}{C_t} = \frac{1}{C_{dl}} + \frac{1}{C_{sc}}$$  \hspace{1cm} [12.4.]

Therefore:

$$C_{sc} = \left[ \frac{1}{C_t} - \frac{1}{C_{dl}} \right]^{-1}$$  \hspace{1cm} [12.5.]

This capacitance as calculated in this manner was plotted as C, 1/C or 1/C$^2$ versus $E$ by means of Cricket Graph®.
12.1.4. Pseudo steady state photoelectrochemical data treatment

Treatment by the data acquisition program

1. Sampling and averaging

The number of data points taken depended on the magnitude of the photocurrent signal generated. In most cases 500, 1000 or 2000 data sets (consisting of potential, photocurrent, phase angle, dark current) were taken with 1 second intervals. Total acquisition time was therefore 50 - 200 seconds per wavelength. The average of the samples was subsequently taken.

2. Conversion to true current and voltage values

The potential value read in this way directly evaluated to the voltage of the specimen. The value of the background (corrosion) current per unit surface area was determined from the voltage value read (1 V corresponds to the full scale of the setting on the PAR 173) by the relationship:

\[ i_{\text{cor}} = \frac{I_{\text{max}} \times E_{\text{read}}}{A} \]  \hspace{1cm} [12.6.]

The value of the photocurrent was determined by the relationship:

\[ i_{\text{ph}} = \frac{E_{\text{read}} \times I_{\text{max}} \times L_{\text{sens}}}{A \times 10} \]  \hspace{1cm} [12.7.]

while the value of the phase angle was determined as:

\[ \theta = \frac{E_{\text{read}}}{0.05} \]  \hspace{1cm} [12.8.]

(the output of the lock-in amplifier is 0.05 V/degree)
The data obtained by the above procedure was saved as an ASCII data file with the columns of the file: (i) potential (ii) photocurrent (iii) phase angle (iv) dark current.

Treatment of data saved by the data acquisition program

1. Correcting data for system throughput

In order to interpret the photoelectrochemical response, it was necessary to correct the data as acquired, for the throughput of the system. The relative throughput of the system was therefore determined as a function of wavelength with the photomultiplier system described in §[7.3.]. The throughput measurements were carried out at the same wavelength values as the photoelectrochemical measurements in order to facilitate easy normalization of the results.

The system throughput as a function of wavelength is given as figure [12.4.1.]. The photocurrent at every wavelength (A/cm²) as stored in the data file described above, was subsequently divided by the system throughput (W/cm²) by means of a custom written Excel® spreadsheet, to get the quantum efficiency of the films in A/W. Because the experimental set-up did not allow for repeatability of absolute throughput with more than 90% accuracy, dimensional units were used wherever possible in subsequent analyses. After the division process, a three point moving average smooth was applied to the data. The resulting data was plotted in suitable formats to elucidate the parameters required.
12.1.5. Cyclic voltammetry photocurrent data treatment

Treatment by the data acquisition program

1. Sampling and averaging

The number of data points acquired was 100 for each of the four channels sampled (potential, current, magnitude of photocurrent, phase angle of photocurrent) in all cases, giving a total of 400 values (100 data sets). These points were taken with intervals of 2.5 ms, giving a total sample time of 1 s for the 100 data sets. The average of each of the 100 sets of the four variables was subsequently taken.

2. Conversion to true current and voltage values

The potential value read in this way directly evaluated to the voltage of the specimen. The value of the background (corrosion) current per unit surface area was determined from the voltage value read (1 V corresponds to the full scale of the setting on the PAR 173) by the relationship:

\[ i_{\text{corr}} = \frac{I_{\text{max}} \times E_{\text{read}}}{A} \]  \[12.9.\]

The value of the photocurrent was determined by the relationship:

\[ i_{\text{ph}} = \frac{E_{\text{read}} \times I_{\text{max}} \times L_{\text{sens}}}{A \times 10} \]  \[12.10.\]

while the value of the phase angle was determined as:

\[ \theta = \frac{E_{\text{read}}}{0.05} \]  \[12.11.\]

(the output of the lock-in amplifier is 0.05 V/degree)
The data obtained by the above procedure was saved as an ASCII data file with the columns of the file: (i) potential (ii) photocurrent (iii) phase angle (iv) dark current.

The steps elaborated in points 1-2 above were carried out at 5 s intervals. At the scan rate of 10 mV/s employed, one data set was thus saved to disk every 50 mV.

Treatment of data saved by the data acquisition program

1. Averaging data from several voltammetric cycles

Because the magnitude of the measured photocurrent was very small due to the thinness of the film formed during voltammetric cycling, and also because the measurement of the photocurrent at each potential had to be completed quickly (measurement could not be carried out for several minutes as in the case of the pseudo steady state photocurrent measurements) the photoresponse was typically measured for 7-15 cycles, and the averages subsequently processed.

The computer program given in §[12.3.6.], was used to sort the continuous file of data sets as produced by the data acquisition program (see description above) into 'bins' with intervals of 50 mV, for both the 'up' and the 'down' scans. During this process, all values deviating more than 1 standard deviation from the mean were discarded. This procedure was necessary in order to ensure that spurious noise did not influence the results obtained. (The experimental apparatus was very sensitive to electrical disturbances in the laboratory) This procedure resulted in less than 2% of the data sets measured being discarded, which is regarded as acceptable.

The average values of the four measured variables was subsequently written to disk as two ASCII files, one for the 'up' scan, and one for the 'down' scan.
2. Interpolation to the same potential values

Because the data acquisition was started at an arbitrary point during the voltammetric scan, and taken thereafter with 10 second intervals, it follows that the data from one run to the next were not taken at exactly the same potential values. For normalization procedures, however it is important to have the data available at exactly the same set of potentials. The data was therefore interpolated by the Quickbasic® program given in §[12.3.2]. A second order Lagrangian interpolation was used. The output of the interpolation file was a ASCII file that could be read by other applications.

3. Correcting data for system throughput

In order to interpret the photoelectrochemical response, it was necessary to correct the data as taken for the throughput of the system. The relative throughput of the system was therefore determined as a function of wavelength with the photomultiplier system described in §[7.3.]. The throughput measurements were carried out at the same wavelength values as the photoelectrochemical measurements in order to facilitate easy normalization of the results.

The system throughput as a function of wavelength is given as figure [12.4.1.]. The photocurrent at every wavelength (A/cm²) as stored in the data file described above, was subsequently divided by the system throughput (W/cm²) by means of a custom written Excel® spreadsheet, to get the quantum efficiency of the films in A/W. Because the experimental set-up did not allow for repeatability of absolute throughput with more than 90% accuracy, dimensionless units were used wherever possible in subsequent analysis. The resulting data was plotted in suitable formats to elucidate the parameters required.
12.2. Theoretical derivations
12.2.1. Effect of imperfectly compensated solution resistance

To numerically illustrate conditions where such uncompensated resistance can influence results, consider two hypothetical responses of the passive film. Imagine that in the first case the passive film exhibits a CPE with a phase angle very close to 90°, say 89°. Suppose that in the second case the passive film also exhibits CPE like response, but in this case with a phase angle of say 60°. Consider now a very high frequency where the magnitude of the imaginary portion is for purposes of argument 5 (arbitrary units). In the case of the CPE exhibiting a phase angle of of 89° it means that:

\[
\frac{\text{Im}}{\text{Re}} = \tan(89) = 57.29 \quad [12.12.]
\]

For Im = 5 it follows that:

\[
\text{Re} = 0.087 \quad [12.13.]
\]

If now the correction of the ohmic resistance is not entirely accurate, and \( R_s \) is determined to be 0.2, instead of 0.087, an error that is not at all unrealistic, then:

\[
\theta = \tan^{-1}\left(\frac{\text{Im}}{\text{Re}}\right) = \tan^{-1}\left(\frac{5}{0.2}\right) = 87.7^\circ \quad [12.14.]
\]

The error in estimation of the \( R_s \) has therefore caused an error in the phase angle:

\[
\Delta \theta_{\text{err}} = \theta_{\text{actual}} - \theta_{\text{meas}} = 89^\circ - 87.7^\circ = 1.29^\circ \quad [12.15.]
\]

Consider now the case where the phase angle is 60°. In this case let the real component of the film be exactly the same as in the previous case, namely, \( \text{Re} = 0.087 \), then, for a phase angle of 60°:

\[
\text{Im} = \text{Re} \times \tan(\theta) = 0.087 \times \tan(60) = 0.122 \quad [12.16.]
\]
Consider now that the Re again is taken to be 0.2 instead as 0.087 as in the previous case. After correction for the solution resistance, then:

\[
\theta = \tan\left(\frac{\text{Im}}{\text{Re}}\right) = \tan\left(\frac{0.122}{0.2}\right) = 31.38^\circ
\]  

[12.17.]

In this case a \(\Delta\theta_{\text{err}} = \theta_{\text{actual}} - \theta_{\text{meas}} = 60^\circ - 31.38^\circ = 29^\circ\) error thus resulted from the same 0.1 \(\Omega\) error in the measurement of the solution resistance, \(R_s\), as before. It can therefore be seen that even a small error in the correction that is made for the solution resistance \(R_e\), may result in a very large error being made in the determination of the phase angle; this is especially true in cases where the imaginary component, \(\text{Im}\), is very small, such as may be the case in situations where appreciable dispersion is present. From the calculation carried out above it is also clear that this effect becomes more and more pronounced as the value of the constant phase element is decreased.
12.2.2. Mathematical basis of percolation

According to Zallen [Zallen 1983], the term percolation was coined by the mathematician J. M. Hammersley [Hammersley 1957]. In order to illustrate the phenomenon of percolation, while still maintaining simplicity, a 2-d percolation situation will be developed here. These ideas can, however, easily be extended to 3 dimensions. The reader is referred to Zallen [Zallen 1983] for a complete treatment, or to Grimmet [Grimmet 1989] for a more rigorous mathematical treatment.

Consider a square lattice, such as depicted in figure [12.4.2.], in which the fraction of filled sites is increased from 25% through 50% to 75% of all sites filled. Let this fraction of filled sites be p, then p=0 corresponds to the completely unfilled lattice, while p=1 corresponds to the completely filled lattice. In the low concentration regime i.e. p << 1, nearly all the filled sites occur as clusters of size one. If s denotes the cluster size, it is found that the cluster-size distribution is peaked at s=1, and falls off exponentially with increasing s. If s is normalised with respect to the total number of sites n, n(s), the dimensionless distribution function is obtained.

Let $s_{av}$ now denote the average cluster size. For p<<1, $s_{av}$~1. When p is increased to p = 0.25, $s_{av}$ increases to 3.5. As p is increased to 0.5, $s_{av}$ further increases to 20. Note however that all clusters are still finite in size. As p is increased to 0.75, however, a cluster that extends right across the lattice suddenly appears. This cluster is called the unbounded cluster or percolation path. Let P(p) now denote the fraction of the total number of filled sites that belong to the unbounded cluster, and let $p_c$ be the number of filled sites at which the unbounded cluster first appears. By Monte-Carlo simulation, $p_c$ for the two dimensional square lattice has been determined as $p_c = 0.50$. It is clear that while p < $p_c$, P(p) = 0, that is, no unbounded cluster is present. For p > $p_c$, however, P(p) increases rapidly. Figure [12.4.3.] shows the parameters defined here as a function of p. In this figure, $l_{av}$ denotes the average linear dimension of the clusters, and is closely related to $s_{av}$.

Appearance of the infinite network at $p_c$, as described above, forms the basis for the percolation model for passivity [Sieradzki 1986, Newman 1988, Sieradzki 1989, Qian...
Consider the Fe-Cr alloy system, and consider that in order for a site to be filled, it must have a Cr atom on it. At low Cr concentrations, Cr atoms will occur in clusters of one. As the wt% Cr is increased, the average size of a Cr cluster will increase, analogous to the process as described above. At a certain wt% Cr, corresponding to the critical percolation threshold or $p_c$, the infinite or spanning cluster will appear.

Imagine now that an Fe atom is prone to dissolution, while a Cr atom is not. According to this model the ‘loose’ Cr clusters that do not form part of the spanning cluster or infinite network described above, represent islands of imperfect passivity. The Fe-rich areas around these islands will dissolve, leading to the small Cr clusters ‘dropping’ out. This process will continue until the spanning cluster is exposed on the corroding surface. At this point no further dissolution will take place, and the material will passivate. As the spanning cluster is only present in alloys that contain more that the critical wt% Cr, it follows that below this ‘critical’ Cr concentration the material will corrode actively. Above the percolation threshold, enrichment of the surface in the non-dissolving species, in this case Cr will result.

Sieradzki and Newman, in their model, go a little beyond the simple picture presented above. They consider in the first instance, not only two dimensional, but also three dimensional percolation. Furthermore, they consider not only nearest neighbour, but also second and third nearest neighbour percolation. In the simple model presented above, it is assumed that an Fe atom will always dissolve, while a Cr atom will never dissolve if it is part of the infinite cluster. In the real situation, however, Cr exhibits a finite dissolution rate. In order to model the true situation more closely, a finite value for the probability of dissolution of both Fe and Cr are assigned.
12.2.3. Band gap of the passive film material

In general, a change in the sign of the field, changes the sign of the photocurrent. The potential at which this sign changes can be determined by photoelectrochemical techniques, and is called the flat band potential. When recombination is disregarded, the photocurrent of a crystalline semiconductor can be expressed as

\[
I_{ph} = \frac{1}{e} \eta J_0 \exp \left[ \frac{1 - \alpha D_{sc} (\varepsilon / kT)^{1/2} (E - E_{fb})^{1/2}}{(1+\alpha L)} \right]
\]

[12.18.]

where \( D_{sc} \) is the space charge layer thickness or Debye length. The thickness of the space charge layer, \( D_{sc} \), is a function of the donor density \( N_d \) and the dielectric constant \( \varepsilon \), and is given by:

\[
D_{sc} = \left( \frac{\varepsilon_0 kT}{\varepsilon^2 N_d} \right)^{1/2}
\]

[12.19.]

The quantity \( L \) is the diffusion length of the minority carriers (holes in the case of an n-type semiconductor) and is given by:

\[
L = (D\tau)^{1/2}
\]

[12.20.]

where \( D \) is the diffusion coefficient, and \( \tau \) is their lifetime. The above equations hold for the case where charge transfer at the electrode/electrolyte interface is not rate controlling.

If the passive film is the absorbing layer, the number of photons absorbed in the passive film is given by Lambert-Beer’s law:

\[
J_{abs} = J_0 (1 - e^{-\alpha d})
\]

[12.21.]

The above equation is not corrected for reflectance at the metal/film interface. If the semiconductive thin film is too thin to absorb all incident radiation, absorption or reflection
at the metal interface has to be considered. Setting the reflectivity of the metal equal to $R$, with the limiting cases of $R=0$ (no reflection) and $R=1$ (complete reflection, equation [12.21.] changes to:

$$J_{\text{abs}} = [1-e^{-\alpha d}] \left[ 1+R e^{-\alpha d} \right]$$  \[12.22.\]

In the limiting cases, the film thickness is thus counted once and twice respectively. Multiplying out to form a quadratic equation, [12.22.] becomes:

$$J_{\text{abs}} = 1 - e^{-\alpha d} + Re^{-\alpha d} - Re^{-2\alpha d}$$  \[12.23.\]

If the film is very thin and the absorption coefficient, $\alpha$, is not too high, the last two terms in equation [12.23.] cancel ($e^{-\alpha d} \sim \alpha d$ for small $x$), so that the number of photons absorbed becomes proportional to the absorption coefficient.

$$J_{\text{abs}} = 1 - e^{-\alpha d}$$  \[12.24.\]

This equation, in turn becomes, in terms of the photocurrent:

$$i_{\text{ph}} = \eta(1 - e^{-\alpha d})$$  \[12.25.\]

If the exponent term is small then the identity that $1 - e^{-\alpha d} \sim \alpha d$ may be used, and the equation thus becomes:

$$i_{\text{ph}} = \eta \alpha d$$  \[12.26.\]

For a crystalline material, the absorption coefficient, $\alpha$, depends on the photon energy as [Stimming 1986]:

$$\alpha = \frac{A(h\nu-E_g)^n}{h\nu}$$  \[12.27.\]
Substituting equation [12.27.] into equation [12.26.] gives:

\[ i_{ph} = \frac{d\eta A(h\nu-E_g)^n}{hv} \]  \hspace{1cm} [12.28.]

From equation [12.28.] it follows that the band gap of the material can be determined from a plot of \((i_{ph}\nu)^{1/n}\) versus \(\nu\). The coefficient for direct transitions is \(n=1/2\), while for indirect transitions which require phonon participation, \(n=2\).
12.3. Program listings
12.3.1. Potential scan program

actv!=0 'actual voltage value read from the potentiostat
actvmin!=0 'minimum voltage read from potentiostat before overflow warning
actvmax!=0 'maximum voltage read from potentiostat before underflow warning
area!!=0 'sample area
begintime!=0 'the time at the beginning of the scan
brd%=0 'Board Number [same as Slot Number]
chan%=0 'Analog Input Channel Number
count%=0 'Count (Number of readings) = countperchannel% * numchans%
counter1%=0 'counter1% - simple variable used for counting
counter2%=0 'counter2% - simple variable used for counting
countperchannel%=0 'number of data points per channel to be input
curridfac%=0 'we need a fiddlefactor because the 173,273 has dif. log current output conventions
ecorr!=0 'corrosion potential measured
dear%!=0 'computed time exp must end
erange!=0 'range of potential to be scanned
errorr%=0 'errorr% - error value return; for possible errors see error checking routine
espeed!=0 'scan speed in mV/s
inputmode%=0 'inputmode% - 0=differential, 1=single ended
inputrange%=0 'inputrange% - Voltage reference value for A/D 5 or 10 V
logcurr!=0 'value of the log of the current (A/cm^2)
muxmode%=0 'muxmode% - Future for ext. multiplexer use muxmode%=0 for now
NUMCHANS%=0 'nuchans% - number of channels to be scanned
polarity%=0 'polarity% - 0=bipolar, 1=unipolar
pot!=0 'value of the electrode potential
potfiddfac%=0 'fiddlefactor=-1 because the output on the instruments are reversed
nosamppoints%=0 'number of points to average out
samptime%!%==0 'Sample Interval. Length of the sample
seconds%==0 'seconds% - sample interval
status%=0 'status% - status% = 1 => data acq complete, 0=> data acq not yet complete
timebase%==0 'Timebase for conversion pulse generation (0 - 5)
rangei%==0 'the value of the range switch on the potentiostat
timenow%==0 'the value of the time at the time of execution of loop
whichstat%=0 'which potentiostat (1=173, 2=273)
a$="" 'junk variable used among others as temp storage space
beginhour$="" 'variable used to determine start + stop of exp
beginminute$="" 'ditto
beginsec$="" 'ditto
endhour$="" 'ditto
endminute$="" 'ditto
endsec$="" 'ditto
outdatafil$="" 'used for the name of the output data file with the data
INIT%=0
AOCONFIG%==&H10
AOWRITE%==&H11
Aoupdate%==&H12
AOVERSSCALE%==&H13
AICONFIG%==&H20
AIREAD%==&H21
AISCALE%==&H22
AISETUP%==&H23
AICHECK%==&H24
ACLEAR%==&H25
AIMUXCONF%==&H26
DIGOUTPORT%==&H30
DIGOUTLINE%==&H31
DIGINPUT%==&H32
DIGINLINE%==&H33
DIGPRCTRL%==&H34
DIGPRTSTATUS%==&H35
DIGGRCONFIG%==&H36
DIGGRPSTATUS%==&H37
DIGGRPMODE% = &H38
DIGOUTGROUP% = &H39
DIGINGROUP% = &H3A
DAQCONFIG% = &H40
DAQSTART% = &H41
DAQCHECK% = &H42
DAQCLEAR% = &H43
DAQSCALE% = &H44
SCANSETUP% = &H45
SCANSTART% = &H46
SCANCHECK% = &H47
DAQ2CONFIG% = &H49
DAQ2GET% = &H4A
DAQ2TAP% = &H4B
DAQ2CLEAR% = &H4C
DAQ2MEMCONF% = &H4D
DAQTRIGGER% = &H4E
DAQ2GETSTR% = &H80
DAQ2TAPSTR% = &H81
CTRCONF% = &H50
CTRSTOP% = &H51
CTRRESTART% = &H52
CTRRESET% = &H53
CTRSTATE% = &H54
CTREVCOUNT% = &H55
CTREVREAD% = &H56
CTRPULSE% = &H57
CTRSQUARE% = &H58
CTRCLK% = &H59
RTSICONN% = &H60
RTSIDISCONN% = &H61
RTSICLEAR% = &H62
WFGRPSETUP% = &H70
WFGRPPSTART% = &H71
WFGRPPSTOP% = &H72
WFGRPPRESET% = &H73
WFLOAD% = &H74
WFSETUP% = &H75
WFSTART% = &H76
WFSTOP% = &H77
WFPRESET% = &H78
WPCHECK% = &H79
WPOFFSET% = &H7B
LIBRARY "LabDriverLib.rsrc"
LDSysERR% = 0
CALL ldfn(INIT%, LDSysERR%)
CLS
LOCATE 10,10
PRINT "-- POT SCAN (S) VERSION 1.0.6 -- 21 Feb 1989"
FOR counter1%=1 TO 2000
  a$=STR$(SIN(COS(SIN(counter1%))))
NEXT counter1%
brd%=2 'my board is in slot #2
NUMCHANS%=2 'only scan channel 0 and 1
DIM chanvector%(NUMCHANS%)
DIM gainvector%(NUMCHANS%)
chanvector%(0)=0 'the current input channel is 0
gainvector%(0)=1 'current == see comment above
chanvector%(1)=1 'the voltage input channel is 1
gainvector%(1)=4 'potential == see comment above
muxmode% = 0 'future ext multiplexer use = use =0 now
timebase% = 3 'clock pulse for conversion = 100 μs
saminterval% = 3
nosamppoints%=167 'number of points to be averaged
inputmode%=0 'differential
inputrange%=10 '10 V max
polarity%=0 'bipolar
potfidfac%=-1 'necessary because output is the wrong way around
DIM buffer%(NUMCHANS%-1,nosamppoints%) buffer% is used for returning the demultiplexed
CALL ldtn(AICONFIG%,brd%,errorr%,inputmode%,inputrange%,polarity%)
CALL ldtn(DAQCLEAR%, brd%, errorr%)
IF errorr%<>-74 THEN GOSUB chkerr
CALL ldtn(SCANSETUP%, brd%, errorr%, NUMCHANS%, chanvector%(0), gainvector%(0), muxmode%)
IF errorr%<>-74 THEN GOSUB chkerr
CLS
PRINT "The system will now read the corrosion potential"
PRINT "When the value on the screen is stable,"
PRINT "Press T or 'i' to continue"
PRINT
PRINT "Press any key to start Ecorr measurement............................"
a$=INPUT$(1)
CLS
LOCATE 15,10
PRINT "Press T or 'i' to continue if the potential is stable"
ecorragain:
CALL ldtn(SCANSTART%,brd%,errorr%,buffer%(0,0),count%,timebase%,sampinterval%)
IF errorr%<>-74 THEN GOSUB chkerr
CHK1:
errorr%=0
CALL ldtn(SCANCHECK%,brd%,errorr%,status%) 'checks status
IF errorr%<>0 THEN GOSUB chkerr
IF (status% < 1) GOTO CHK1
ecorr!=0
FOR counter1%=0 TO nosamppoints%-1
ecorr!=ecorr!+buffer%(1,counter1%)
NEXT counter1%
ecorr!=potfidfac%*(ecorr!/2048)*(inputrange%/gainvector%(1))
LOCATE 10,10
PRINT ".
LOCATE 10,10
PRINT "The corrosion potential is "; USING "+.###";ecorr!;
PRINT " V versus Ref"
PRINT "Scan speed (mV/s)";espeed!
PRINT "Sample interval in seconds";seconds%
parinput:
CLS
PRINT "The corrosion potential is ";USING "+.###";ecorr!;
PRINT 
PRINT "Which potentiostat is used (1=173, 2=273)";whichstat%
INPUT "What is the specimen area (cm2)";area!
IF whichstat%<>1 THEN
INPUT "What is the value of the current range switch (A) ";rangei!
INPUT "What is the minimum allowable 173 V (return for 0.5 default)";a$
IF a$="" THEN LET actvmin!=.5 ELSE LET actvmin!=VAL(a$)
INPUT "What is the maximum allowable 173 V (return for 3.5 default)";a$
IF a$="" THEN LET actvmax!=3.5 ELSE LET actvmax!=VAL(a$)
curfidfac%=-1 '173 has positve output in log i mode
ELSE
INPUT "What is the value of the current corresponding to 0.0 V (A) ";rangei!
curfidfac%!-1 'the 273 has negative output in log I mode
END IF
INPUT "Total potential range to be scanned (V)";erange!
INPUT "Scan speed (mV/s)";espeed!
INPUT "Sample interval in seconds";seconds%
PRINT "Estimated # of points are";erange!/((espeed!/1000)*seconds%)
INPUT "Actual number of data pairs (I-V) to be read";countperchannel%
INPUT "Name of output file";outdatfil$
PRINT "Satisfied with all parameters (Y/N)"
a$=INPUT$(1)
IF a$="N" OR a$="n" THEN GOTO parinput

CLS
PRINT "Enable the cell"
PRINT "Press any key to to start measurements"
PRINT "Then start the scan"
a$=INPUT$(1)
OPEN outdatfil$ FOR OUTPUT AS #1
OPEN "clip:" FOR OUTPUT AS #2
begintime!=TIMER
endtime!=begintime!+countperchannel%*seconds%
begintime!=(begintime!/3600)
beginhour$=STR$(INT(begintime!))
begintime!=begintime!-VAL(beginhour$)
beginminute$=STR$(INT(begintime!*60))
begintime!=begintime!*60-VAL(beginminute$)
beginsec$=STR$(INT(begintime!*60))
IF endtime!>86400! THEN endtime!=endtime!-86400!
endtime!=(endtime!/3600)
endhour$=STR$(INT(endtime!))
endtime!=endtime!-VAL(endhour$)
endminute$=STR$(INT(endtime!*60))
endtime!=endtime!*60-VAL(endminute$)
endsec$=STR$(INT(endtime!*60))

'so that clock changes at midnight

CLS
LOCATE 5,10
PRINT "Beginning time:

LOCATE 5,25

"

PRINT beginhour$+":"+beginminute$+":"+beginsec$
LOCATE 6,10
PRINT "Proj. ending time:
LOCATE 6,25
PRINT endhour$+":"+endminute$+":"+endsec$
LOCATE 15,7
PRINT "Press T or 'i' to interrupt at any time and save only collected values"
LOCATE 10,10
PRINT "log I (A/cmA2)";TAB(25);"Pot (V versus ref):";TAB(40);"Actual V read"
FOR counterl%=1 TO countperchannel%
CALLldfn(SCANSTART%,brd%,errorr%,buffer%(0,0),count%,timebase%,sampinterval%)
IF errorrco-74 THEN GOSUB chkerr
CHK:
errorr%=0
CALL ldfn(SCANCHECK%,brd%,errorr%,status%) 'checks status of background acquisition
chkerr
GOSUB
IF (status% o 1) GOTO CHK
pot!=0
logcurr!=0
FOR counter2%=0 TO nosamppoints%-1
logcurr!=logcurr!+buffer%(0,counter2%)
pot!=pot!+buffer%(1,counter2%)
NEXT counter2%
logcurr!=curfidfac%*(logcurr!/nosamppoints%)
pot!=pot!/nosamppoints%
logcurr!=(logcurr!/2048)*(inputrange%/gainvector%(0))
actv!=logcurr!
logcurr!=LOG(EXP((LOG(rangei!)/LOG(10)-logcurr!)*LOG(10))/area!)/LOG(10)
pot! =potfidfac%*(pot!/2048)*(inputrange%/gainvector%(1))
LOCATE 11,10
PRINT"
LOCATE 11,10

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PRINT USING "###.#####":logcurr!
PRINT TAB(25);
PRINT USING "###.#####":pot!
PRINT TAB(40);
PRINT USING "###.#####":actv!
IF whichstat%=1 THEN
IF actv<actvmin! OR actv>actvmax! THEN SOUND 600,5,255,0 END IF
PRINT #1, logcurr!;CHR$(9);pot! 'x=first=current
PRINT #2, logcurr!;CHR$(9);pot!
a$=INKEY$
IF a$="i" OR a$="I" THEN
' the user interrupted the acq don't read the other values
counterchannel%=counter1% ' only this no of values already read
GOTO clos END IF
chk2:
IF TIMER<begintime! THEN
timenow!=TIMER + 86400! 'past midnight during run
ELSE
timenow!=TIMER 'not past midnight during run
ENDIF
IF (timenow<begintime!+counter1%*seconds%) GOTO chk2 NEXT counter1%
clos:
CLOSE #1
CLOSE #2
CLS
LOCATE 10,10
PRINT "All done"
FOR counter1%=1 TO 2000
a$=STR$(SIN(COS(SIN(counter1%))))
NEXT counter1%
STOP
chkerr:
IF (errorr% = -1) THEN CLS: LOCATE 10,15:PRINT"***Device Manager Error ***":STOP
IF (errorr% = -60) THEN CLS: LOCATE 10,15:PRINT"***Not our board ***":STOP
IF (errorr% = -61) THEN CLS: LOCATE 10,15:PRINT"***Bad board number ***":STOP
IF (errorr% = -62) THEN CLS: LOCATE 10,15:PRINT"***Bad GAIN ***":STOP
IF (errorr% = -63) THEN CLS: LOCATE 10,15:PRINT"***Bad channel number ***":STOP
IF (errorr% = -64) THEN CLS: LOCATE 10,15:PRINT"***Function not supported on this board ***":STOP
IF (errorr% = -65) THEN CLS: LOCATE 10,15:PRINT"***Port parameter out of range ***":STOP
IF (errorr% = -66) THEN CLS: LOCATE 10,15:PRINT"***Port not configured for output ***":STOP
IF (errorr% = -67) THEN CLS: LOCATE 10,15:PRINT"***Port does not handle handshaking ***":STOP
IF (errorr% = -68) THEN CLS: LOCATE 10,15:PRINT"***Port cannot be assigned to a group ***":STOP
IF (errorr% = -69) THEN CLS: LOCATE 10,15:PRINT"***Bad input value ***":STOP
IF (errorr% = -70) THEN CLS: LOCATE 10,15:PRINT"***Incomplete A/D ***":STOP
IF (errorr% = -71) THEN CLS: LOCATE 10,15:PRINT"***Input value out of range ***":STOP
IF (errorr% = -72) THEN CLS: LOCATE 10,15:PRINT"***Data Acquisition in progress ***":STOP
IF (errorr% = -73) THEN CLS: LOCATE 10,15:PRINT"***Counter in use ***":STOP
IF (errorr% = -74) THEN CLS: LOCATE 10,15:PRINT"***No Data Acquisition ***":STOP
IF (errorr% = -75) THEN CLS: LOCATE 10,15:PRINT"***Overflow in Data Acquisition ***":STOP
IF (errorr% = -76) THEN CLS: LOCATE 10,15:PRINT"***Overrun in Data Acquisition ***":STOP
IF (errorr% = -77) THEN CLS: LOCATE 10,15:PRINT"***Bad count. Scan count must be mult. of no. of ch. ***":STOP
IF (errorr% = -78) THEN CLS: LOCATE 10,15:PRINT"***Bad board type ***":STOP
IF (errorr% = -79) THEN CLS: LOCATE 10,15:PRINT"***Counter not configured for event counting ***":STOP
IF (errorr% = -80) THEN CLS: LOCATE 10,15:PRINT"***Counter reserved for data acq. only ***":STOP
IF (errorr% = -81) THEN CLS: LOCATE 10,15:PRINT"***Port currently assigned to a group ***":STOP
IF (errorr% = -82) THEN CLS: LOCATE 10,15:PRINT"***No port assigned to group specified ***":STOP
IF (errorr% = -83) THEN CLS: LOCATE 10,15:PRINT"***Group not configured for output ***":STOP
IF (errorr% = -84) THEN CLS: LOCATE 10,15:PRINT"***Invalid signal direction specified ***":STOP
IF (errorr% = -91) THEN CLS: LOCATE 10,15:PRINT"***RTSI line in use ***":STOP
IF (errorr% = -92) THEN CLS: LOCATE 10,15:PRINT"***No RTSI line available ***":STOP
IF (errorr% = -93) THEN CLS: LOCATE 10,15:PRINT"***Signal in use ***":STOP
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IF (error% = -94) THEN CLS: LOCATE 10,15:PRINT "***No DMA board ***":STOP
IF (error% = -95) THEN CLS: LOCATE 10,15:PRINT "***No DMA channel available ***":STOP
IF (error% = -96) THEN CLS: LOCATE 10,15:PRINT "***Waveform setup call required ***":STOP
IF (error% = -97) THEN CLS: LOCATE 10,15:PRINT "***Analog output channel in use ***":STOP
IF (error% = -98) THEN CLS: LOCATE 10,15:PRINT "***Waveform load call required" ***":STOP
IF (error% = -99) THEN CLS: LOCATE 10,15:PRINT "***Specified channel has been assigned to a group ***":STOP
IF (error% = -100) THEN CLS: LOCATE 10,15:PRINT "***No waveform operation executed ***":STOP
IF (error% = -101) THEN CLS: LOCATE 10,15:PRINT "***Only one WFGREP SETUP call per board allowed ***":STOP
IF (error% = -108) THEN CLS: LOCATE 10,15:PRINT "***Not enough memory ***":STOP
IF (error% = -110) THEN CLS: LOCATE 10,15:PRINT "***Labdriver not configured for double buffered mode ***":STOP
IF (error% = -111) THEN CLS: LOCATE 10,15:PRINT "***Acquired data overwritten ***":STOP
IF (error% = -112) THEN CLS: LOCATE 10,15:PRINT "***Number samples requested not yet available ***":STOP
IF (error% = -113) THEN CLS: LOCATE 10,15:PRINT "***Acquisition complete before no of samples requested available ***":STOP
IF (error% = -114) THEN CLS: LOCATE 10,15:PRINT "***Block size parameter does not conform to an integer mult of no of channels ***":STOP
IF (error% = -115) THEN CLS: LOCATE 10,15:PRINT "***DAQ2MEM CONFIG executed after DAQ2 CONFIG ***":STOP
IF (error% = -120) THEN CLS: LOCATE 10,15:PRINT "***No trigger value found ***":STOP
IF (error% = -121) THEN CLS: LOCATE 10,15:PRINT "***Analog trigger did not occur before timeout ***":STOP
RETURN
12.3.2. Interpolation program

ON ERROR GOTO ertrap
DIM datvalues!(10),xout!(10),yout!(10),x!(10),y!(10),intvalues!(10),outvalues!(10)
loops%=0
startover:
loops%=loops%+1
CLS
INPUT "Number of columns in the data file (return for default of 2)";a$
IF a$="" THEN LET colsdat%=2 ELSE LET colsdat%=VAL(a$)
INPUT "Column number of X values (return for default of 2)";a$
IF a$="" THEN LET xcol%=2 ELSE LET xcol%=VAL(a$)
INPUT "Column number of Y values (return for default of 1)";a$
IF a$="" THEN LET ycol%=1 ELSE LET ycol%=VAL(a$)
INPUT "Degree of interpolation to be used (return for default of 2)";a$
IF a$="" THEN LET degree%=2 ELSE LET degree%=VAL(a$)
datname$=FILES$(1,"TEXT")
ERASE datvalues!
DIM datvalues!(1000,colsdat%)
rawvals%=0 'dummy only read sub will determine
ERASE xout!,yout!
DIM xout!(degree%), yout!(degree%)
errflag%=0
CALL readtext(datname$,rawvals%,colsdat%,datvalues!())
ERASE x!,y!
DIM x!(1000),y!(1000)
FOR i%=1 TO rawvals%
x!(i%)=datvalues!(i%,xcol%)
y!(i%)=datvalues!(i%,ycol%)
NEXT i%
INPUT "Print calculated values (return for no)";a$
IF a$="" OR a$="N" OR a$="n" THEN LET doprint%=0 ELSE LET doprint%=1
IF loops%<>1 THEN INPUT "Do you want to use the same values to interpolate at (return for yes)";a$
IF a$="n" OR a$="N" OR loops%=1 THEN
INPUT "Number of columns in the intval file (return for default of 2)";a$
IF a$="" THEN LET colsinvalfile%=2 ELSE LET colsinvalfile%=VAL(a$)
INPUT "Column number of values to interpolate at (return for default of 1)";a$
IF a$="" THEN LET intvalcol%=1 ELSE LET intvalcol%=VAL(a$)
INPUT "Column number occurrence to be used (return for default of 2)";a$
IF a$="" THEN LET occcol%=2 ELSE LET occcol%=VAL(a$)
inname$=FILES$(1,"TEXT")
nointtvals%=0 'dummy value only - routine will determine
ERASE intvalvalues!
DIM intvalvalues!(1000,colsintvalfile%)
CALL readtext(inname$,nointtvals%,colsinvalfile%,intvalvalues!())
END IF
ERASE outvalues!
DIM outvalues!(1000,3)
FOR f%=1 TO nointtvals%
intx=!intvalvalues!(f%,intvalcol%)
occ=!intvalvalues!(f%,occcol%)
CALL interpolextract(x!(),y!(),rawvals%,xout!(),yout!(),degree%,intx!,occ!,errflag%)
IF errflag%<>1 THEN
CALL lagrange(intx!,inty!,xout!(),yout!(),degree%)
outvalues!(f%,1)=inty!
outvalues!(f%,2)=intx!
outvalues!(f%,3)=errflag%
ELSE
outvalues!(f%,1)=0
outvalues!(f%,2)=0
outvalues!(f%,3)=errflag%
END IF
IF doprint% = 1 THEN PRINT "Xint ", outvalues!(f%, 2), "Yint ", outvalues!(f%, 1), "Error ", errflag%
NEXT%
CLS
PRINT "Do you want to do another interpolation (return for yes) ?"
a$ = INPUT$(1)
IF a$ <> "N" AND a$ <> "n" THEN GOTO startover
STOP
ertrap:
IF ERL = 42 AND ERR = 11 THEN
RESUME NEXT
ELSE
CLS
LOCATE 10, 20
PRINT "error ", ERR; " in "; ERL
a$ = INPUT$(1)
STOP
ENDIF
SUB interpolextract(xbigin!(1), ybigin!(1), noxbig%, xsmallout!(1), ysmallout!(1), deg%, xint!, occno%, errflag%)
ocnocntr% = 0 'initialize = no occurrences yet found
errflag% = 0
middle% = INT(deg% / 2)
FOR j% = 1 TO noxbig% - 1
IF ((xint! < xbigin!(j% + 1)) AND (xint! > xbigin!(j%)) OR ((xint! > xbigin!(j% + 1)) AND (xint! < xbigin!(j%))) OR xint! = xbigin!(j%) THEN 'up or down sweep
nocnocntr% = nocnocntr% + 1
IF nocnocntr% = nocno% THEN
IF (j% - middle%) >= 1 OR (j% - middle%) <= noxbig% THEN
FOR k% = 0 TO deg%
IF (j% + k% - middle%) > noxbig% THEN
xsmallout!(k%) = xbigin!(noxbig%)
ysmallout!(k%) = ybigin!(noxbig%)
erflag% = 2
ELSEIF (j% + k% - middle%) < 1 THEN
xsmallout!(k%) = xbigin!(1)
ysmallout!(k%) = ybigin!(1)
erflag% = 2
ELSE
xsmallout!(k%) = xbigin!(j% + k% - middle%)
ysmallout!(k%) = ybigin!(j% + k% - middle%)
ENDIF
NEXT k%
ENDIF 'long condition
END IF
NEXT k%
ELSE
errflag% = 1
END IF 'nocnocntr%
END IF 'long condition
END SUB
SUB lagrange(xint!, yint!, x!(1), y!(1), deg%)
DIM l!(deg%)
yint! = 0
FOR cnt2% = 0 TO deg%
l!(cnt2%) = 1 'initialise
FOR cnt1% = 0 TO deg%
42 IF cnt1% <> cnt2% THEN LET l!(cnt2%) = l!(cnt2%) * (xint! - x!(cnt1%)) / (x!(cnt2%) - x!(cnt1%))
NEXT cnt1%
yint! = yint! + l!(cnt2%) * y!(cnt2%)
NEXT cnt2%
END SUB
SUB readtext(textfilename$, entries%, cols%, values!(2))
fileno% = 10
OPEN textfilename$ FOR INPUT AS #fileno%
entries% = 0
END SUB
WHILE NOT EOF(fileno%)  
  LINE INPUT #fileno%,a$ 
  entries%=entries%+1  
WEND  
CLOSE #fileno%  
OPEN textfilename$ FOR INPUT AS #fileno%  
FOR i%=1 TO entries%  
  LINE INPUT #fileno%,a$  
  FOR j%=1 TO cols%  
    IF j%<cols% THEN  
      tabpos%=INSTR(a$,CHR$(9))  
      length%=LEN(a$)  
      values!(i%,j%)=VAL(LEFT$(a$,tabpos%-1))  
      a$=RIGHT$(a$,length%-tabpos%) 'lop off the value already  
    ELSE  
      values!(i%,j%)=VAL(a$)  
    END IF  
  NEXT j%  
NEXT i%  
CLOSE #fileno%  
END SUB  
SUB writetext(textfilename$,entries%,cols%,values!(2))  
fileno%=11  
fileno2%=12  
OPEN textfilename$ FOR OUTPUT AS #fileno%  
OPEN "clip:" FOR OUTPUT AS #fileno2%  
OPEN "clip:" FOR OUTPUT AS #fileno2%  
FOR i%=1 TO entries%  
  FOR j%=1 TO cols%  
    IF j%<cols% THEN  
      PRINT #fileno%, values!(i%,j%);CHR$(9);  
      PRINT #fileno2%, values!(i%,j%);CHR$(9);  
    ELSE  
      PRINT #fileno%, values!(i%,j%);  
      PRINT #fileno2%, values!(i%,j%);  
    END IF  
  NEXT j%  
NEXT i%  
CLOSE #fileno%  
CLOSE #fileno2%  
END SUB
12.3.3. HP data transfer program

DIM f$(300,8),f(300,8)
ON ERROR GOTO errhnd

mainmenu:
CLS
PRINT "1 - Import a file from the HP"
PRINT "2 - Crunch an imported file"
PRINT "3 - Exit program"
PRINT "Choose 1-3"
rept:
a$=INPUT$(1)
a=VAL(a$)
IF a>3 OR a<1 THEN GOTO rept
ON a GOSUB import,crunch,quit
GOTO mainmenu

import:
GOSUB getnewfil
OPEN fil$ FOR OUTPUT AS #2
CLS
OPEN "com1:1200,e,7,1" FOR INPUT AS 1
begin$="false"
WHILE begin$<"BEGIN"
LINE INPUT #1,begin$
WEND
nextres:
INPUT #1,version$
IF INSTR(version$,"END")<>0 THEN
PRINT #2,"END"
CLOSE #1
CLOSE #2
RETURN
END IF
PRINT version$
PRINT #2,version$
INPUT #1,subversion$
PRINT subversion$
PRINT #2,subversion$
INPUT #1,t1$
PRINT t1$
PRINT #2,t1$
INPUT #1,n$
PRINT n$
PRINT #2,n$
FOR i%=1 TO VAL(n$)
FOR j%=1 TO 5
INPUT #1,f$(i%,j%)=VAL(f$(i%,j%))
f$(i%,j%)=STR$(f(i%,j%))
NEXT j%
PRINT #2,f$(i%,1);CHR$(9);f$(i%,2);CHR$(9);f$(i%,3);CHR$(9);f$(i%,4);CHR$(9);f$(i%,5)
PRINT f$(i%,1),f$(i%,2),f$(i%,3),f$(i%,4),f$(i%,5)
NEXT i%
GOTO nextres

crunch:
DIM opfil$(50)
CLS
GOSUB openfil
openfil$=fil$
OPEN openfil$ FOR INPUT AS #1
GOSUB getnewfil
openfiles=1 'no OUTPUT FILES OPEN yet, ONLY 1 INPUT FILE
nextres2:

50 INPUT #1, version$
IF INSTR(version$,"END")<>0 THEN
ERASE opfil$
    "so that is clear for next run"
FOR k=1 TO openfiles
CLOSE # k
NEXT k
RETURN
ENDIF
PRINT version$

60 INPUT #1, subversion$
PRINT subversion$

70 INPUT #1, t1$
PRINT t1$

80 INPUT #1, n$
PRINT VAL(n$)

90 potfilename$=fil$+"/"+MIDS(t1$2,5)+"A"+MIDS(t1$8,2) "prefix+acc file NAME
91 yetopen$="false" "force through
FOR i=2 TO 50
IF opfil$(i)=potfilename$ THEN
yetopen$="true"
fileno=i

100 hed$=MIDS(t1$4,4)+"/"
101 PRINT
    # fileno, hed$+"F"; CHR$(9); hed$+"Re"; CHR$(9); hed$+"Im"; CHR$(9); hed$+"Er"; CHR$(9); hed$+"Res"; CHR$(9); hed$+"log f"; CHR$(9); hed$+"log z"; CHR$(9); hed$+"theta"
END IF
NEXT i
IF yetopen$="false" THEN
    inc # open files (number excludes the input file)
fileno=openfiles
opfil$(openfiles)=potfilename$
OPEN potfilename$ FOR OUTPUT AS # fileno
hed$=MIDS(t1$4,4)+"/
PRINT # fileno, hed$+"F"; CHR$(9); hed$+"Re"; CHR$(9); hed$+"Im"; CHR$(9); hed$+"Er";
PRINT # fileno, CHR$(9); hed$+"Res"; CHR$(9); hed$+"log f"; CHR$(9);
PRINT # fileno, hed$+"log z"; CHR$(9); hed$+"theta"
END IF
FOR i%=1 TO VAL(n$)
110 LINE INPUT #1, a$
    FOR j%=1 TO 5
    IF j%<>5 THEN
        tabpos%=INSTR(a$, CHR$(9))
        length%=LEN(a$)
        f$(i%,j%)=LEFT$(a$, tabpos%-1)
        f(i%,j%)=VAL(LEFT$(a$, tabpos%-1))
        PRINT f(i%,j%); a$=RIGHT$(a$, length%-tabpos%) 'lop off the value already
    ELSE
        f$(i%,j%)=a$
        f(i%,j%)=VAL(a$)
    END IF
    NEXT j%
errhndflag=0
f$(i%,6)=STR$(LOG(f(i%,1))/LOG(10))

120 IF errhndflag=1 THEN
errhndflag=0
f$(i%,1)="ERR"
f$(i%,2)="ERR"
f$(i%,3)="ERR"
f$(i%,4)="ERR"

f$(i%,5)="ERR"
f$(i%,6)="ERR"
f$(i%,6)="ERR"
f$(i%,7)="ERR"
f$(i%,8)="ERR"
ENDIF
PRINT # fileno,f$(i%,1);CHR$(9);f$(i%,2);CHR$(9);f$(i%,3);CHR$(9);f$(i%,4);
PRINT # fileno,CHR$(9);f$(i%,5);CHR$(9);f$(i%,6);CHR$(9);f$(i%,7);CHR$(9);f$(i%,8)
PRINT f$(i%,1);CHR$(9);f$(i%,2);CHR$(9);f$(i%,3);CHR$(9);f$(i%,4);CHR$(9);
PRINT f$(i%,5);CHR$(9);f$(i%,6);CHR$(9);f$(i%,7);CHR$(9);f$(i%,8)
NEXT i%
FOR k=VAL(n$)+1 TO 99
PRINT # fileno,"
NEXT k
GOTO nextres2
getnewfil:
fil$=FILES$(0,"Output file name")
IF fil$="" THEN
CLS
INPUT "Do you want to quit";a$
IF a$="Y" OR a$="y" THEN
GOTO quit
ELSE
CLS
GOTO getnewfil
END IF
RETURN
openfil:
fil$=FILES$(1,"TEXT")
IF fil$="" THEN
CLS
INPUT "Do you want to quit";a$
IF a$="Y" OR a$="y" THEN
GOTO quit
ELSE
CLS
GOTO openfil
END IF
RETURN
quit:
END
errhnd:
errcnt=errcnt+1
IF ERR=5 OR ERR=11 AND ERL=110 THEN
errhndflag=1
CLS
PRINT "Error while extracting data"
FOR pauser=1 TO 100
px=SIN(pauser)
NEXT pauser
RESUME 120
END IF
IF ERR=5 AND ERL=50 THEN
version$="Error in reading version"
CLS
PRINT "Error while reading version"
FOR pauser=1 TO 100
px=SIN(pauser)
NEXT pauser
RESUME 60
END IF
IF ERR=5 AND ERL=60 THEN
  subversion$="Error in reading subversion"
  CLS
  PRINT "Error while reading subversion"
  FOR pauser=1 TO 100
    px=SIN(pauser)
  NEXT pauser
  RESUME 70
END IF
IF ERR=5 AND ERL=70 THEN
  t$="Error in reading title"
  CLS
  PRINT "Error while reading title"
  FOR pauser=1 TO 100
    px=SIN(pauser)
  NEXT pauser
  RESUME 80
END IF
IF ERR=5 AND ERL=80 THEN
  CLS
  PRINT "Error";ERR;" detected - cannot recover - press any key"
  PRINT "(Cannot read number of data points)"
  a$=INPUT$(1)
  GOTO mainmenu
END IF
IF ERR=5 AND ERL=90 THEN
  potfilename$="Errfil"+STR$(errcnt)
  CLS
  PRINT "Error while extracting filename"
  FOR pauser=1 TO 100
    px=SIN(pauser)
  NEXT pauser
  RESUME 91
END IF
IF ERR=5 AND ERL=100 THEN
  hed$="Errfil"+STR$(errcnt)
  CLS
  PRINT "Error while extracting filename"
  FOR pauser=1 TO 100
    px=SIN(pauser)
  NEXT pauser
  RESUME 101
END IF
IF ERR=5 AND ERL=110 THEN
  errhndflag=1
  CLS
  PRINT "Error while reading raw string"
  FOR pauser=1 TO 100
    px=SIN(pauser)
  NEXT pauser
  RESUME 120
END IF
IF ERR=5 AND ERL=6 THEN
  CLS
  PRINT "Error";ERR;" detected - cannot recover - press any key"
  PRINT "(Cannot read number of data points)"
  a$=INPUT$(1)
  GOTO mainmenu
END IF
12.3.4. Pseudo steady state photocurrent program

rept:
CLEAR, 100000L, 10000
area%=0 'area of the specimen
beep%=0 'beep flag in case of over or underflow in the voltage read
brd%=0 'brd% - Board Number (same as Slot Number)
curr%=0 'current value read
count%=0 'no of points to be input
counter%=0 'simple counter
terror%=0 'errorr% - error return; for possible errors see error checking routine
fiddlefactor%=1 'necessary because the par 173 potential sign is wrong
inputloops%=0 'flag that allows looping until user is satisfied with setup
inputmode%=0 'inputmode% - 0=differential, 1=single ended
inputrange%=0 'inputrange% - Voltage reference value for A/D 5 or 10 V
maxpercent%=0 'max percentage of full inputrange at which to sound beep
minpercent%=0 'min percentage of full inputrange to sound beep
muxmode%=0 'muxmode% - Future for ext. multiplexer use muxmode%=0 for now
numchans%=0 'number of channels to be scanned
pangle%=0 'phase angle
pcurrent%=0 'photocurrent
polarity%=0 'polarity% - 0=bipolar, 1=unipolar
pot%=0 'potential
sampinterval%=0 'sampinterval% - Sample Interval. Length of the sample
status%=0 'status% - status%=1 => data acq complete, 0=> data acq not yet complete
topec%0 'force one pass thru a loop
t stor%=0 'flag to see if the last value was stored
tim%=0 'time for acq at one wavelength
timebase%=0 'timebase% - Timebase for conversion pulse generation (0 - 5)
vcurr%=0 'actual voltage read on the current channel
Vpangle%=0 'actual voltage read on the angle channel
Vpcurrent%=0 'actual voltage read on the photocurrent channel
Vpot%=0 'actual voltage read on the potential channel
wlength%=0 'wavelength measured
wcounter%=0 'counter to see how many points done, prim for det if first round or not
w$= " junk variable used among others as temp storage space
outdatfil$=" used for the name of the output data file with the data
INIT%= 0
REM ** LabDriver Analog Output function codes
AOCONFIG%= &H10
AOWRITES%= &H11
AOUPDATE%= &H12
AOVSCALE%= &H13
REM ** LabDriver Analog Input function codes
AICONFIG%= &H20
AIRREAD%= &H21
AISCALE%= &H22
AISETUP%= &H23
AICHECK%= &H24
ACLEAR%= &H25
AIMUXCONFIG%= &H26
DIGOUTPORT%= &H30
DIGOUTLINE%= &H31
DIGINPORT%= &H32
DIGINLINE%= &H33
DIGFRTCONFG%= &H34
DIGFRTSTATUS%= &H35
DIGGRPCONFG%= &H36
DIGGRPSTATUS%= &H37
DIGGRPMODE%= &H38
DIGOUTGROUP%= &H39
DIGINGROUP%= &H3A
DAQCONFIG% = &H40  
DAQSTART% = &H41  
DAQCHECK% = &H42  
DAQCLEAR% = &H43  
DAQSCALE% = &H44  
SCANSETUP% = &H45  
SCANSTART% = &H46  
SCANCHECK% = &H47  
DAQ2CONFIG% = &H49  
DAQ2GET% = &H4A  
DAQ2TAP% = &H4B  
DAQ2CLEAR% = &H4C  
DAQ2MEMCONFIG% = &H4D  
DAQTRIGGER% = &H4E  
DAQ2GETSTR% = &H80  
DAQ2TAPSTR% = &H81  
CTRCONFIG% = &H50  
CTRSTOP% = &H51  
CTRRESTART% = &H52  
CTRRESET% = &H53  
CTREVSTATE% = &H54  
CTREVCOUNT% = &H55  
CTRPULSE% = &H57  
CTRSQUARE% = &H58  
CTRCLOCK% = &H59  
RTSICONN% = &H60  
RTSIDISCONN% = &H61  
RTSCLEAR% = &H62  
WFGRPSETUP% = &H70  
WFGRPSSTART% = &H71  
WFGRPSSTOP% = &H72  
WFGRPRESET% = &H73  
WFLOAD% = &H74  
WFSETUP% = &H75  
WFSTART% = &H76  
WFSTOP% = &H77  
WFRESET% = &H78  
WFCHECK% = &H79  
WFOFFSET% = &H7B  
LIBRARY "LabDriverLib.rsrc"  
LDSSysERR% = 0  
CALL ldfn(INT%, LDSysERR%)  
CLS  
LOCATE 10,10  
PRINT "-. Pcurr versus WLength  VERSION 1.0.4 -- 19 April 1989 --"  
FOR counterl%=1 TO 2000  
a$=STR$(SIN(COS(SIN(counterl%))))  
NEXT counterl% 

brd%=2 'my board is in slot #2  
nuchans%=4 '!!!!!!$&%^&^%^&^%^$^&^&^ <====My swearing because I said 3 here  
DIM chanvector%(nuchans%)  
DIM gainvector%(nuchans%)  
chanvector%(0)=1  
chanvector%(1)=2  
chanvector%(2)=3  
chanvector%(3)=5  
gainvector%(0)=4 'potential == see comment above  
gainvector%(1)=1 'vector == see comment above  
gainvector%(2)=1 'angle == see comment above  
gainvector%(3)=4 'current == see comment above  
timebase%= 4 'clock pulse for conversion = 1 ms  
inputmode%=0 'differential  
inputrange%=10 '10 V max
polarity%=0 'bipolar -10 to 10 V
muxmode%=0
CALL ldfn(AICONFIG%,brd%,errorr%,inputmode%,inputrange%,polarity%)
CALL ldfn(DAQCLEAR%, brd%, errorr%)
IF errorr%<>-74 THEN GOSUB chkerr
CLS
outdatfil$=FILES$(0,"Output file name")
INPUT "Specimen area (cm2) (default is 1)";a$
IF a$="" THEN
  area!=1
  PRINT area!
ELSE
  area!=VAL(a$)
  PRINT area!
END IF
INPUT "Sound beep for underflow % (default is 10 wt%)";a$
IF a$="" THEN
  minpercent!=.1
  PRINT minpercent!
ELSE
  minpercent!=VAL (a$)/100
  PRINT minpercent!
END IF
INPUT "Sound beep for overflow % (default is 90%)";a$
IF a$="" THEN
  maxpercent!=.9
  PRINT maxpercent!
ELSE
  maxpercent!=VAL(a$)/100
  PRINT maxpercent!
END IF
OPEN outdatfil$ FOR OUTPUT AS #1
OPEN "clip:" FOR OUTPUT AS #2
wlength!=250 'initial proposed starting value
stopp%=0 'force one pass true
stor%=0 'flag to see if the last value was stored
wcounter%=0 'counter to see how many points done, prim for det if first round or not
WHILE stopp%=0
  wcounter%=wcounter%+1
  infcorr%=0 'force one pass through next loop
  newwlength!=wlength!+10
  inploops%=0
  WHILE infcorr%=0
    inploops%=inloops%+1
    CLS
    IF wcounter%>1 THEN
      IF stor%=1 AND inploops%=1 THEN
        PRINT "The prev wavelength was (nm)";wlength!;" and was stored"
      ELSEIF stor%=0 AND inploops%=1 THEN
        PRINT "The prev wavelength was (nm)";wlength!;" and was not stored"
      ELSEIF inploops%!>1 THEN
        PRINT "The prev wavelength was (nm)";wlength!;" and measmt was not taken"
    END IF
    ELSE
      PRINT
    END IF
    IF wcounter%>1 THEN
      PRINT
    END IF
  END WHILE
  wlength!=VAL(a$)
PRINT wlength!
ENDIF
INPUT "Number of points to be input per wavelength (default is 1000)";a$
IF a$="" THEN
  countperchannel%=1000
  PRINT countperchannel%
ELSE
  countperchannel%=VAL(a$)
  PRINT countperchannel%
ENDIF
INPUT "Sample interval (ms) (2<=int<=32767,default is 25)";a$
IF a$="" THEN
  sampinterval%=25
  PRINT sampinterval%
ELSE
  sampinterval%=VAL(a$)
  PRINT sampinterval%
ENDIF
INPUT "Range setting on Pstat (default is 10e-6 A)";a$
IF a$="" THEN
  rangei!=.00001
  PRINT USING "+.##^^^";rangei!
ELSE
  rangei!=VAL(a$)
  PRINT USING "+.##^^^";rangei!
ENDIF
INPUT "Lockin sensitivity (V/10 V) (default is 500e-6)";a$
IF a$="" THEN
  locksens!=.0005
  PRINT USING "+.##^^^";locksens!
ELSE
  locksens!=VAL(a$)
  PRINT USING "+.##^^^";locksens!
ENDIF
ELSE
INPUT "New wavelength (nm) (return for 10 nm increment on prev stored value)";a$
IF a$="" THEN
  IF stor%=1 THEN
    wlength!=newwlength!
  ELSE
    wlength!=wlength!
  ENDIF
  PRINT wlength!
ELSE
  wlength!=VAL(a$)
  PRINT wlength!
ENDIF
INPUT "Number of points to be input per wavelength (Return for prev value)";a$
IF a$="" THEN
  countperchannel%=countperchannel%
  PRINT countperchannel%
ELSE
  countperchannel%=VAL(a$)
  PRINT countperchannel%
ENDIF
INPUT "Sample interval (ms) (2<=int<=32767,Return for prev value)";a$
IF a$="" THEN
  sampinterval%=sampinterval%
  PRINT sampinterval%
ELSE
  sampinterval%=VAL(a$)
  PRINT sampinterval%
ENDIF
INPUT "Range setting on Pstat (Return for prev value)";a$
IF a$="" THEN
rangei!=rangei!
PRINT USING "+#.##^^^";rangei!
ELSE
rangei!=VAL(a$)
PRINT USING "+#.##^^^";rangei!
ENDIF

INPUT "Lockin sensitivity (V/10 V) (Return for prev value)";a$
IF a$="" THEN
locksens!=locksens!
PRINT USING "+#.##^^^";locksens!
ELSE
locksens!=VAL(a$)
PRINT USING "+#.##^^^";locksens!
ENDIF
ENDIF

count%=countperchannel%*numchans%
tim!=(count%*sampinterval%)/1000!
stor%=0 'reinitialise for the next round
PRINT "The time per frequency acquisition is ";tim!;" (s)"
LOCATE 20,10
PRINT "If points, time is not OK press 'N', else press any other key"
a$=INPUT$(1)
IF a$<"N" AND a$&"n" THEN
LET infcorr%=1
WEND

IF wcounter%=1 THEN
DIM buffer%(numchans%-1,countperchannel%)
ELSE
ERASE buffer%
DIM buffer%(numchans%-1,countperchannel%)
ENDIF
CLS
LOCATE 10,20
PRINT "Acquisition in progress - Please be patient"
CALL ldfn(SCANSETUP%,brd%,errorr%,numchans%,chanvector%(0),gainvector%(0),muxmode%)
IF errorr%<>-74 THEN GOSUB chkerr
CALL ldfn(SCANSTART%,brd%,errorr%,buffer%(0,0),count%,timebase%,sampinterval%)
IF errorr%<>-74 THEN GOSUB chkerr
CHK:
errorr%=0
CALL ldfn(SCANCHECK%,brd%,errorr%,status%) 'checks status of background acquisition
IF errorr%<>-74 THEN GOSUB chkerr
IF (status% < 1) GOTO CHK
pot!=0
pcurrent!=0
pangle!=0
curr!=0
FOR counterl%=0 TO countperchannel%-1
pot!=pot!+buffer%(0,counter1%)
pcurrent!=pcurrent!+buffer%(1,counter1%)
pangle!=pangle!+buffer%(2,counter1%)
curr!=curr!+buffer%(3,counter1%)
NEXT counter1%
pot!=pot!/countperchannel%
pcurrent!=pcurrent!/countperchannel%
pangle!=pangle!/countperchannel%
curr!=curr!/countperchannel%
vpot!=(pot!/2048)*(inputrange%/gainvector%(0))
vpcurrent!=(pcurrent!/2048)*(inputrange%/gainvector%(1))
pangle!=(pangle!/2048)*(inputrange%/gainvector%(2))
vcurr!=(curr!/2048)*(inputrange%/gainvector%(3))
pot!=fiddlefactor%*(pot!/2048)*(inputrange%/gainvector%(0))
pcurrent!=(pcurrent!/2048)*(inputrange%/gainvector%(1))
rangei!*locksens!10

355
LOCATE 3,20
PRINT "Instrument settings"
PRINT "Number of points to be input per wavelength":countperchannel%
PRINT "Sample interval (ms)":sampinterval%
PRINT "Range setting on Pstat (A) ";
PRINT USING "+#.##A^":rangei!
PRINT "Lockin sensitivity (V/10 V) ";
PRINT USING "+#.###":locksens!
PRINT "Acquisition time per point (s)":time!
LOCATE 10,20
PRINT "Real value":;TAB(40);"Actual voltage"
PRINT
PRINT "Wavelength (nm)";
PRINT TAB(20);
PRINT USING "+####":wlength!
PRINT "Pot (V)";
PRINT TAB(20);
PRINT USING "+#.###":pot!
PRINT TAB(40);
PRINT USING "+#.###":vpot!
PRINT "Current (A/cm^2)";
PRINT TAB(20);
PRINT USING "+#.###":curr!
PRINT TAB(40);
PRINT USING "+#.###":vpcurrent!
PRINT "Phase angle (Deg)";
PRINT TAB(20);
PRINT USING "+#.###":pangle!
PRINT TAB(40);
PRINT USING "+###.##":pangle!
FOR counterl%=1 TO 3
SOUND 600,5,255,0
NEXT counterl%
ELSE
SOUND 200,5,255
NEXT counterl%
END IF
LOCATE 20,20
PRINT "Print this to the output files ?"
a$=INPUT$(1)
IF a$<"N" AND a$<"n" THEN
PRINT #1, wlength!;CHR$(9);pot!;CHR$(9);curr!;CHR$(9); pcurrent!;CHR$(9);pangle!
PRINT #2, wlength!;CHR$(9);pot!;CHR$(9);CHR$(9);curr! pcurrent!;CHR$(9);pangle!
stor%=1
LOCATE 18,10
PRINT "Press any key to do next frequency, (N) to exit loop ......"
a$=INPUT$(1)
IF a$="N" OR a$="n" THEN stop%=1
IF (error%=-1) THEN CLS: LOCATE 10,15:PRINT "***Device Manager Error"*:STOP
IF (error%=-60) THEN CLS: LOCATE 10,15:PRINT "***Not our board"*:STOP
IF (error%=-61) THEN CLS: LOCATE 10,15:PRINT "***Bad board number"*:STOP
IF (error%=-62) THEN CLS: LOCATE 10,15:PRINT "***Bad GAIN"*:STOP
IF (error%=-63) THEN CLS: LOCATE 10,15:PRINT "***Bad channel number"*:STOP
IF (error%=-64) THEN CLS: LOCATE 10,15:PRINT "***Function not supported on this board"*:STOP
IF (error%=-65) THEN CLS: LOCATE 10,15:PRINT "***Port parameter out of range"*:STOP
IF (error%=-66) THEN CLS: LOCATE 10,15:PRINT "***Port not configured for output"*:STOP
IF (error%=-67) THEN CLS: LOCATE 10,15:PRINT "***Port does not handle handshaking"*:STOP
IF (error%=-68) THEN CLS: LOCATE 10,15:PRINT "***Port cannot be assigned to a group"*:STOP
IF (error%=-69) THEN CLS: LOCATE 10,15:PRINT "***Bad input value"*:STOP
IF (error%=-70) THEN CLS: LOCATE 10,15:PRINT "***Incomplete A/D"*:STOP
IF (error%=-71) THEN CLS: LOCATE 10,15:PRINT "***Input value out of range"*:STOP
IF (error%=-72) THEN CLS: LOCATE 10,15:PRINT "***Data Acquisition in progress"*:STOP
IF (error%=-73) THEN CLS: LOCATE 10,15:PRINT "***Counter in use"*:STOP
IF (error%=-74) THEN CLS: LOCATE 10,15:PRINT "***No Data Acquisition"*:STOP
IF (error%=-75) THEN CLS: LOCATE 10,15:PRINT "***Overflow in Data Acquisition"*:STOP
IF (error%=-76) THEN CLS: LOCATE 10,15:PRINT "***Overrun in Data Acquisition"*:STOP
IF (error%=-77) THEN CLS: LOCATE 10,15:PRINT "***Bad count. Scan count must be mult. of no. of ch."*:STOP
IF (error%=-78) THEN CLS: LOCATE 10,15:PRINT "***Bad board type"*:STOP
IF (error%=-79) THEN CLS: LOCATE 10,15:PRINT "***Counter not configured for event counting"*:STOP
IF (error%=-80) THEN CLS: LOCATE 10,15:PRINT "***Counter reserved for data acqu. only"*:STOP
IF (error%=-81) THEN CLS: LOCATE 10,15:PRINT "***Port currently assigned to a group"*:STOP
IF (error%=-82) THEN CLS: LOCATE 10,15:PRINT "***No port assigned to group specified"*:STOP
IF (error%=-83) THEN CLS: LOCATE 10,15:PRINT "***Group not configured for output"*:STOP
IF (error%=-90) THEN CLS: LOCATE 10,15:PRINT "***Invalid signal direction specified"*:STOP
IF (error%=-91) THEN CLS: LOCATE 10,15:PRINT "***RTSI line in use"*:STOP
IF (error%=-92) THEN CLS: LOCATE 10,15:PRINT "***No RTSI line available"*:STOP
IF (error%=-93) THEN CLS: LOCATE 10,15:PRINT "***Signal in use"*:STOP
IF (error%=-94) THEN CLS: LOCATE 10,15:PRINT "***No DMA board"*:STOP
IF (error%=-95) THEN CLS: LOCATE 10,15:PRINT "***No DMA channel available"*:STOP
IF (error%=-96) THEN CLS: LOCATE 10,15:PRINT "***Waveform setup call required"*:STOP
IF (error%=-97) THEN CLS: LOCATE 10,15:PRINT "***Analog output channel in use"*:STOP
IF (error%=-98) THEN CLS: LOCATE 10,15:PRINT "***Waveform load call required"*:STOP
IF (error%=-99) THEN CLS: LOCATE 10,15:PRINT "***Specified channel has been assigned to a group"*:STOP
IF (error%=-100) THEN CLS: LOCATE 10,15:PRINT "***No waveform operation executed"*:STOP
IF (error%=-101) THEN CLS: LOCATE 10,15:PRINT "***Only one WFGRPSETUP call per board allowed"*:STOP
IF (error%=-108) THEN CLS: LOCATE 10,15:PRINT "***Not enough memory"*:STOP
IF (error%=-110) THEN CLS: LOCATE 10,15:PRINT "***Labdriver not configured for double buffered mode"*:STOP
IF (error%=-111) THEN CLS: LOCATE 10,15:PRINT "***Acquired data overwritten"*:STOP
IF (error%=-112) THEN CLS: LOCATE 10,15:PRINT "***Number samples requested not yet available"*:STOP
IF (error%=-113) THEN CLS: LOCATE 10,15:PRINT "***Acquisition complete before no of samples requested available"*:STOP
IF (error%=-114) THEN CLS: LOCATE 10,15:PRINT "***Block size parameter does not conform to an integer mult of no of channels"*:STOP
IF (error%=-115) THEN CLS: LOCATE 10,15:PRINT "***DAQ2MEMCONFIG executed after DAQ2CONFIG"*:STOP
IF (error%=-120) THEN CLS: LOCATE 10,15:PRINT "***No trigger value found"*:STOP
IF (error%=-121) THEN CLS: LOCATE 10,15:PRINT "***Analog trigger did not occur before timeout"*:STOP
RETURN
12.3.5. Cyclic voltammetry photocurrent program

rept:
CLEAR, 100000!, 10000

' Variable declaration part

'simple variables
acqtime%=0 'time to acquire data
area%=0 'area of the specimen
beep%=0 'beep flag in case of over or underflow in the voltage read
brd%=0 'brd% - Board Number (same as Slot Number)
curr%=0 'current value read
counter%=0 'no of points to be input
counter%=0 'simple counter
datapairs%=0 'counter for the number of data pairs
i%=0 'counter
error%=0 'error% - error value return; for possible errors see error checking routine
fiddlefactor%=-1 'necessary because the par 173 potential sign is wrong
inprice%=0 'flag that allows looping until user is satisfied with setup
inputmode%=0 'inputmode% = 0=differential, 1=single ended
inputrange%=0 'inputrange% - Voltage reference value for A/D 5 or 10 V
interrupt%=0 'interrupt% of the experiment flag
mapcurpot%=0 'potential at the max photocurrent
maxpercent%=0 'max percentage of full inputrange at which to sound beep
minpercent%=0 'min percentage of full inputrange to sound beep
muxmode%=0 'muxmode% - Future for ext. multiplexer use muxmode%=0 for now
numchans%=0 'number of channels to be scanned
pangle%=0 'phase angle
pcurrent%=0 'photocurrent
polarity%=0 'polarity% - 0=bipolar, 1=unipolar
pot%=0 'potential
loud%=0 'sound volume
soft%=0 'sound volume

tampinterval%=0'sampinterval% - Sample Interval. Length of the sample

'sampie variables
status%=0 'status% - status%=1 => data acq complete, 0=> data acq not yet complete
time%=0 'time for acq at one wavelength
timebase%=0 'timebase% - Timebase for conversion pulse generation (0 - 5)

'timeout%=0 'time out of input loop
timein%=0 'time in input loop
storstart%=0 'flag to control if data stored or not
vprint%=0 'voltage read pot
vangle%=0 'voltage read phaseangle
vcurrent%=0 'voltage read pcurr
vcurr%=0 'voltage read current
wlength%=0 'wavelength measured
wcounter%=0 'counter to see how many points done, prim for det if first round or not

'string variables
as="" 'junk variable used among others as temp storage space
outdatfil$="" 'used for the name of the output data file with the data

array variables
'buffer%() is used for returning the demultiplexed data
'chanvector%() vector with channel sequence
'gainvector%() vector with gain values

' Labdriver initialisation (LabDriverInit.bas)
INIT% = 0
AOCONFIG% = &H10
AOWRITE% = &H11
AOUPDATE% = &H12
AOVSCALE% = &H13
AICONFIG% = &H20
AIREAD% = &H21
AISCALE% = &H22
AISETUP% = &H23
AICHECK% = &H24
AICLEAR% = &H25
AIMUXCONFIG% = &H26
DIGOUTPORT% = &H30
DIGOUTLINE% = &H31
DIGINPORT% = &H32
DIGINLINE% = &H33
DIGPRTCONFIG% = &H34
DIGPRTSTATUS% = &H35
DIGGRPCONFIG% = &H36
DIGGRPSTATUS% = &H37
DIGGRPMODE% = &H38
DIGOUTGROUP% = &H39
DIGINGROUP% = &H4A
DAQCONF% = &H40
DAQSTART% = &H41
DAQCHECK% = &H42
DAQCLEAR% = &H43
DAQSCALE% = &H44
SCANSETUP% = &H45
SCANSTART% = &H46
SCANCHECK% = &H47
DAQ2CONF% = &H49
DAQ2GET% = &H4A
DAQ2TAP% = &H4B
DAQ2CLEAR% = &H4C
DAQ2MEMCONFIG% = &H4D
DAQTRIGGER% = &H4E
DAQ2GETSTR% = &H80
DAQ2TAPSTR% = &H81
CTRCONFIG% = &H50
CTRSTOP% = &H51
CTRESTART% = &H52
CTRESET% = &H53
CTRSTATE% = &H54
CTREVCOUNT% = &H55
CTREVREAD% = &H56
CTRPULSE% = &H57
CTRSQUARE% = &H58
CTRCLK% = &H59
RTSICONN% = &H60
RTSIDISCONN% = &H61
RTSICLEAR% = &H62
WFGRPSETUP% = &H70
WFGRPSTART% = &H71
WFGRPSTOP% = &H72
WFGRPRESET% = &H73
WFLoad% = &H74
WFSKET% = &H75
WFSTART% = &H76
WFSTOP% = &H77
WFRESET% = &H78
WFCHECK% = &H79
WFOFFSET% = &H7B
LIBRARY "LabDriverLib.rsrc"
LDSysERR% = 0
CALL ldfn(IN1T%, LDSysERR%)
' Start of main program
'Setup of parameters part
brd%=2 'my board is in slot #2
'MAY ONLY SPECIFY 2, 4 OR 8!!!!!!!!!!!!IIII!!!II!1f!!11!!If!!!!!!!!!!!!!
'channel no 1 is the potential
'channel no 2 is the lockin vector R
'channel no 3 is the lockin angle
'channel no 5 is the current value
numchans%=4
DIM chanvector%(numchans%)
DIM gainvector%(numchans%)
'MAY ONLY SPECIFY 2, 4 OR 8!!!!!!!!!!!!IIII!!!II!1f!!11!!If!!!!!!!!!!!!!
'channel no 1 is the potential
'channel no 2 is the lockin vector R
'channel no 3 is the lockin angle
'channel no 5 is the current
chanvector%(0)=1
chanvector%(1)=2
chanvector%(2)=3
chanvector%(3)=5
'MAY ONLY SPECIFY 2, 4 OR 8!!!!!!!!!!!!IIII!!!II!1f!!11!!If!!!!!!!!!!!!!
gainvector%(0)=4 'potential == see comment above
gainvector%(1)=1 'vector == see comment above
gainvector%(2)=1 'angle == see comment above
gainvector%(3)=4 'current == see comment above
timebase%= 3 'clock pulse for conversion = 0.1 ms
'now for board dip switch settings
inputmode%=0 'differential
inputrange%=10 '10 V max
polarity%=0 'bipolar -10 to 10 V
muxmode%=0
'MAY ONLY SPECIFY 2, 4 OR 8!!!!!!!!!!!!IIII!!!II!1f!!11!!If!!!!!!!!!!!!!
'initialise the analog input circuitry for above parameter values
CALL ldffn(AICONFIG%,brd%,errorr%,inputmode%,inputrange%,polarity%)
'MAY ONLY SPECIFY 2, 4 OR 8!!!!!!!!!!!!IIII!!!II!1f!!11!!If!!!!!!!!!!!!!
'clearing of data acq. circuitry
CALL ldffn(DAQCLEAR%, brd%, errorr%)
IF errorr%<>-74 THEN GOSUB chkerr
'MAY ONLY SPECIFY 2, 4 OR 8!!!!!!!!!!!!IIII!!!II!1f!!11!!If!!!!!!!!!!!!!
'get information
infcorr%=0
WHILE infcorr%=0
CLS
outdatfil$=FILES$(0,"Output file name")
INPUT "Specimen area (cm2) (default is 1)";a$
IF a$="" THEN
area!=1
PRINT area!
ELSE
area!=VAL(a$)
PRINT area!
END IF
INPUT "Seconds between each data point (default is 5 seconds)";a$
IF a$="" THEN
seconds%=5
PRINT seconds%
ELSE
seconds%=VAL(a$)
PRINT seconds%
END IF
INPUT "Number of points to be input (default is 100)";a$
IF a$="" THEN
countperchannel%=100
PRINT countperchannel%
ELSE
countperchannel%=VAL(a$)
PRINT countperchannel%

INPUT "Sample interval (.1*ms) (2<=int<=32767, default is 25)"; a$
IF a$="" THEN
    sampinterval%=25
    PRINT sampinterval%
ELSE
    sampinterval%=VAL(a$)
    PRINT sampinterval%
ENDIF
acqtime!=sampinterval%*.0001*countperchannel%*4
PRINT "(Time to acquire ;acqtime; "s)"
INPUT "Range setting on Pstat (default is 10e-6 A)"; a$
IF a$="" THEN
    rangei!=.00001
    PRINT USING "+#.##^^^"; rangei!
ELSE
    rangei%=VAL(a$)
    PRINT USING "+#.##^^^"; rangei!
ENDIF
INPUT "Lockin sensitivity (V/10 V) (default is 500e-6)"; a$
IF a$="" THEN
    locksens!=.0005
    PRINT USING "+#.##^^^"; locksens!
ELSE
    locksens%=VAL(a$)
    PRINT USING "+#.##^^^"; locksens!
ENDIF
PRINT "Beep for over and underflows (Y/N)"
a$=INPUT$(1)
IF a$="Y" OR a$="y" THEN
    loud%=100
    soft%=50
ELSE
    loud%=0
    soft%=0
ENDIF
'calculate the number of points in total to be input
count%=countperchannel%*numchans%
LOCATE 20,10
PRINT "Any key to continue, 'n' or 'N' to repeat input parameters"
a$=INPUT$(1)
IF a$<"N" AND a$<"n" THEN LET infcorr%=1
WEND
CLS
LOCATE 18,10
PRINT "Press 'r' or 'R' to reset max/mins"
LOCATE 19,10
PRINT "Press 'T' or 'L' to set lockin amplification"
LOCATE 20,10
PRINT "Press 'b' or 'B' to start storing values"
LOCATE 21,10
PRINT "Press 'q' or 'Q' to stop experiment"
LOCATE 9,10
PRINT "Vi iph fi"
' the OUTPUT FILES
OPEN outdatfil$ FOR OUTPUT AS #1
'dimension the storage space for this number of points
DIM buffer%(numchans%-1,countperchannel%)
'reset the max + min values before entering into loop
mapot!=-1E+10
mapangle!=-1E+10
mapcurrent!=-1E+10
macurr!=-1E+10
mipot!=1E+10
mipangle!=1E+10
mipcurrent!=1E+10
micurr!=1E+10

'loop while the person does not interrupt the scan
interrupt%=0
datapairs%=0
storstart%=0 'don't store at start
beginintime=TIMER
WHILE interrupt%=0
datapairs%=datapairs%+1
  'Initialize circuitry for a scanned data acquisition
  CALL ldfn(SCANSETUP%, brd%, errorr%, numchans%, chanvector%(0), gainvector%(0), muxmode%)
  IF errorr%<>-74 THEN GOSUB chkerr
  'Acquire DATA
  CALL ldfn(SCANSTART%, brd%, errorr%, buffer%(0,0), count%, timebase%, sampinterval%)
  IF errorr%<>-74 THEN GOSUB chkerr
  CHK:
  errorr%=0
  CALL ldfn(SCANCHECK%, brd%, errorr%, status%) 'checks status of background acquisition
  IF errorr%<>-74 THEN GOSUB chkerr
  IF (status%<>1) GOTO CHK
  'now determine the true average value of the potential, photocurrent, angle
  pot!=0
  pcurrent!=0
  pangle!=0
  curr!=0
  'calc true values
  FOR counterl%=0 TO countperchannel%-1
    pot!=pot! +buffer%(0,counterl%)
    pcurrent!=pcurrent!+buffer%(1,counterl%)
    pangle!=pangle!+buffer%(2,counterl%)
    curr!=curr!+buffer%(3,counterl%)
  NEXT counterl%
  'calculate true voltages
  vpot!=((pot!/countperchannel%)/2048)*(inputrange%/gainvector%(0))
  vpangle!=((pangle!/countperchannel%)/2048)*(inputrange%/gainvector%(2))
  vpcurrent!=((pcurrent!/countperchannel%)/2048)*(inputrange%/gainvector%(1))
  vcurr!=((curr!/countperchannel%)/2048)*(inputrange%/gainvector%(3))

  'sound warning if the lockin is overflowing/underflowing or the pstat current is too great
  *** underflows ***
  IF vpcurrent!<1 THEN
    SOUND 523,2,soft%,0
    LOCATE 1,10
    PRINT "pcurrent underflow"
  END IF
  IF vpot!<-2.45 THEN
    SOUND 659,2,soft%,0
    LOCATE 2,10
    PRINT "pot underflow"
  END IF
IF ABS(vcurr!)<.1 THEN
    SOUND 784.2,soft%,0
    LOCATE 3,10
    PRINT "current underflow"
ENDIF

'*** overflows ***
IF vpcurrent!>9 THEN
    SOUND 523.5,loud%,0
    LOCATE 4,10
    PRINT "pcurrent overflow"
ENDIF

IF vpot!>2.45 THEN
    SOUND 659.5,loud%,0
    LOCATE 5,10
    PRINT "pot overflow"
ENDIF

IF ABS(vcurr!)>.9 THEN
    SOUND 784.5,loud%,0
    LOCATE 6,10
    PRINT "current overflow"
ENDIF

pot!=fiddlefactor%*((pot!/countperchannel%)/2048)*(inputrange%/gainvector%(0))
pcurrent!=((pcurrent!/countperchannel%)/2048)*(inputrange%/gainvector%(1))*rangei!*locksen!/10/area!
pangle!=((pangle!/countperchannel%)/2048)*(inputrange%/gainvector%(2))/.05
curr!=((curr!/countperchannel%)/2048)*(inputrange%/gainvector%(3))*rangei!/area!

'*** take action on user interrupt ***
a$=INKEY$
IF a$="R" OR a$="r" THEN
    'reset the max + min values
    mapot!=-1E+10
    mapangle!=-1E+10
    mapcurrent!=-1E+10
    macurr!=-1E+10
    mipot!=1E+10
    mipangle!=1E+10
    mipcurrent!=1E+10
    micurr!=1E+10
END IF

'only start storing after the user specifies
IF a$="b" OR a$="B" THEN
    storstart%=1
    LOCATE 20,10
    PRINT "Press 's' or 'S' to stop storing values"
ENDIF

IF a$="S" OR a$="s" THEN
    storstart%=0
    LOCATE 20,10
    PRINT "Press 'b' or 'B' to start storing values"
ENDIF

IF a$="q" OR a$="Q" THEN
    interrupt%=1
END IF
IF a$="I" OR a$="L" THEN
  timein!=TIMER
  LOCATE 17,20
  INPUT "New lockin sensitivity (V/10 V)";locksens!
  LOCATE 17,20
  PRINT " 
  timeout!=TIMER
  'to not let the next few points be on each other set time
  'on by time it took to get info
  begintime!=begintime!+(timeout!-timein!)
ENDIF
'reset for next command
a$=""

'accumulate min and max values
IF vpcurrent!>mapcurrent! THEN
  mapcurrent!=vpcurrent!
  mapcurpot!=pot!
END IF
IF vpcurrent!<mipcurrent! THEN
  mipcurrent!=vpcurrent!
END IF
IF vcurr!>macurr! THEN
  macurr!=vcurr!
END IF
IF vcurr!<micurr! THEN
  micurr!=vcurr!
END IF
IF vpot!>mappot! THEN
  mappot!=vpot!
END IF
IF vpot!<mippot! THEN
  mippot!=vpot!
END IF
IF vpangle!>mapangle! THEN
  mapangle!=vpangle!
END IF
IF vpangle!<mipangle! THEN
  mipangle!=vpangle!
END IF
LOCATE 10,10
PRINT " 
LOCATE 10,10
PRINT USING "+#.###";pot!;
PRINT " 
PRINT USING "+#.###^^^";curr!;
PRINT " 
PRINT USING "+###.##";pcurrent!;
PRINT " 
PRINT USING "+#####";pangle!;

IF storstart%=1 THEN
  PRINT #1,pot!;CHR$(9);curr!;CHR$(9); pcurrent!;CHR$(9);pangle!
  PRINT "Value stored"
ENDIF
ELSE
    PRINT " Value not stored"
ENDIF

LOCATE 11,3
PRINT " "
LOCATE 11,3
PRINT "R1 V";
LOCATE 11,10
PRINT USING "+#.###";vpot!;
PRINT " ";
PRINT USING "+#.###";vcurl!;
PRINT " ";
PRINT USING "+#.###";vpcurrent!;
PRINT " ";
PRINT USING "+#.###";vpangle!;

LOCATE 12,3
PRINT " "
LOCATE 12,3
PRINT "Vmax ";
LOCATE 12,10
PRINT USING "+#.###";mapot!;
PRINT " ";
PRINT USING "+#.###";macurr!;
PRINT " ";
PRINT USING "+#.###";mapcurrent!;
PRINT " ";
PRINT USING "+#.###";mapangle!;
PRINT " (;
PRINT USING "+#.###";mapcurpot!;
PRINT ");"

LOCATE 13,3
PRINT " "
LOCATE 13,3
PRINT "Vmin ";
LOCATE 13,10
PRINT USING "+#.###";mipot!;
PRINT " ";
PRINT USING "+#.###";micurr!;
PRINT " ";
PRINT USING "+#.###";mipcurrent!;
PRINT " ";
PRINT USING "+#.###";mipangle!;

'wait until the time is right for the next run
WHILE TIMER<begintime!+datapairs%*seconds%
    hang around here
WEND

'clear upper corner of screen
FOR i%=1 TO 6
    LOCATE i%,1
    PRINT " 
NEXT i%

WEND
CLOSE #1
LOCATE 15,10
PRINT "All done. Press any key to exit, (R) to repeat the calibration"
a$=INPUT$(1)
This subroutine checks for possible Data Acquisition Errors and prints an appropriate message.

chkerr:
IF (error% = -1) THEN CLS: LOCATE 10,15:PRINT "**Device Manager Error" **":STOP
IF (error% = -60) THEN CLS: LOCATE 10,15:PRINT "**Not our board" **":STOP
IF (error% = -61) THEN CLS: LOCATE 10,15:PRINT "**Bad board number" **":STOP
IF (error% = -62) THEN CLS: LOCATE 10,15:PRINT "**Bad GAIN" **":STOP
IF (error% = -63) THEN CLS: LOCATE 10,15:PRINT "**Bad channel number" **":STOP
IF (error% = -64) THEN CLS: LOCATE 10,15:PRINT "**Function not supported on this board" **":STOP
IF (error% = -65) THEN CLS: LOCATE 10,15:PRINT "**Port parameter out of range" **":STOP
IF (error% = -66) THEN CLS: LOCATE 10,15:PRINT "**Port not configured for output" **":STOP
IF (error% = -67) THEN CLS: LOCATE 10,15:PRINT "**Port does not handle handshaking" **":STOP
IF (error% = -68) THEN CLS: LOCATE 10,15:PRINT "**Port cannot be assigned to a group" **":STOP
IF (error% = -69) THEN CLS: LOCATE 10,15:PRINT "**Bad input value" **":STOP
IF (error% = -70) THEN CLS: LOCATE 10,15:PRINT "**Incomplete A/D" **":STOP
IF (error% = -71) THEN CLS: LOCATE 10,15:PRINT "**Input value out of range" **":STOP
IF (error% = -72) THEN CLS: LOCATE 10,15:PRINT "**Data Acquisition in progress" **":STOP
IF (error% = -73) THEN CLS: LOCATE 10,15:PRINT "**Counter in use" **":STOP
IF (error% = -74) THEN CLS: LOCATE 10,15:PRINT "**No Data Acquisition" **":STOP
IF (error% = -75) THEN CLS: LOCATE 10,15:PRINT "**Overflow in Data Acquisition" **":STOP
IF (error% = -76) THEN CLS: LOCATE 10,15:PRINT "**Overrun in Data Acquisition" **":STOP
IF (error% = -77) THEN CLS: LOCATE 10,15:PRINT "**Bad count. Scan count must be mult. of no. of ch." **":STOP
IF (error% = -78) THEN CLS: LOCATE 10,15:PRINT "**Bad board type" **":STOP
IF (error% = -79) THEN CLS: LOCATE 10,15:PRINT "**Counter not configured for event counting" **":STOP
IF (error% = -80) THEN CLS: LOCATE 10,15:PRINT "**Counter reserved for data acq. only" **":STOP
IF (error% = -81) THEN CLS: LOCATE 10,15:PRINT "**Port currently assigned to a group" **":STOP
IF (error% = -82) THEN CLS: LOCATE 10,15:PRINT "**No port assigned to group specified" **":STOP
IF (error% = -83) THEN CLS: LOCATE 10,15:PRINT "**Group not configured for output" **":STOP
IF (error% = -90) THEN CLS: LOCATE 10,15:PRINT "**Invalid signal direction specified" **":STOP
IF (error% = -91) THEN CLS: LOCATE 10,15:PRINT "**RTSI line in use" **":STOP
IF (error% = -92) THEN CLS: LOCATE 10,15:PRINT "**No RTSI line available" **":STOP
IF (error% = -93) THEN CLS: LOCATE 10,15:PRINT "**Signal in use" **":STOP
IF (error% = -94) THEN CLS: LOCATE 10,15:PRINT "**No DMA board" **":STOP
IF (error% = -95) THEN CLS: LOCATE 10,15:PRINT "**No DMA channel available" **":STOP
IF (error% = -96) THEN CLS: LOCATE 10,15:PRINT "**Waveform setup call required" **":STOP
IF (error% = -97) THEN CLS: LOCATE 10,15:PRINT "**Analog output channel in use" **":STOP
IF (error% = -98) THEN CLS: LOCATE 10,15:PRINT "**Waveform load call required" **":STOP
IF (error% = -99) THEN CLS: LOCATE 10,15:PRINT "**Specified channel has been assigned to a group" **":STOP
IF (error% = -100) THEN CLS: LOCATE 10,15:PRINT "**No waveform operation executed" **":STOP
IF (error% = -101) THEN CLS: LOCATE 10,15:PRINT "**Only one WFGRPSETUP call per board allowed" **":STOP
IF (error% = -108) THEN CLS: LOCATE 10,15:PRINT "**Not enough memory" **":STOP
IF (error% = -110) THEN CLS: LOCATE 10,15:PRINT "**Labdriver not configured for double buffered mode" **":STOP
IF (error% = -111) THEN CLS: LOCATE 10,15:PRINT "**Aquired data overwritten" **":STOP
IF (error% = -112) THEN CLS: LOCATE 10,15:PRINT "**Number samples requested not yet available" **":STOP
IF (error% = -113) THEN CLS: LOCATE 10,15:PRINT "**Acquisition complete before no of samples requested available" **":STOP
IF (error% = -114) THEN CLS: LOCATE 10,15:PRINT "**Block size parameter does not conform to an integer mutl of no of channels" **":STOP
IF (error% = -115) THEN CLS: LOCATE 10,15:PRINT "**DAQ2MEMCONFIG executed after DAQ2CONFIG" **":STOP
IF (error% = -120) THEN CLS: LOCATE 10,15:PRINT "**No trigger value found" **":STOP
IF (error% = -121) THEN CLS: LOCATE 10,15:PRINT "**Analog trigger did not occur before timeout" **":STOP
RETURN
12.3.6. Cyclic voltammetry photocurrent averaging program

restart:
CLS
CLEAR, 500000&
OPTION BASE 1
'pol pcurr - a program to crunch the data acquired by the data acquisition
'venables
'regular
binno%=0 'which bin indicator
cols%=0
'number of columns in the input file
cnt1%=0
'counter
cnt2%=0
'counter
crit!=0
'percentage of the max value that is considered to be an error
datapairs%=0
'number of data lines in the input file
datapairsup%=0
'number of data lines up
datapairsdo%=0
'number of data lines down
deltail%=0
'increment in the potential (det if sweep is up or down)
incv!=0
'pot inc for bins
nobins%=0
'number of bins to throw values in
nodevs%=0
'number of standard devs to consider
maxv!=0
'max pot for bins
minv!=0
'min pot for bins
maxup!=0
'max avg pcurr value in the downarray
maxdo!=0
'max avg pcurr value in the downarray
titleflag%=0
'flag to control if the titles are printed
'in file ="
'infil"=
'input file name
outfil$=""
'output file name
fil$=""
'variable used by the get filename subs

'array
DIM datass(8000,4)
DIM up(8000,4)
DIM do(8000,4)
DIM binsup(500,5)
DIM binsdo(500,5)
DIM statsup(500,2)
DIM statsdo(500,2)
DIM fbinsup(500,6)
DIM fbinsdo(500,6)
'program pol pcurr
'the output from pol pcurr is in the format potential, current, pcurr, pangle
',
'-----------------------------------------------
'input of information section
'-----------------------------------------------
'get the input/output file names
GOSUB openfil
infil$=fil$
GOSUB genewfil
outfil$=fil$
'get the min,max, inc for bins
INPUT "What is the max potential (V)";maxv!
INPUT "What is the min potential (V)";minv!
INPUT "What is the potential increment (V)";incv!
INPUT "Number of sdevs to consider (V)";nodevs%
INPUT "% of max value that is the error limit";crit!
crit!=crit!/100 'convert to fraction
INPUT "Print title in files (Y/N)";a$
367
IF a$="Y" OR a$="y" THEN LET titleflag%=1

'readin and manipulation section

'read the file and break it into variables
CLS
LOCATE 10,20
PRINT "*** Reading values - please be patient ***"
cols%=4
CALL readtext(infil$, datapairs%, cols%, datas!())

'calculate the differences and put in up or down arrays
CLS
LOCATE 10,20
PRINT "*** Calculating up and down arrays - please be patient ***"

'first initialise counters
datapairsup%=0 'number of data lines up
datapairsdo%=0 'number of data lines down
FOR cnt1%=1 TO datapairs%-1
    delta!=datas!(cntl%+1,1)-datas!(cntl%,1)
    IF delta!>0 THEN
        'value must be put in the up array
        datapairsup%=datapairsup%+1
        FOR cnt2%=1 TO cols%
            up!(datapairsup%, cnt2%)=datas!(cntl%, cnt2%)
        NEXT cnt2%
    ELSE
        datapairsdo%=datapairsdo%+1
        FOR cnt2%=1 TO cols%
            do!(datapairsdo%, cnt2%)=datas!(cntl%, cnt2%)
        NEXT cnt2%
    END IF
NEXT cnt1%
CLS
LOCATE 10,20
PRINT "*** Calculating initial bins - please be patient ***"

'throw in bins
nobins%=INT((maxv!-minv!)/incv!)+1

'first the uparray
FOR cnt1%=1 TO datapairsup%
    'bin structure is as follows
    'col1= sum(V), col2=sum(I), col3=sum(Ipc), col4=sum(Ipc^2), col5=# vals
    binno%=INT((up!(cntl%,1)-minv!)/incv!)+1
    'may have to put initialise bins to zero statement in first
    'put values in bins
    binsup!(binno%,1)=binsup!(binno%,1)+up!(cntl%,1)
    binsup!(binno%,2)=binsup!(binno%,2)+up!(cntl%,2)
    binsup!(binno%,3)=binsup!(binno%,3)+up!(cntl%,3)
    binsup!(binno%,4)=binsup!(binno%,4)+up!(cntl%,3)^2
    binsup!(binno%,5)=binsup!(binno%,5)+1
NEXT cnt1%

'now the downarray
FOR cnt1%=1 TO datapairsdo%
    'bin structure is as follows
    'col1= sum(V), col2=sum(I), col3=sum(Ipc), col4=sum(Ipc^2), col5=# vals
    binno%=INT((do!(cntl%,1)-minv!)/incv!)+1
    'may have to put initialise bins to zero statement in first
    'put values in bins
    binsdo!(binno%,1)=binsdo!(binno%,1)+do!(cntl%,1)
    binsdo!(binno%,2)=binsdo!(binno%,2)+do!(cntl%,2)
    binsdo!(binno%,3)=binsdo!(binno%,3)+do!(cntl%,3)
NEXT cnt1%
binsdo!(binno%, 4) = binsdo!(binno%, 4) + do!(cnt1%, 3)^2
binsdo!(binno%, 5) = binsdo!(binno%, 5) + 1

NEXT cnt1%
CLS
LOCATE 10, 20
PRINT "+++++++ Calculating initial stats - please be patient ++++

'calculate the statistical values of interest
'the structure of the stats are
'coll1-avg pcurr
'col 2- sigma
'first the uparray
maxup! = 0
FOR cntl% = 1 TO nobins%
  'see lotus manual for following formula (p. 89)
  IF binsup!(cntl%, 5) > 0 THEN
    statsup!(cntl%, 1) = binsup!(cntl%, 3) / binsup!(cntl%, 5)
    statsup!(cntl%, 2) = ((binsup!(cntl%, 4) * binsup!(cntl%, 5) -
      statsup!(cntl%, 1)^2) / (binsup!(cntl%, 5) * (binsup!(cntl%, 5) - 1)))^.5
  ELSE
    'there is nothing in this bin
    statsup!(cntl%, 1) = 0
    statsup!(cntl%, 2) = 0
  END IF
NEXT cnt1%
'calc max
FOR cntl% = 1 TO nobins%
  IF statsup!(cntl%, 1) > maxup! THEN LET maxup! = statsup!(cntl%, 1)
NEXT cnt1%

'now the downarray
maxdo! = 0
FOR cntl% = 1 TO nobins%
  'see lotus manual for following formula (p. 89)
  IF binsdo!(cntl%, 5) > 0 THEN
    statsdo!(cntl%, 1) = binsdo!(cntl%, 3) / binsdo!(cntl%, 5)
    statsdo!(cntl%, 2) = ((binsdo!(cntl%, 4) * binsdo!(cntl%, 5) -
      statsdo!(cntl%, 1)^2) / (binsdo!(cntl%, 5) * (binsdo!(cntl%, 5) - 1)))^.5
  ELSE
    'there is nothing in this bin
    statsdo!(cntl%, 1) = 0
    statsdo!(cntl%, 2) = 0
  END IF
NEXT cnt1%
'calc max
FOR cntl% = 1 TO nobins%
  IF statsdo!(cntl%, 1) > maxdo! THEN LET maxdo! = statsup!(cntl%, 1)
NEXT cnt1%

'+++++++ Calculating final bins - please be patient +++

'now throw in bins again, this time, discarding all value more than two st dev away
CLS
LOCATE 10, 20
PRINT "+++++++ Calculating final bins - please be patient +++

'first the uparray
FOR cnt1% = 1 TO datapairsup%
  'final bin structure is as follows
  'coll1= avg(V), col2=avg(I), col3=avg(Ipc), col4=std dev pc, col5=# vals kept, col6=# vals disc
binno% = INT((up!(cntl%,1)-minv!)/incv!)+1
'may have to put initialise bins to zero statement in first
'put values in bins if they are fit to
'+++++++++++++++++++++++++++++++++++++++++++++++++++++++
uplim! = statsup!(binno%,1)+statsup!(binno%,2)*nodevs%
downlim! = statsup!(binno%,1)-statsup!(binno%,2)*nodevs%
'+++++++++++++++++++++++++++++++++++++++++++++++++++++++
IF (up!(cntl%,3)>uplim! OR up!(cntl%,3)<downlim!) AND ABS(up!(cntl%,3)-
downlim!)>crit!*maxup! THEN
    fbinsup!(binno%,6) = fbinsup!(binno%,6)+1
ELSE
    fbinsup!(binno%,1) = fbinsup!(binno%,1)+up!(cntl%,1)
    fbinsup!(binno%,2) = fbinsup!(binno%,2)+up!(cntl%,2)
    fbinsup!(binno%,3) = fbinsup!(binno%,3)+up!(cntl%,3)
    fbinsup!(binno%,4) = fbinsup!(binno%,4)+up!(cntl%,3)^2
    fbinsup!(binno%,5) = fbinsup!(binno%,5)+1
ENDIF
NEXT cntl%
'calc stdev, avg's
FOR cntl%=1 TO nobins%
    IF fbinsup!(cntl%,5)>1 THEN
        'sdevs first - needs sigmas not averages
        IF (fbinsup!(cntl%,4)*fbinsup!(cntl%,5)-
            fbinsup!(cntl%,3)A2)/(fbinsup!(cntl%,5)*(fbinsup!(cntl%,5)-1))>0 THEN
            fbinsup!(cntl%,4) = ((fbinsup!(cntl%,4)*fbinsup!(cntl%,5)-
                fbinsup!(cntl%,3)^2)/(fbinsup!(cntl%,5)*(fbinsup!(cntl%,5)-1)))^0.5
        ELSE
            fbinsup!(cntl%,4) = -99
        ENDIF
    fbinsup!(cntl%,1) = fbinsup!(cntl%,1)/fbinsup!(cntl%,5)
    fbinsup!(cntl%,2) = fbinsup!(cntl%,2)/fbinsup!(cntl%,5)
    fbinsup!(cntl%,3) = fbinsup!(cntl%,3)/fbinsup!(cntl%,5)
ENDIF
IF fbinsup!(cntl%,5)=1 THEN
    'sdevs first - needs sigmas not averages
    fbinsup!(cntl%,4) = -99
    fbinsup!(cntl%,1) = fbinsup!(cntl%,1)/fbinsup!(cntl%,5)
    fbinsup!(cntl%,2) = fbinsup!(cntl%,2)/fbinsup!(cntl%,5)
    fbinsup!(cntl%,3) = fbinsup!(cntl%,3)/fbinsup!(cntl%,5)
ENDIF
IF fbinsup!(cntl%,5)<1 THEN
    fbinsup!(cntl%,1) = 0
    fbinsup!(cntl%,2) = 0
    fbinsup!(cntl%,3) = 0
    fbinsup!(cntl%,4) = 0
ENDIF
NEXT cntl%
'now the downarray
FOR cntl%=1 TO datapairsdo%
    IF fbinsup!(cntl%,5)>1 THEN
        'sdevs first - needs sigmas not averages
        IF (fbinsup!(cntl%,4)*fbinsup!(cntl%,5)-
            fbinsup!(cntl%,3)A2)/(fbinsup!(cntl%,5)*(fbinsup!(cntl%,5)-1))>0 THEN
            fbinsup!(cntl%,4) = ((fbinsup!(cntl%,4)*fbinsup!(cntl%,5)-
                fbinsup!(cntl%,3)^2)/(fbinsup!(cntl%,5)*(fbinsup!(cntl%,5)-1)))^0.5
        ELSE
            fbinsup!(cntl%,4) = -99
        ENDIF
    fbinsup!(cntl%,1) = fbinsup!(cntl%,1)/fbinsup!(cntl%,5)
    fbinsup!(cntl%,2) = fbinsup!(cntl%,2)/fbinsup!(cntl%,5)
    fbinsup!(cntl%,3) = fbinsup!(cntl%,3)/fbinsup!(cntl%,5)
ENDIF
IF fbinsup!(cntl%,5)=1 THEN
    'sdevs first - needs sigmas not averages
    fbinsup!(cntl%,4) = -99
    fbinsup!(cntl%,1) = fbinsup!(cntl%,1)/fbinsup!(cntl%,5)
    fbinsup!(cntl%,2) = fbinsup!(cntl%,2)/fbinsup!(cntl%,5)
    fbinsup!(cntl%,3) = fbinsup!(cntl%,3)/fbinsup!(cntl%,5)
ENDIF
IF fbinsup!(cntl%,5)<1 THEN
    fbinsup!(cntl%,1) = 0
    fbinsup!(cntl%,2) = 0
    fbinsup!(cntl%,3) = 0
    fbinsup!(cntl%,4) = 0
ENDIF
NEXT cntl%
'final bin structure is as follows
'coll= avg(V), col2=avg(I), col3=avg(Ipc), col4=stdev pc, col5=# vals kept, col6=# vals disc
binno% = INT((do!(cntl%,1)-minv!)/incv!)+1
'may have to put initialise bins to zero statement in first
'put values in bins if they are fit to
'+++++++++++++++++++++++++++++++++++++++++++++++++++++++
duplim! = statsdo!(binno%,1)+statsdo!(binno%,2)*nodevs%
downlim! = statsdo!(binno%,1)-statsdo!(binno%,2)*nodevs%
'+++++++++++++++++++++++++++++++++++++++++++++++++++++++
IF (do!(cntl%,3)>duplim! OR do!(cntl%,3)<downlim!) AND ABS(do!(cntl%,3)-
downlim!)>crit!*maxdo! THEN
    fbinsdo!(binno%,6) = fbinsdo!(binno%,6)+1
ELSE
    fbinsdo!(binno%,1) = fbinsdo!(binno%,1)+do!(cntl%,1)
    fbinsdo!(binno%,2) = fbinsdo!(binno%,2)+do!(cntl%,2)
fbinsdo!(binno%,3)=fbinsdo!(binno%,3)+do!(cntl%,3)
fbinsdo!(binno%,4)=fbinsdo!(binno%,4)+do!(cntl%,3)^2
fbinsdo!(binno%,5)=fbinsdo!(binno%,5)+1
END IF

NEXT cnt1%
CLS
'calc stdv, avg's
FOR cntl%=1 TO nobins%
  IF fbinsdo!(cntl%,5)>0 THEN
    'sdevs first - needs sigmas not averages
    fbinsdo!(cnt1%,4)=((fbinsdo!(cnt1%,4)*fbinsdo!(cntl%,5)-
                      fbinsdo!(cntl%,3)^2)/(fbinsdo!(cntl%,5)*(fbinsdo!(cntl%,5)-1)))^0.5
    fbinsdo!(cntl%,1)=fbinsdo!(cntl%,1)/fbinsdo!(cntl%,5)
    fbinsdo!(cntl%,2)=fbinsdo!(cntl%,2)/fbinsdo!(cntl%,5)
    fbinsdo!(cntl%,3)=fbinsdo!(cntl%,3)/fbinsdo!(cntl%,5)
  ELSE
    fbinsdo!(cntl%,1)=0
    fbinsdo!(cntl%,2)=0
    fbinsdo!(cntl%,3)=0
    fbinsdo!(cntl%,4)=0
  END IF

NEXT cntl%
'write the output file
CLS
LOCATE 10,20
PRINT "*** Writing output - please be patient ***"
IF titleflag%=0 THEN
  title$=""
ELSE
  title$="* E"+CHR$(9)+"I"+CHR$(9)+"Iph"+CHR$(9)+"SD Iph"+CHR$(9)+"# used"+CHR$(9)+"# disc"
END IF
CALL writetext(outfil$+"/up",nobins%-1,6,fbinsup!(),title$)
CALL writetext(outfil$+"/do",nobins%-1,6,fbinsdo!(),title$)
quit:
CLS
LOCATE 20,20
PRINT "*** 'R' to repeat, any other key to exit ***"
a$=INPUT$(1)
IF a$="R" OR a$="r" THEN GOTO restart
STOP
'$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
'get filename to open routine
'=====================================================================================================================

openfil:
fil$=FILES$(1,"TEXT")
IF fil$="" THEN
  CLS
  LOCATE 20,20
  PRINT "*** Do you want to quit ? ***"
  a$=INPUT$(1)
  IF a$="Y" OR a$="y" THEN
    GOTO quit
  ELSE
    CLS
    GOTO openfil
  END IF
END IF
RETURN

'----------------------------------------------------------

'get new filename routine
'----------------------------------------------------------

getnewfil:
fil$=FILE$(0, "Output file name")
IF fil$="" THEN
    CLS
    INPUT "Do you want to quit"; a$
    IF a$="Y" OR a$="y" THEN
        GOTO quit
    ELSE
        CLS
        GOTO getnewfil
    END IF
ENDIF
RETURN

'----------------------------------------------------------

'subroutine to read a text file, and to break it into variables
'the text file is assumed to be the same as written by Excel
'etc.
'SUB readtext(textfilename$, entries%, cols%, values!(2)) STATIC

'Version information
'1.0.0 - 17 February 1989
'1) Preliminary version
'
description of variables

Passed variables

'textfilename$ = Name of the text file to be read in and broken up (supplied)
'entries% = number of the entries found in the text file (determined by sub)
'cols% = number of columns in the text file to be read (supplied)
'values! = a 2 D matrix with cols% columns and enough rows for entries%
    must be dimensioned before calling.

Local variables

'fileno% = number assigned to the text file that is opened
'i%,j% simple counters
'a$ text value used for storage of the line read in

fileno%=10

OPEN textfilename$ FOR INPUT AS #fileno%
'get the number of pairs in order to determine the sizes of the matrices
entries%=0
WHILE NOT EOF(fileno%)
    LINE INPUT #fileno%, a$
    entries%=entries%+1
WEND
CLOSE #fileno%
OPEN textfilename$ FOR INPUT AS #fileno%
FOR i%=1 TO entries%
    LINE INPUT #fileno%, a$
    FOR j%=1 TO cols%
        IF j%=cols% THEN
            tabpos%=INSTR(a$, CHR$(9))
        ELSE
            tabpos%=tabpos%+1
        END IF
        values%(i%,j%)=a$(tabpos%)
    NEXT j%
NEXT i%
length% = LEN(a$)
values!(i%,j%) = VAL(LEFT$(a$, tabpos%-1))
a$ = RIGHTS(a$, length%-tabpos%) 'lop off the value already 'extracted put rest back in.
ELSE
   values!(i%,j%) = VAL(a$)
ENDIF
NEXT j%
NEXT i%
CLOSE #fileno%
END SUB

'write calculated values to output

SUB writetext(textfilename$, entries%, cols%, values!(2), title$) STATIC
'check information
'1.0.0 - 17 February 1989
'1) Preliminary version
'description of variables

'Passed variables
'textfilename$ = name of the file to be written
'entries%=number of the entries to be written (supplied)
'cols% = number of columns in the text file to be written (supplied)
'values! = a 2 D matrix with cols% columns and entries% rows with data
'title$ = string containing the first line of the file not printed if = ""

'Local variables

'i%,j% simple counters
'fileno% = number assigned to the text file that is written
'fileno2% = number assigned to the clipboard

fileno% = 11
fileno2% = 12

OPEN textfilename$ FOR OUTPUT AS #fileno%
OPEN "clip:" FOR OUTPUT AS #fileno2%

IF title$ <> "" THEN
   PRINT #fileno%, title$
   PRINT #fileno2%, title$
ENDIF
FOR i%=1 TO entries%
   IF values!(i%,5) > 0 THEN
      FOR j%=1 TO cols%
         'first the current, then the voltage
         IF j% << cols% THEN
            'must print a tab character after the entry
            PRINT #fileno%, USING " +.###^A^", values!(i%,j%);
            PRINT #fileno2%, USING " +.###^A^", values!(i%,j%);
            PRINT #fileno2%, CHR$(9);
         ELSE
            'last entry in line => no tab
            PRINT #fileno%, USING " +.###^A^", values!(i%,j%);
            PRINT #fileno2%, USING " +.###^A^", values!(i%,j%);
         END IF
      NEXT j%
      'print a LF after each line on the clipboard and the text file written
   END IF
NEXT i%
PRINT #fileno%,
PRINT #fileno2%,
END IF
NEXT i%
CLOSE #fileno%
CLOSE #fileno2%
END SUB
12.4. Figures - Appendices
Figure [12.4.1.] Photomultiplier response (A/W) and total system light flux (W/cm²) as a function of wavelength.
Figure [11.4.2.] Site percolation on the square lattice, illustrating various cluster sizes (s) for three values of p, the fraction of filled sites. For p = 0.75, an unbounded cluster is present. From Zallen [Zallen 1983].
Figure [11.4.3.] Characteristic percolation parameters as a function of the fraction of bonds filled, $p$ [Zallen 1983].
BIOGRAPHICAL NOTE

Birth

1962, Cape Town, South Africa

Education

Graduate

Undergraduate
1982 - 1986: University of Pretoria, Department of Chemical Engineering, B.Eng with distinction.

Fellowships, Scholarships and Awards

Autumn 1989: H. H. Uhlig Award in Corrosion, Presented by the Greater Boston Section of the National Association of Corrosion Engineers.

Autumn 1987: Fulbright Scholarship, Institute for International Education.


Professional Affiliations

The British Institute of Chemical Engineers
The Electrochemical Society
The National Association of Corrosion Engineers
The South African Institute of Chemical Engineers
The South African Institute of Professional Engineers