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A STUDY OF THE ELECTROCHEMICAL PHENOMENA
OCCURRING DURING THE CORROSION
OF ARMCO IRON IN METHANOL SOLUTIONS

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF
THE UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

MAY 1996

By

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ACKNOWLEDGMENTS

I would, first and foremost, like to thank my mother, Miriam Boucher, for her undaunting faith in me. I would also like to thank my chemistry advisor, George Andermann, for all his support and encouragement and my electrochemistry advisor, Bruce Liebert, for providing such outstanding equipment. There have been many people who have helped me in my research endeavors at the Materials Research Lab and at facilities here at the University of Hawaii, Manoa. I would like to acknowledge their assistance. Finally, I would like to thank my friends, Jean Cullingham and Eugene Smotkin, for it was their faith in my abilities that helped me through the difficult parts.

This research was initially supported by DOE grant #DE-FG01-90CE50310 awarded to Hawaii Natural Energy Institute, School of Ocean Engineering, Science and Technology at University of Hawaii, Manoa and I would like to thank them for their contribution. The Chemistry Department also helped to support my research and without their financial support you would not be reading this dissertation. This work has benefited from the facilities and equipment made available to Stanford University by the NSF-MRSEC Program through the Center for Materials Research at Stanford University.

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ABSTRACT

The corrosion behavior of Armco iron in 0 and 5 mM tetrabutylammonium perchlorate (TBAP) methanol solution was followed for two weeks using Electrochemical Impedance Spectroscopy (EIS). Equivalent circuit modeling of the EIS spectra showed a ten-fold decrease in the charge transfer resistance and a thousand-fold decrease in the surface film resistance when TBAP was in the solution.

Comparison of the behavior as a function of potential of the circuit element values, for Armco iron in 50 mM phosphoric acid (H₃PO₄) methanol solution, obtained from fitting the EIS spectra with nested versus series equivalent circuits, to the qualitative behavior predicted by theory, showed the series equivalent circuit gave a better match to theory. The corrosion rate for Armco iron in 50 mM H₃PO₄ methanol solution was 0.294 mpy.

EIS spectra measured as a function of potential, for Armco iron in 0 mM, 50 mM and 100 mM lithium perchlorate (LiClO₄) methanol solutions and fit using the series equivalent circuit, suggested that, LiClO₄ affected the thickness and nature of the thin film at the surface and the corrosion rate of Armco iron. The corrosion rates for Armco iron in 0 mM, 50 mM and 100 mM LiClO₄ methanol solutions were, for an anodic Tafel slope of 0.120 V/dec, 0.0209 mpy, 0.0981 mpy and 0.0295 mpy, respectively, and for an anodic
Tafel slope of 0.552 V/dec, 0.0452 mpy, 0.183 mpy, and 0.0564 mpy, respectively.

Overall cathodic and anodic reactions were suggested by analyzing the solution and surface deposits formed when Armco iron was galvanostatically treated at current densities of 2 to 4 μA/cm² in methanol. Several anodes developed a resistive yellow film proposed to be iron oxymethoxide. The cathodes developed dark deposits possibly an iron oxide or oxyhydroxide. The galvanostatically treated electrodes were analyzed using X-ray Emission Spectroscopy, Scanning Electron Microscopy with and without elemental detection, Fourier Transform Infra-Red Diffuse Reflectance Spectroscopy, X-ray Photoelectron Spectroscopy and X-ray Diffraction. The solutions resulting from the galvanostatic treatment were analyzed by Gas-Solid Chromatography and Atomic Absorption Spectroscopy.
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<th>Description</th>
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<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>Cf</td>
<td>film capacitance</td>
</tr>
<tr>
<td>Cstray</td>
<td>stray capacitance</td>
</tr>
<tr>
<td>EDS</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>eqn</td>
<td>equation</td>
</tr>
<tr>
<td>FTIRDRS</td>
<td>Fourier Transform Diffuse Reflectance Infra-Red Spectroscopy</td>
</tr>
<tr>
<td>GC/MS</td>
<td>Gas Chromatography/Mass Spectrometry</td>
</tr>
<tr>
<td>GSC</td>
<td>Gas-Solid Chromatography</td>
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<tr>
<td>IR</td>
<td>Infra-Red</td>
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<tr>
<td>mM</td>
<td>milli molar</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>ndl</td>
<td>frequency exponent for Qdl</td>
</tr>
<tr>
<td>nf</td>
<td>frequency exponent for Qf</td>
</tr>
<tr>
<td>Qdl</td>
<td>double layer constant phase element</td>
</tr>
<tr>
<td>Qf</td>
<td>film constant phase element</td>
</tr>
<tr>
<td>Raman</td>
<td>Raman Spectroscopy</td>
</tr>
<tr>
<td>Rct</td>
<td>charge transfer resistance</td>
</tr>
<tr>
<td>Rf</td>
<td>film resistance</td>
</tr>
<tr>
<td>Rs</td>
<td>solution resistance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Spectroscopy</td>
</tr>
<tr>
<td>TBAP</td>
<td>Tetrabutyl Ammonium Perchlorate</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
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<tr>
<td>XES</td>
<td>X-ray Emission Spectroscopy</td>
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<tr>
<th>Acronym</th>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>µA</td>
<td>micro amperes</td>
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CHAPTER 1: INTRODUCTION

1.1 Objectives

The primary objective of this work was to elucidate the overall reactions that occur and their overall rates during the corrosion of Armco iron in "pristine" electrolyte-free methanol. The second objective was to investigate the effects of various additions to the methanol, such as perchlorate salts and phosphoric acid, on the rate of corrosion and on the formation of passive films. The third objective was to more thoroughly characterize the surface after corrosion had occurred by correlating the electrochemical results with the ex-situ techniques X-Ray Emission Spectroscopy, Fourier Transform Diffuse Reflectance Infra-Red Spectroscopy, Raman Spectroscopy, X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy with and without elemental detection.

1.2 Structure of the Dissertation

Chapter One describes the general motivation, goals and background for the research. Chapter Two presents a brief review of the theoretical considerations involved in corrosion studies and the details of how the Electrochemical Impedance spectra were analyzed. Chapter Three discusses the
experimental equipment and techniques used in this research project. Chapter Four presents the electrochemical experimental results and discusses the implications of these results. Chapter Five presents the result of the many techniques used to analyze the surfaces of the Armco iron electrodes and characterize the deposits that formed on them. Chapter Six contains the results of the various chemical analyses conducted upon the methanol solutions after corrosion had occurred. Finally, Chapter Seven presents the conclusions reached as a result of the many experiments which have been carried out.

1.3 Motivation of the Research

Corrosion of metals has been a problem for thousands of years. "The cost to society of corrosion and its prevention is staggering: it has been estimated to be about $200 billion per annum in the United States alone, corresponding to $800 per capita per year."¹ Due to water's being the most common solvent on the planet, most of the research on corrosion has been done for aqueous systems. One of the most important and studied systems is iron in aqueous solutions and a number of review articles are available².

The consideration of methanol as a replacement fuel for gasoline and diesel fuels in the transportation sector³,⁴,⁵ and its increased use as a feedstock in the chemical industry
has called attention to its corrosive properties. As can be seen from Table 1.1, methanol has substantially different chemical properties from both water and traditional hydrocarbon fuels. Thus, it is not surprising that the corrosion of metals in methanol exhibits different rates and reaction mechanisms than the corrosion of metals in either traditional hydrocarbon fuels or aqueous systems.

The three main factors which determine the nature and rate of corrosion (excluding temperature and pressure) are: one, the nature of the metal surface, two, the solution composition and three, the electrical potential. By changing the solvent from water to methanol, all three factors are changed. The films which form on the surface are of a different composition. Methanol has a much lower dielectric constant than water, 32 versus 78, respectively. Under a 1 atm pressure of oxygen at 25°C, oxygen is almost ten times as soluble in methanol (10.3 mM) than in water (1.0 mM). And finally, the reaction kinetics, and quite probably the mechanisms of the reactions themselves, are changed which causes the equilibrium electrical potential to shift.

1.4 Review of Relevant Corrosion Literature

Since the early 1970's, society's attempts to move away from petrochemicals as the main provider of fuel and chemical feedstocks, has increased interest in the corrosion
Table 1.1 Solvent properties of methanol, water and benzene.

<table>
<thead>
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<th>Methanol</th>
<th>Water</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>32</td>
<td>18</td>
<td>78</td>
</tr>
<tr>
<td>static dielectric constant at 20°C</td>
<td>32</td>
<td>78</td>
<td>2</td>
</tr>
<tr>
<td>Dipole moment at 20°C</td>
<td>1.7</td>
<td>1.8</td>
<td>0</td>
</tr>
<tr>
<td>Resistivity at 20°C (MΩcm)</td>
<td>1</td>
<td>18</td>
<td>3</td>
</tr>
<tr>
<td>Resistivity with 0.3 M HCl at 20°C (Ωcm)</td>
<td>50</td>
<td>10</td>
<td>&gt;1x10^6</td>
</tr>
<tr>
<td>Dynamic viscosity at 20°C (mPa/s)</td>
<td>0.72</td>
<td>0.98</td>
<td>0.72</td>
</tr>
<tr>
<td>Density at 20 °C (kg/l)</td>
<td>0.79</td>
<td>1.0</td>
<td>0.87</td>
</tr>
<tr>
<td>Surface tension at 20°C (mN/M)</td>
<td>71</td>
<td>21</td>
<td>29</td>
</tr>
<tr>
<td>Vapor pressure at 20°C (mbar)</td>
<td>120</td>
<td>22</td>
<td>100</td>
</tr>
<tr>
<td>Boiling point at 1 atm (°C)</td>
<td>65</td>
<td>100</td>
<td>80</td>
</tr>
</tbody>
</table>
properties of organic solvents. Corrosion is an electrochemical process and hence the primary techniques used to study it are electrochemical. Readers who are unfamiliar with the terminology used in corrosion studies are referred to Chapter 2 for a brief introduction to the fundamental concepts and language of electrochemistry.

One corrosion phenomenon which is not discussed in Chapter 2 is passivation. In many metals, including iron, nickel, chromium, titanium and cobalt, the corrosion rate decreases above some critical anodic potential. This corrosion resistance, despite the high potential driving force, is defined as passivity. Passivity is caused by the formation of a thin, protective, corrosion product surface film that acts as a barrier to the anodic dissolution reaction\(^\text{10}\).

1.4.1 Armco Iron in Methanol Solutions

Farina, et.al.\(^\text{11}\) used potentiodynamic measurements to investigate the electrochemical behavior of Armco iron in a base solution of degassed 0.10 M LiClO\(_4\) methanol or dimethylformamide. Their counter electrode was platinum and they used a saturated calomel reference electrode (SCE). The anodic behavior was investigated as a function of water content (200, 460, 5000, and 10,000 ppm), lithium chloride content (10 mM and 20 mM) and sulfuric acid content (10 mM
and 1 mM). Coulometric tests showed that the iron dissolves as Fe$^{2+}$. Their samples exhibited pitting in the solutions with added water, a more diffuse pitting when chloride ions were added, and finally general attack in the acidic solutions. In the absence of aggressive ions, such as, H$^+$ or Cl$^-$, passive behavior was observed for water contents above 5000 ppm. They briefly looked at the cathodic behavior of Armco iron in oxygen saturated, 0.01 M sulfuric acid solutions and in nitrogen deaerated 0.01 M sulfuric acid solutions. Oxygen saturation increased the open circuit potential by about 150 mV, leading the authors to speculate that oxygen reduction is the cathodic reaction. Furthermore, in the deaerated solution, there were two cathodic processes: the first was ascribed to residual oxygen reduction with a Tafel slope of 180 mV/dec. and the second, which occurred at potentials of less than -1 V, was speculated to be hydrogen evolution with a Tafel slope of 110 mV/dec.

The anodic polarization behavior of Armco iron in methanol solutions was also studied by Mazza, et.al.\textsuperscript{12}. The base solution used in his study was deaerated methanol containing 0.1 M LiClO$_4$ and less than 100 ppm water. Their counter electrode was platinum and they used a saturated calomel reference electrode (SCE). They added water (100 ppm and 5000 ppm), acid (0.1 mM H$_2$SO$_4$) and chloride ions (0.1 mM NaCl) to the methanol to investigate their effects on the corrosion process. They pretreated their Armco iron samples
in 3 M sulfuric acid for 10 minutes at a potential of -700 mV versus SCE to remove any preexisting surface film. They found the shapes of the polarization traces to be strongly dependent upon the rate at which the potential was increased. This was attributed to passive film formation that occurred to a greater extent at the slower scan rates.

Mazza, et.al. also found that the behavior was strongly affected by the presence of water, acid or chloride ions in the methanol solution with the presence of both acid and chloride ions leading to the greatest corrosion. They determined that the presence of the acid in the methanol prevents the formation of a passive film until the current density (current per cm²) exceeds 0.1 mA/cm² and this passive film is not very stable. On the other hand, the chloride ions were believed to decrease the protection of the passive film.

1.4.2 Pure Iron in Methanol Solutions

1.4.2.1 Research at Keio University Chemistry Department

In a series of papers, a research group at Keio University in Japan has investigated the corrosion of 99.99% pure iron in various methanol solutions. Sakakibara, et.al.\textsuperscript{13}, investigated the corrosion of iron under a nitrogen atmosphere in several different methanol solutions containing
450 ppm water plus a 0.1 M concentration of one of the following salts: LiClO$_4$, LiCl, LiBr or NaI. They used Cyclic Voltammetry and Anodic Polarization to investigate the electrochemical behavior of these systems and XPS to investigate the passive surface films formed on the iron electrode surfaces.

Sakakibara found that an iron electrode polished in air forms a ferric oxyhydroxide film that is on the order of 10 nm thick. This film was found to render their iron electrodes passive in the LiClO$_4$ methanol solution. Breakdown of the film was observed in the solutions containing 0.1 M LiCl, LiBr or NaI. The electrodes polarized in these solutions showed pitting corrosion with the pitting potentials following the same trend as in aqueous borate buffer, namely, $I^- > Br^- > Cl^-$. 

To determine if the electrode would form a film in the solution, the final polishing of an iron electrode was done inside a glove box (oxygen <0.01 ppm and water <50 ppm). When this "film free" electrode was immersed for five hours in 0.1 M LiClO$_4$ methanol solution, a film formed on the electrode surface. A comparison of the oxygen 1s$_{1/2}$ XPS spectra of the film to the XPS spectra of what the authors believed to be ferrous methoxide showed excellent agreement. This led the authors to speculate that the film was composed of ferrous methoxide. The only problem with this conclusion is that their oxygen 1s$_{1/2}$ XPS spectra shows two peaks;
whereas, ferrous methoxide should only exhibit one peak. One possible explanation of this may be that the film they observed is some type of ferric oxymethoxide.

After this initial research, these same researchers\textsuperscript{14,15} studied the effects of complexing agents on the polarization behavior of iron in 0.1 M LiClO\textsubscript{4} methanol solution (<150 ppm water) containing 100 µM concentration of one of the following complexing agents: ethylene diamine, 2,2-bipyridine, acetylacetone, catechol, 1, 10-phenanthroline and 2,3-dimercapto-1-propanol. The complexing agents showed little effect on the cathodic reaction which became diffusion limited at current densities of 5 to 10 µA/cm\textsuperscript{2} in all cases. All of the complexing agents increased the anodic current density, except for catechol, which formed a dark red protective complex on the electrode surface and shifted the open circuit potential roughly 200 mV in the positive direction. The acceleration of anodic dissolution current was in the order: ethylene diamine < 2,2-bipyridine < 1, 10-phenanthroline << 2,3-dimercapto-1-propanol.

The presence of 2,3-dimercapto-1-propanol in the solution shifted the open circuit potential by roughly 200 mV in the negative direction. The authors also proposed the following overall reaction:

\[
\text{Fe} + 2\text{CH}_3\text{OH} \rightarrow \text{Fe(OCH}_3)_2 + \text{H}_2 \quad (1.1)
\]
However, they had no evidence of hydrogen evolution and proposed that it occurs via the following reduction half reaction:

\[
2\text{CH}_3\text{OH} + 2e^- \rightarrow 20\text{CH}_3^- + \text{H}_2
\]  

(1.2)

To further study the effects of 2.3-dimercapto-1-propanol and catechol in 0.1 M LiClO₄ methanol solution (<100 ppm water) on the polarization behavior of iron, the group at Keio University measured the polarization behavior of iron at concentrations from 10 µM to 3 M of the complexing agents. The corrosion deposits were studied ex-situ by both Fourier Transform Infra-red Spectroscopy (FTIR) and XPS.

The anodic current density increased, the open circuit potential shifted to more negative values and the cathodic limiting current density increased with increasing concentrations of 2.3-dimercapto-1-propanol. Examination of the electrode surface film by XPS and FTIR after exposure to 10 µM or to 1 M 2.3-dimercapto-1-propanol methanol solutions suggested the absence of an iron methoxide film. The anodic current density decreased, the open circuit potential shifted to more positive values and the cathodic limiting current density increased with increasing concentrations of catechol. Examination of the electrode surface film by XPS and FTIR after exposure to 10 µM or to 1 M catechol methanol solutions
suggested the presence of an iron catechol complex at the surface.

In a recent paper\textsuperscript{16}, the effect of the addition of ferric chloride to 0.1 M LiClO\textsubscript{4} methanol solution (<80 ppm water) on the polarization behavior of iron has been studied. The concentrations used ranged from 10 µM to 0.1 M ferric chloride. The corrosion current was dramatically affected by the presence of the ferric chloride in the solution. The value of the corrosion current was strongly dependent upon the ferric chloride concentration and went from 0.56 µA/cm\textsuperscript{2} in 10 µM ferric chloride to 1350 µA/cm\textsuperscript{2} in 0.1 M ferric chloride. The cathodic current density was once again diffusion limited and the diffusion limiting current for the cathodic reaction increased with increasing concentrations of ferric chloride, suggesting that the cathodic reaction in the presence of ferric ions is:

\[ \text{Fe}^{3+} + 1\text{e}^- \rightarrow \text{Fe}^{2+} \quad (1.3) \]

XPS analysis of the surface deposit formed indicated methoxide at the surface of the film and only iron oxide below that. FTIR of the layer showed significant bands at 1020 and 584 cm\textsuperscript{-1} which the authors used to identify the layer as \( \text{Fe}_3\text{O}_4 \). Other bands evident in the FTIR spectra occur at 800, 750, 675, 650 and 475 cm\textsuperscript{-1} and their presence suggests
that the surface layer might actually be a mixture of various iron oxides and oxyhydroxide and not simply magnetite.

1.4.2.2 Research on Iron in Methanol Solutions by other Groups

Brossia, et.al.\textsuperscript{17} recently studied the effects of the presence of low levels (mM) of aggressive species (sulfuric acid, sodium chloride and sodium sulfate) on the corrosion behavior of iron (99.9985%) in 0.1 M NaClO\textsubscript{4} methanol solutions at two water concentrations (<500 ppm and 5000 ppm). They found the corrosion rate and open circuit potential to be most strongly affected by the presence of sulfuric acid. At both water contents, the open circuit potential was shifted 200 mV positive in the 1 mM sulfuric acid solutions; the corrosion rate also increased, by a factor of 16 at the lower water content and a factor of 4 at the higher water content. The presence of sodium chloride and sodium sulfate had a much smaller effect with almost no change in the open circuit potential and at most a doubling of the corrosion rate.

By studying the cathodic behavior of methanol on a platinum electrode they found the proposed hydrogen evolution as the cathodic reaction for acidified solutions. They proposed that the effects of water on the corrosion rates in
acidic methanol solution are due to the presence of water reducing the mobility of protons\textsuperscript{18}.

In neutral solutions, they observed oxygen reduction even in deaerated solutions at potential above $-1\,\text{V}$ versus SSC (a methanol silver/silver chloride reference electrode). For the dominant cathodic reaction on iron in neutral methanol solutions, they proposed the following oxygen reduction reaction:

$$O_2 + \text{CH}_3\text{OH} + 4\text{e}^- \rightarrow 2\text{CH}_3\text{O}^- + 2\text{OH}^-$$ \hspace{1cm} (1.4)

The polarization behavior of iron (99.999\% pure) in degassed, 0.1 M LiClO$_4$ alcoholic solutions (methanol, ethanol, n-propanol, n-butanol and 2-chloro-ethanol) was investigated as a function of water content (0.05\%, 0.5\%, 1.0\%, 2\%, 5\%, 10\%, 50\% and 100\%) by DeAnna\textsuperscript{19}. For iron in methanol solutions, he found that the corrosion current increases and the open circuit potential shifted to more negative values as the water content was increased; however, the limiting cathodic current was essentially unaffected. He did not observe passivation for iron in methanol solutions at any water concentration.

In a survey of several different metals in acidic methanol solutions, Mansfield\textsuperscript{20} investigated the polarization behavior of iron (the purity is not given). No passivation was observed in 0.2 M sulfuric acid methanol solutions (400
Additions of water up to 10% in the 0.2 M sulfuric acid solution was not able to cause the iron sample to passivate, but it did cause the open circuit potential to shift from -500 mV to a more positive potential of -380 mV. Large pits were observed on the surfaces after polarization.

1.4.3 Surface Studies on Iron with Methanol

A research group at Princeton University has extensively studied the reactions of small molecules at well characterized iron surfaces and a review of their work was recently published. They have studied the decomposition of methanol on clean Fe(110) surfaces and on oxygen modified Fe(110) surfaces using High Resolution ElectronEnergy Loss Spectroscopy (HREELS), Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and Temperature Programmed Reaction Spectroscopy (TPRS).

In studies of methanol decomposition on clean Fe(110) surfaces, methanol was found, upon adsorption, to undergo a facile O-H bond scission at 113K and form an overlayer of adsorbed methoxy. The methoxy overlayer was characterized by HREELS giving vibrational frequencies at low doses of 345, 630, 1020, 1445 and 2930 cm⁻¹. Upon annealing to 295K the detected HREELS vibrational frequencies were shifted to 405, 1035, 1445 and 2890 cm⁻¹. As the temperature is increased,
hydrogen desorbs. The methoxy species then decomposes at 450K via a rate limiting C-H bond scission and desorbs as hydrogen and carbon monoxide.

The decomposition of methanol on oxygen modified Fe(110) surfaces was also investigated. The surfaces have been well characterized\textsuperscript{23}. On Fe(110) surfaces that have been exposed to oxygen and subsequently annealed at 923K, the oxygen atoms have been shown to occupy the four fold hollow site. The presence of adsorbed oxygen on the Fe(110) surface significantly alters the decomposition of methanol\textsuperscript{24,25}. The methanol still adsorbs via an O-H scission to form a methoxy overlayer; however, the oxygen adsorbed on the surface poisons the decomposition of methanol into carbon monoxide. A new reaction pathway is opened up and the methanol molecules decompose into formaldehyde on these oxygen modified Fe(110) surfaces.

\section*{1.4.4 Corrosion in Organic Solvents}

In a study of the corrosion of metals in solutions of organic solvents containing dissolved hydrogen chloride, \cite{Hronsky26} investigated the corrosion of zinc (99.96\% pure), iron (99.45\% pure), aluminum (99.59\% pure) and 304 stainless steel, chrome(17.4\%)-nickel(9.1\%), by weight loss measurements. The three types of solvents investigated were protic solvents (methanol, ethanol, 1-propanol and 1-
butanol), dipolar aprotic (acetone, ethyl acetate, diethyl ether and 1,4-dioxane), and aprotic (vinylidene chloride and benzene). The corrosion rates in selected organic solvents exceeded the rate of corrosion in water. The protic-aprotic properties, viscosity and electrolytic resistivity of the solvent are of particular importance in determining the rate of corrosion. Also important is the solubility of the corrosion products in the solvent; when this is high, it can lead to high corrosion rates.

A review of the literature by Kelly and Moran\textsuperscript{27} regarding the passivity of metals in organic solutions revealed two opposing observations. Some workers have found that passivation is not observed in anhydrous solutions, but small additions of water lead to the formation of a passive oxide film. Other workers have found that metals passivate in anhydrous solution and additions of water lead to attack on the metal. All of the work where passivity was not observed in anhydrous solutions was carried out in highly acidified solutions. All of the work where passivation of the surface was observed was carried out in neutral or very weakly acidic solutions.
CHAPTER 2: THEORY AND MODELING

2.1 Basic Electrochemistry

The corrosion of metals is the result of the electrochemical oxidation of the metal by its environment. The metal is oxidized and some substance, such as oxygen or hydronium ions, is reduced. Corrosion is an interfacial phenomenon occurring at the phase boundary between the metal and the surrounding liquid or gas. Oxidation of the metal results from charge transfer reactions occurring across the phase boundary. The rate of the oxidation half-reaction, which is the rate at which the metal is dissolving, is controlled not only by the usual chemical factors, temperature, pressure and the concentrations of reactants and products, but also by the potential gradient across the interphase and the presence of a film or defect sites on the electrode surface.

The following discussion is intended to briefly review the basic theory of the electrochemical factors that determine the rate of charge transfer across a metal solution interface. The basic terminology, common types of electrochemical experiments and the conventions used in this research will be reviewed.
2.1.1 The Components of a Classic Electrochemical Cell

A classic electrochemical cell is shown schematically in figure 2.1. This cell contains three electrodes and a solution. The working electrode is the electrode being investigated. The counter electrode completes the electrical circuit and an external power supply is used to apply a potential between the working electrode and the counter electrode. The third electrode is the reference electrode. The reference electrode is a well defined and reproducible electrode with a stable potential. The recorded potential is the potential difference between the working electrode and the reference electrode.

2.1.1.1 The Electrochemical Potential

In electrostatic theory, the difference in potential is measured by the work required to move a test charge from one point to another and is determined only by distribution of electronic point charges in the medium. If, however, the test charge moves across an interface between two different phases, besides the electrostatic contribution, there will be a chemical contribution to the work required. Since there is no way to separate effects of these two terms, it is
Figure 2.1. Schematic illustration of a typical electrochemical cell.
theoretically impossible to measure a purely electrostatic potential difference between two phases. What can be measured is the sum of the chemical and electrostatic terms. Furthermore, even the overall potential drop across a single phase boundary cannot be measured. There have been many attempts to measure the potential difference across a solution metal interface, but there is a fundamental problem that arises\textsuperscript{28}. In order to make the measurement another interface must be introduced to the electrochemical cell. Once an additional metal electrode has been added to the system, one can readily measure the potential difference between two metal electrodes and any changes in the potential difference. It is this difference in the electrochemical potential between two electrodes that is generally called the electrochemical potential.

2.1.1.2 Reference Electrodes

An ideal reference electrode has a very well defined and difficult to change potential difference across its interface. Such electrodes are referred to as non-polarizable, since their interfaces are difficult to polarize. This behavior is the result of having very facile charge-transfer reactions across their interface. Any attempt to change the potential difference across the interface drives these facile charge-transfer reactions rather than
inducing charge separation and the building up of a potential gradient. If a non-polarizable electrode is used in an electrochemical cell, then changes in the potential difference between the reference electrode and the working electrode will be due to changes in the potential across the working electrode-solution interface.

It has long been the convention in electrochemistry to record potential differences against the Normal Hydrogen Electrode (NHE), also known as the Standard Hydrogen Electrode (SHE). This electrode consists of a platinized platinum electrode submerged in an aqueous solution at unit activity of H⁺ in equilibrium with hydrogen gas at a partial pressure of one atmosphere. This reference electrode is quite difficult to maintain and other reference electrodes, such as the silver/silver chloride or the saturated calomel reference electrode, are more commonly used.

2.1.1.3 Sign Conventions

One of the most confusing aspects of electrochemical research is that there are two different sign conventions in common usage. The sign convention used in this research is the American convention. The anode is the electrode where the oxidation half-reaction occurs and is at the more positive potential. The cathode is the electrode where the reduction half-reaction occurs and is at the more negative
potential. A positive current is cathodic and results in the working electrode being the cathode. A negative current is anodic and results in the working electrode being the anode.

2.1.2 The Electrode-Solution Interface

Far away from the electrode surface in what is called the bulk solution the equilibrium forces are spherically symmetric and atoms and molecules experience only solution forces. Ions may or may not be solvated and randomly diffuse through the solution. Solvent molecules likewise move randomly through the solution interacting with each other and ions via van der Waals forces, dipole-dipole interactions and perhaps hydrogen bonding. The solution is electrically neutral and, in the absence of an externally applied field, free from potential gradients. The solvent molecules and ions which make up the solution have some average distribution and local structure due to their interactions.

The presence of an electrode in the solution creates a phase boundary between the solid electrode and the liquid solution. The solvent molecules and ions will be interrupted in their random walk through the solution. They may be attracted to the electrode or they may be repelled. One thing is certain; the presence of the electrode will change the distribution of the solvent molecules and ions near enough to interact with it. The question is: What will the
new distribution of the solvent molecules and ions be under the influence the electrode surface?

The phase boundary between the bulk solution and bulk of the electrode is known as the interphase. The interphase region extends less than 100 Å into the solution. In this complicated region, electrostatic and chemical interactions between the electrode, solvent molecules and ions determine the molecular structure and the macroscopic properties of the interphase. The interphase region as a whole must be electrically neutral; however, charge separation occurs with the electrode surface being oppositely charged from the solution in the interphase region. There is a long history of the development of the theoretical description of the interphase.

In all of the models, the metal surface is considered to be a structured layer of positively charged metal ions embedded in a sea of free conduction band electrons. The potential of the electrode determines how many electrons are in the conduction band. Since the excess charge on a conductive object resides on the surface of that object, the potential of the electrode determines whether the surface of the electrode is neutral (potential of zero charge, pzc), positively charged (potentials positive of the pzc) or negatively charged (potentials negative of the pzc).

The first model of the interphase was given in 1879 by Helmholtz. The Helmholtz Model proposes, that depending
upon the charge of the electrode surface, a layer of oppositely charged ions electrostatically adsorbs on the electrode surface from the solution. The two layers of charge behave like a parallel plate capacitor so the capacitance of the Helmholtz model is given by:

\[ C_H = -\left( \frac{\varepsilon A}{4\pi d} \right) \]  

(2.1)

where \( \varepsilon \) is the static dielectric constant of the substance between the plates, \( A \) is the surface area of the electrode and \( d \) is the distance between the plates (in this case the radius of the ions adsorbed on the electrode surface). The static dielectric constant, \( \varepsilon \), is a measure of the polarizability of a substance or rather a measure of its ability to separate charge.

An illustration of the Helmholtz Model is shown in figure 2.2. In this example, the potential on the electrode is negative leading to an excess negative charge on the electrode surface. This causes positive ions in the solution to be attracted through electrostatic interactions and creates two layers of charge separated by the radius of the adsorbed ions.

Using the ion radius for \( d \) and the static dielectric constant of the solution, the Helmholtz model can qualitatively predict the behavior of the interfacial
Figure 2.2 Illustration of the Double Layer Model proposed by Helmholtz. This is for the case where the electrode potential is negative of the pzc, and therefore, has an excess of electrons at its surface which cause the positive ions in the solution to adsorb giving rise to a capacitive behavior.
capacitance. It gives reasonable results for very concentrated solutions, but it is inadequate for a number of reasons. The Helmholtz model neglects any contribution of the solvent molecules to the double layer capacitance; and furthermore, the thermal motions of the solution molecules and ions would never permit such a rigid structure in the interphase. It also neglects the chemical interactions between the metal and the solutes and between the metal and the solvent. Although this model does not accurately predict the size or potential behavior of the interfacial capacitance, it does explain the existence of the capacitive behavior across an interface.

The next attempt to model the interface came from Gouy in 1903 and Chapman in 1913. This model is called the Gouy-Chapman model and is shown in figure 2.3. This is the diffuse model of the interphase structure and is a decent description of the interphase double layer behavior in very dilute solutions. There is charge buildup in the solution near the surface in response to excess charge on the electrode surface, but it is not rigidly held in position like in the Helmholtz model. The ions are attracted to the surface electrostatically, but are also subject to random thermal motion.
Figure 2.3 Illustration of the Gouy-Chapman Diffuse Double Layer Model. In this case, the electrode potential is negative of the pzc and has an excess of electrons at its surface which cause the positive ions in the solution to be electrostatically attracted to the electrode. This electrostatic attraction is in competition with the thermal motions of the ions and so the charged region in the solution extends out away from the electrode surface.
Starting from the Boltzmann equation for the concentration of the $i^{th}$ ionic species, $C_i(x)$, at a distance $x$ from the surface,

$$C_i(x) = C_i^0 \exp \left( \frac{-Z_i F V_x}{RT} \right) \quad (2.2)$$

where $V_x$ represents the potential at a distance $x$ from the metal surface (with respect to the potential in the bulk solution which is taken as zero) and $Z_i$ is the charge on the ion. The concentration is determined by the ratio of the ion's electrostatic energy ($Z_i F V_x$) to their average thermal energy, $RT$.

By essentially following the derivation\textsuperscript{34} of the Debye-Huckel theory, which is used to describe the interactions of ions in solution, the capacitance of the interphase can be solved for using well known electrostatic and thermodynamic principles. The interphase capacitance predicted by the Gouy-Chapman model, for a symmetrical electrolyte (e.g., NaCl or LiClO$_4$), is:

$$C_{GC} = |z| F \left\{ \frac{\varepsilon}{2 \pi RT} C^0 \right\} \frac{1}{2} \cosh \left[ \frac{|z| F V_0}{2RT} \right] \quad (2.3)$$
where \( z \) is the ionic charge, \( C^0 \) is the bulk concentration of the ions and \( V_0 \) is the potential difference across the entire interphase.

The largest flaw is this model is that Gouy and Chapman treated the ions as point charges. This leads to unrealistic numbers of ions near the surface\(^{35} \). Other approximations made during the derivation are the neglect of ion-ion interactions in the energy of adsorption and assuming that \( \varepsilon \) is constant over the interphase region.

A better model was proposed in 1924 by Stern\(^{36} \). He realized that both the Helmholtz model and the Gouy-Chapman model are valid and in fact exist at an interphase simultaneously. Thus, the Stern model shown in figure 2.4 is a synthesis of the two previous descriptions of the interphase with a compact layer of ions at the surface and a diffuse space charge region extending out into the solution. These two capacitive layers are connected in series; and hence, the Stern model predicts that the double layer capacitance will be:

\[
\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{GC}} \tag{2.4}
\]

where \( C_H \) is the capacitance of the compact Helmholtz layer given by eqn. 2.1 and \( C_{GC} \) is the capacitance of the diffuse Gouy-Chapman layer given by eqn. 2.3.
Figure 2.4 A schematic drawing of the Stern model of the interfacial region. This model includes both a compact Helmholtz layer and a diffuse Gouy-Chapman layer.
It was shown by Grahame\textsuperscript{37} that the Gouy-Chapman model gives good quantitative agreement with experiment for a mercury electrode in solutions containing a non-specifically adsorbed electrolyte. So far only electrostatic interactions have been considered and all three models only consider the electrostatic interactions of the electrode surface with the ions in solution. However, there are many other interactions which occur at the interface. A complete description of the interphase region must take these other effects into account.

The following discussion will be limited to a qualitative description of these other factors\textsuperscript{38}. To begin with, the electrode surface will be solvated and these adsorbed molecules will contribute to the double layer capacitance by orienting opposite of the potential field. A schematic representation of this effect is shown in figure 2.5.

The orientation of solvent molecules in the interphase region has been shown\textsuperscript{39}, for the silver(111) surface in water, to extend at least three molecular diameters from the surface and to be dependent upon the charge of the metal. In fact, the water molecules were shown to flip as the externally applied potential on the metal is changed from a negative surface potential to a positive potential.
Figure 2.5  A schematic drawing of the polarization of the solvent molecules in the interfacial region. The polarization of the solvent molecules is due to the electrostatic attraction of the excess electron density at the electrode surface.
Furthermore, as shown in figure 2.6, the ions in solution may be solvated and this solvation sheath will prevent them from adsorbing onto the electrode surface. In general, smaller ions tend to be more strongly solvated and this is why, in figure 2.6, the cation is shown as solvated. Anions are typically larger and often do not have a solvation sheath. Ions which are not strongly solvated can adsorb onto the surface. An ion adsorbed directly onto the electrode surface is referred to as contact or specifically adsorbed.

Lastly, the ions may chemically interact very strongly with the electrode surface and this force can be stronger than the electrostatic repulsion. When this occurs, anions will be adsorbed onto a negatively charged surface. Similarly, cations which chemically interact strongly with the electrode surface may be adsorbed onto the electrode surface.

These solvent and chemical effects cause the behavior of the interphase region to be more complex than the behavior predicted by the Stern Model. Thus the actual capacitive behavior of an electrochemical interface is dependent upon the concentration and type of ions dissolved in solution, the solvent and the electrode material.
Figure 2.6 A schematic drawing of some of the other types of behavior believed to occur in the interphase. In this diagram, the cations are solvated, the anions are not solvated, the solvent molecules near the interface are polarized, there is an anion contact adsorbed on the electrode surface and an excess of positive charge inside the diffuse layer.
2.1.3 Charge Transfer Reactions

As previously stated, corrosion occurs when a metal is oxidized via a charge transfer reaction at the electrode surface. The general current-potential relationship for a simple one electron charge transfer reaction:

\[ A^+ + e^- \rightarrow A \]  \hspace{1cm} (2.5)

which is called the Butler-Volmer equation can be found in any elementary electrochemistry text:\textsuperscript{40}:

\[ i = i_0 \left[ \exp\left(-\left(1-\beta\right)\frac{F\eta}{RT}\right) - \exp\left(\beta\frac{F\eta}{RT}\right) \right], \]  \hspace{1cm} (2.6)

where \( i \) is the current in amperes, \( i_0 \) is the exchange current in amperes, \( \beta \) is the symmetry factor, \( F \) is Faraday's constant, \( R \) is the gas constant, \( T \) is the temperature and \( \eta \), the overpotential, is the deviation in the potential difference across the interface from its equilibrium value. The symmetry factor represents the ratio of the effect of potential on the electrochemical free energy of activation to its effect on the electrochemical free energy of the overall reaction.

The equilibrium exchange current density, \( i_0 \), is a measure of the rate of the reaction which occurs (in opposite
directions at equal rates) at an interface at equilibrium where the net reaction rate is zero. The basic chemical rate of reaction and the rate of reaction due to the equilibrium potential difference across the interface are contained in \( i_0 \). The expression for \( i_0 \) for the reaction shown in eqn. 2.5 is:

\[
i_0 = i_f = Fk_f C_{A^+} \exp\left(-\left(1 - \beta\right) F V_{eq} / RT\right) \tag{2.7}
\]

\[
i_0 = |i_b| = \left|-Fk_b C_A \exp\left(\beta F V_{eq} / RT\right)\right| \tag{2.8}
\]

where \( k_f \) (\( k_b \)) is the forward (backward) chemical rate constant, \( C_{A^+} \) (\( C_A \)) is the concentration of \( A^+ \) (\( A \)), \( V_{eq} \) is the equilibrium potential difference across the interface and the other factors are as defined for eqn. 2.6.

It is interesting to note at this point that for unit activities of products and reactants at 25°C the equilibrium potential difference measured relative to NHE is what is commonly call the standard electrochemical potential or the electromotive force (emf). Further inspection of eqns. 2.6, 2.7 and 2.8 reveals that the charge transfer current at a given potential difference is dependent upon the equilibrium exchange current density and the deviation of the potential difference from its equilibrium value.
Corrosion occurs as a result of different electrochemical charge transfer reactions occurring simultaneously and in opposite directions at a surface. The current across a corroding interface will be equal to the sum of the cathodic half reaction's current and the anodic half reaction's current at any given potential. It is convenient, since these currents are exponential functions of potential, to plot the logarithm of the magnitude of the current versus potential when evaluating the behavior of charge transfer reactions. Figure 2.7 shows the current behavior of two different charge transfer reactions and the behavior of their sum as a function of potential. The reactions chosen were:

\[
\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe(s)}
\]  \hspace{1cm} (2.9)

\[
2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{H}_2\text{O}
\]  \hspace{1cm} (2.10)

The equilibrium potentials at 25 °C were estimated using the Nernst equation for a pH of 8, a ferrous ion concentration of 10 nM and an oxygen pressure of 1 atm. The exchange current densities were taken from Bockris (1 μA for the reaction in eqn. 2.9 and 10 fA for the reaction in eqn. 2.10) and a value of 0.5 was taken for the symmetry factor. In figure 2.7, the two currents become equal at a potential of -0.4 V and this point is called the open circuit
Figure 2.7 A Tafel plot of the current behavior of two different charge transfer reactions and the behavior of their sum as a function of potential.
potential. The open circuit potential is the value of the potential when the corroding system is at equilibrium. At open circuit, the net current approaches zero and the anodic current is proportional to the rate of metal dissolution.

As shown by figure 2.7, for a corroding system the current is still exponentially dependent upon the potential in a corroding system; however, the cathodic reaction is different from the anodic reaction. Thus when studying corrosion, the empirically determined Tafel equation, which is conventionally expressed in base 10, is used:

\[ i = i_{corr}\left[10^\left(-\eta\right)-10^\left(\eta\right)\right], \]  

\[(2.11)\]

where \( i \) is the net current, \( i_{corr} \) is the corrosion current, \( B_a \) is the anodic Tafel slope and \( B_c \) is the cathodic Tafel slope. For small values of \( \eta/B \), a Taylor expansion (retaining only the first two terms) of eqn. 2.11 leads to the current-potential relationship:

\[ i = i_{corr}\left[\left(\frac{2.3\eta}{B_a}\right) - \left(-\frac{2.3\eta}{B_c}\right)\right]. \]  

\[(2.12)\]

After simplification and rearrangement, we arrive at the Stern and Geary form of eqn. 2.11, good for low \( \eta/B \) values:
\[ i_{\text{corr}} = \left( \frac{\text{Ba} \times \text{Bc}}{\text{Ba} + \text{Bc}} \right) \times \frac{i}{2.3 \eta} = \left( \frac{\text{Ba} \times \text{Bc}}{\text{Ba} + \text{Bc}} \right) \times \frac{1}{2.3 R_p}, \] (2.13)

where \( R_p \) is the polarization resistance, the resistance to the applied field. In the absence of other processes \( R_p \) is the charge transfer resistance or in other words the resistance of the interface to the transfer of charge across it.

Equations 2.11, 2.12 and 2.13 are for the case where the current response to an applied potential is due only to charge transfer reactions occurring at the surface. They assume there is no film present on the surface and that the solution resistance is negligible.

Unfortunately for the scientist trying to study corrosion, these two assumptions rarely hold true and the measured resistance often contains three contributions to the overall resistance: solution resistance, charge transfer resistance and the surface film resistance. What is needed is a way to separate the interface, the film and the solution effects to obtain the charge transfer resistance that can then be converted to \( i_{\text{corr}} \) and the rate of corrosion.

Fortunately, a technique exists which allows the effects of the solution resistance, the film resistance and the charge transfer resistance to be separated. This is possible, because these different processes have different time constants. Thus by varying the perturbation rate it is
often possible to separate them. The technique is called Electrochemical Impedance Spectroscopy (EIS) and it works by measuring the current response to an applied sinusoidal potential perturbation over a wide range of frequencies. EIS has been shown\textsuperscript{42, 43, 44, 45, 46} to be a powerful tool for studying corrosion.

2.2 Electrochemical Impedance Spectroscopy

Impedance is the result of generalizing Ohm's Law to describe circuits containing capacitors and inductors; thus, impedance is the complex transfer function from current to potential. Although the impedance concept has been known for a long time\textsuperscript{47}, it was only with the advent of computerized data acquisition systems\textsuperscript{48} which allow experiments to be carried out with ease that the use of impedance spectroscopy to investigate electrochemical systems has become common. Electrochemical Impedance Spectroscopy combines a phase sensitive voltmeter with a variable frequency sine-wave generator to obtain the impedance of a system as a function of the frequency of an applied sinusoidal perturbation.

The impedance response to a sinusoidal perturbation at a frequency, $\omega$, is expressed in complex notation as:

$$Z(\omega) = Z'(\omega) - jZ''(\omega)$$  \hspace{1cm} (2.14)
where $Z'$ is the resistance portion of the impedance and $Z''$ is the reactance portion of the impedance. It can also be expressed as a magnitude and phase shift, $\phi$:

$$|Z(\omega)| = \sqrt{(Z'(\omega))^2 + (Z''(\omega))^2}$$  \hspace{1cm} (2.15)

$$\phi(\omega) = \text{inv} \tan \left(\frac{Z''(\omega)}{Z'(\omega)}\right)$$ \hspace{1cm} (2.16)

These two different expressions of the impedance transfer function give rise to the most common types of impedance plots. A Nyquist plot is the result of plotting the impedance of a system as $-Z''$ versus $Z'$. A Bode plot (actually two plots combined in one) is the result of plotting the log of the magnitude of the impedance and the phase shift of the impedance as a function of the log of the frequency.

2.3 Chemical Significance of Equivalent Circuit Elements

EIS spectra over all frequencies theoretically contain all the information accessible by electrical experiments regarding the system being investigated. The trick is to extract the information for each separate process from the spectra. The most common method of EIS data analysis is equivalent circuit fitting. The impedance of the electrode system is measured over a large frequency range and, using a
nonlinear least squares fitting program, an equivalent circuit is fit to the data.

The equivalent circuit uses a combination of classical electrical components, such as, resistors, capacitors and inductors, to approximate the experimental response of the electrochemical system about a fixed potential. This method has proved to be a powerful technique for extracting the response of each different electrochemical process occurring in the system during the experiment.

If equivalent circuit modeling is accepted as being a reasonable way to describe the processes occurring across the interphase, then the efficacy of a specific equivalent circuit can be tested. The equivalent circuit can be fit to EIS spectra taken at different applied potentials and if the current response of the various components behaves as predicted by electrochemical theory, then the equivalent circuit is deemed a reasonable model of the system. For example, as seen in eqn. 2.11, theory predicts that the charge transfer resistance will be an exponential function of the applied potential.

Although it would be convenient if all electrochemical processes could be modeled using electrical components, they cannot and this is one of the main criticisms which equivalent circuit modeling has received. The equivalent circuit is a very simplified model of the behavior of the interfacial and solution processes and in some cases these
electrical analogies are incapable of adequately describing electrochemical processes.

One way in which the equivalent circuit's ability to model the EIS spectra has been improved, is through the use of special circuit elements that do not occur in electrical circuits. These equivalent circuit elements were developed in response to the phenomenological behavior observed in electrochemical experiments. The most common deviation from classical electronics type behavior occurs in the capacitive behavior and this is accounted for by using a constant phase element in place of a capacitor in the equivalent circuit. The constant phase element will be discussed in more detail in section 2.3.3.

2.3.1 Resistors

The electrical resistance of an object characterizes its ability pass a direct electrical current. This property is called resistivity, $\rho$, and is usually given in units of ohm meters ($\Omega m$) or ohm centimeters ($\Omega cm$). Resistance is the constant in Ohm's Law which relates electrical potential to current:

$$V = iR$$  \hspace{1cm} (2.17)
The electrical resistance of an object is given by:

\[ R = \frac{\rho L}{A}, \]  

(2.18)

where \( \rho \) is the resistivity of the material, \( L \) is the length of the object and \( A \) is the cross sectional area. One can see that resistance is a linear transfer function of current to potential.

In electrochemical systems, there are three commonly observed phenomena which cause resistive behavior. First, electrical current passing through a solid encounters a certain resistance to its flow. The metal electrode and the wires attaching the electrochemical system to the measurement device have resistance. In the experiments discussed in this dissertation, this resistance is too small (on the order of \( 10^{-2} \Omega \)) to contribute significantly to the response of the system.

Oxides are semiconductors or insulators and exhibit much larger resistivities than metals. An oxide film formed on the surface of an electrode may contribute a significant resistance to the electrochemical response of the system. An oxide film's resistance is determined by eqn. 2.18 and is proportional to the resistivity of the oxide, the thickness of the film and inversely proportional to the surface area of the electrode.
Another process which causes resistance to the flow of current is the opposition of the solution to the passage of ions through it. The solution passes a current by ion migration and diffusion and, depending upon the solvent and the concentration of ions dissolved in the solution, a wide range of solution resistivities is observed. For example, ultra pure water has a resistivity of 18 MΩcm; whereas, 1 M HCl solution has a resistivity of 4 Ωcm and 1 M HCl methanol solution has a resistivity of 23 Ωcm.

The solution resistance in a planar electrode configuration also follows the behavior of eqn. 2.18 and has been shown to be the high frequency limit of the impedance. One obvious way to minimize the solution resistance is by adding ions (supporting electrolyte) to decrease the solution resistivity. Another way to minimize the solution resistance is to reduce the effective thickness of the solution layer between the reference electrode and the working electrode. This can be accomplished by using a Luggin capillary.

The Luggin capillary is essentially a narrow glass tube filled with bulk solution; one end of the tube is brought close to the working electrode surface and the other end is connected to the reference electrode. The effective thickness of the solution layer between the reference electrode and the working electrode is the distance between capillary tip and the working electrode; and hence, the solution resistance is reduced.
Finally, in order for a current to flow from the electrode into the solution, charge transfer must occur across the electrode-solution interface. As was shown in eqn. 2.12, for small potential perturbations, the charge transfer current is a linear function of overpotential. This means that a resistance can be used to approximate the charge transfer response to a small applied potential perturbation. This resistance is called the charge transfer resistance.

2.3.2 Capacitors

Capacitors are composed of two electrical conductors separated by a nonconducting medium which store charge on their conducting surfaces. A capacitor has the property:

\[ Q = CV, \]  
(2.19)

where \( Q \) is the coulombs of charge stored in the capacitor, \( C \) is the capacitance in terms of farads (F) and \( V \) is the potential applied across the capacitor in volts (V). Taking the derivative of eqn. 2.19 with respect to time gives:

\[ \frac{dQ}{dt} = i = C \frac{dV}{dt}. \]  
(2.20)
Thus, the current response of a capacitor is more complicated than that of a resistor. The current is not simply proportional to the potential difference, but to the rate of change of the potential.

When a potential is applied externally to two conductors separated by a nonconducting dielectric material, negative charge builds up on one and positive charge builds up on the other. Capacitance, like a resistance, depends on the materials involved and their geometry. For a parallel-plate capacitor, the following equation can be used to calculate the capacitance:

\[
C = \frac{\varepsilon}{4\pi} \left( \frac{A}{d} \right), \tag{2.21}
\]

where \(\varepsilon\) is the static dielectric constant of the nonconducting media, \(A\) is the surface area of each plate and \(d\) is the distance between the plates. The typical ceramics used in making capacitors have dielectric constants in the range from 6 to 10.

If a sinusoidal potential wave is applied across a capacitor, its derivative will be:

\[
\frac{dV}{dt} = \frac{d(V_0 \sin(\omega t + \phi))}{dt} = \omega V_0 \cos(\omega t + \phi), \tag{2.22}
\]
and inserting this result into eqn 2.20 yields a capacitor current response of:

\[ i = C \omega V_0 \cos(\omega t + \phi) \]  \hspace{1cm} (2.23)

\[ i = C \omega V_0 \sin(\omega t + \phi + 90). \]  \hspace{1cm} (2.24)

In other words, the sinusoidal current response of a capacitor will have a phase shift of 90 degrees relative to the applied potential and its amplitude will be directly proportional to the capacitance.

In electrochemical studies, there are two main processes which result in capacitive behavior. One is the presence of a nonconducting film on the surface of the electrode. This means that when a potential is applied across the electrochemical cell some of the energy goes to polarizing the film. If the applied potential is sinusoidal, the current response of the oxide film at the electrode surface will be phase shifted and have a frequency dependent amplitude.

As discussed in more detail in section 2.1.2, another process which exhibits capacitive behavior is the response of the interphase to an applied potential.

Although the capacitance of the double layer is, strictly speaking, a function of potential, for small potential perturbations this effect can be neglected and the
response of the double layer to a sinusoidal potential perturbation can be modeled using a capacitor. The double layer is not, in fact, a true capacitor and one way to compensate for this is to use a constant phase element in its place in the equivalent circuit.

### 2.3.3 Constant Phase Elements

It is well established that the dielectric properties of many liquids and solids are frequency dependent\(^{54}\). The frequency dependence of the dielectric constant is reflected in the capacitive response of the liquid or solid to an ac perturbation and this response has been mathematically described by a constant phase element\(^{55,56}\). This constant phase element is often used in equivalent circuits in place of a capacitor.

The constant phase element (CPE) differs from a capacitor in that its frequency dependence varies from \(-1<n<1\). A CPE is equivalent to a capacitor (if \(n=1\)), to a Warburg diffusion impedance (if \(n=1/2\)), to a resistor (if \(n=0\)) and to an inductor (if \(n=-1\)). A Warburg diffusion impedance is the transfer function between current and potential which results when the diffusion equations are solved for a sinusoidal potential perturbation\(^{57}\). It has been mathematically described in many different ways and is

50
described in the admittance representation, the inverse of impedance, as:

\[ Y^*(\omega) = Y_0(i\omega)^n \left[ \cos\left(\frac{n\pi}{2}\right) + i \sin\left(\frac{n\pi}{2}\right) \right], \]  \hspace{1cm} (2.25)

where \( Y_0 \) and \( n \) are the adjustable parameters and \( \omega \) is the frequency\(^58\).

### 2.3.4 Simulation of Constant Phase Element Behavior

The circuits shown in figure 2.8a and 2.8b are Randles' type equivalent circuits used in the absence of any surface thin film. The Randles' circuit represents a simple charge transfer reaction occurring at a film free electrode surface. In these circuits, the first resistance is due to the solution and connecting wire resistance. The resistance in parallel with either a capacitor (figure 2.8a) or a CPE (figure 2.8b) represents the charge transfer resistance. The capacitor or CPE corresponds to the double layer behavior in the interphase region.
a. Randles' circuit using a capacitor to model the double layer.

b. Randles' circuit using a CPE to model the double layer behavior.

Figure 2.8 Randles' type equivalent circuits. These circuits are used to model electrochemical systems containing only a simple charge transfer reaction and double layer in the interphase region.
To further explore the CPE behavior, synthetic data was generated for the Randles' type equivalent circuit shown in figure 2.8b. The values for \( R_s \), \( R_{ct} \) and \( Q_{dl} \) were fixed at 1 kohm, 100 kohm and 10 \( \mu \)Farads, respectively, while the value of \( n \) was varied from 0.5 to 1.0. The results are plotted in Fig. 2.9 in the Nyquist format and in Fig. 2.10 in the Bode format.

Fig. 2.9 is the Nyquist plot of the synthetic data that shows the real part of the impedance versus the imaginary part. For \( n = 1 \), the CPE is equivalent to a capacitor and the shape of the plot is a semicircle. The intersection of the semicircle on the high frequency (left) side is the solution resistance and the intersection on the low frequency (right) side is the sum of the solution and polarization or charge transfer resistance. It can be seen that the semicircle is depressed by decreasing \( n \).

Fig. 2.10 is a Bode plot of the same data, but this time the logarithm of the magnitude and phase shift of the impedance are plotted versus the logarithm of the frequency. The phase shift peak broadens, shifts to higher frequencies and its maximum decreases with \( n \) while the slope of the log of the magnitude of the impedance decreases with \( n \).
Figure 2.9 Nyquist plot of the impedance of the equivalent circuit shown in figure 2.8b. The values for $R_s$, $R_{ct}$ and $Q_{dl}$ were fixed at 1 kohm, 100 kohm and 10 μF, respectively, while the value of $n$ was varied from 0.5 to 1.0.
Figure 2.10 Bode plot of the impedance of the equivalent circuit shown in figure 2.8b. The values for $R_s$, $R_{ct}$ and $Q_{dl}$ were fixed at 1 kΩ, 100 kΩ and 10 μF, respectively, while the value of $n$ was varied from 0.5 to 1.0.
2.4 EIS Modeling

2.4.1 Equivalent Circuits versus Mechanistic Modeling

Another approach to analyzing impedance data is to simulate the spectra from the chemical reaction mechanism\textsuperscript{59, 60, 61}. In this approach, the kinetic parameters for the various steps in the reaction mechanism are adjusted until a good fit is obtained for the impedance spectra. Typically, the EIS spectra are taken at several different applied potentials and the model parameters are adjusted until a good fit to the impedance spectra at the various applied potentials is obtained.

While mechanistic modeling approach takes a more fundamental view of the electrochemical reactions occurring at the interface, it is also somewhat self-fulfilling in that the kinetic parameters are adjustable. Thus, any model that has the right limiting reaction behavior can be made to fit the impedance spectra. Additionally, there are several parameters, such as the distances from the surface to the inner and outer Helmholtz planes, the number of available surface reaction sites and the surface concentrations of reactants, intermediates and products that must be estimated in the absence of experimental information. However, this approach can offer much insight into the microscopic picture.
of the processes that occur at the interface and in the interphase region.

Equivalent circuit modeling is a simpler approach than mechanistic modeling; and furthermore, the electrochemical parameters are extracted from the impedance spectra using fewer adjustable parameters and by mathematically fitting the model to the spectra. This type of modeling works best for simple systems where a charge transfer reaction is the rate determining step in the reaction mechanism; in other words, when Tafel behavior is observed and the reaction rate is potential dependent.

2.4.2 Equivalent Circuits Used in Modeling the Data

The equivalent circuits used to analyze the data are shown in Fig. 2.11. These circuits have been associated with electrodes that have surface thin films\textsuperscript{62,63,64}. Since the Armco iron electrode contained surface films, these equivalent circuits were used to model the data. The presence of a surface film on the electrode surface has been confirmed experimentally, as will be discussed in Chapters 4 and 5. The equivalent circuits that were chosen to fit the EIS data were the simplest that were able to reproduce the spectral features.
a. Series circuit, $R_s(R_{ct}Q_{dl})(R_fQ_f)$, with a CPE for thin film capacitance.

b. Nested circuit, $R_s(R_{ct}(Q_{dl}(R_fQ_f)))$, with $R_{ct}$ parallel to the rest of the circuit elements and a CPE for the thin film capacitance.

Figure 2.11 Equivalent circuits associated with electrodes containing surface films.
The first resistor, $R_s$, is the resistance of the solution and the connecting wires. This is the high frequency limit of the impedance. In Fig. 2.11a, one resistor, $R_{ct}$, and CPE, $Q_{dl}$, in parallel are associated with the electrode/solution interactions. This resistance is due to the charge transfer at the electrode surface. The CPE is due to the formation of the double layer in the interphase region between the sample and the solution. This CPE is dependent upon the applied potential due to changes in the double layer structure. The CPE behavior of the double layer can be quite complex and is dependent upon the surface, the solvent and the electrolyte present.

The second parallel resistor, $R_f$, and CPE, $Q_f$, in parallel is associated with the film on the electrode surface. The resistance is due to the resistivity of the film and the CPE is due to the film's dielectric nature. Hence, $R_f$ should increase with film thickness and $Q_f/C_f$ decrease with film thickness.

Fig. 2.11b shows a similar equivalent circuit to the one in Fig. 2.11a, but this circuit is nested. In Fig. 2.11b, the thin film elements, $R_f$ and $Q_f$, and the double layer CPE are in parallel with the charge transfer resistance. Note that there is somewhat of a fundamental difference between the nested and the series circuits. In the nested circuit, shown in Fig. 2.11b, the current can flow through either the
charge transfer path or the double-layer/film path, where as in the series case it must flow through both.

A short hand notation is often used in describing the equivalent circuits, where elements enclosed in parentheses are in parallel and elements adjacent to each other are in series. Using this notation, the equivalent circuit in figure 2.11a is represented by \( R_s(R_{ct}Q_{dl})(R_fQ_f) \) and the equivalent circuit in figure 2.11b is represented by \( R_s(R_{ct}(Q_{dl}(R_fQ_f))) \).

It has been shown by Silverman\(^6^5\) that there are ambiguities in using equivalent circuits. Silverman showed that the overall impedance of the series circuit in Fig. 2.11a after simplification is:

\[
Z = R_s + \frac{R_{ct}R_fQ_{dl}\left(1+\frac{Q_f}{Q_{dl}}\right) + R_{ct}Q_fQ_{dl} + R_fQ_fQ_{dl}}{R_{ct}R_f + R_{ct}Q_f + R_fQ_{dl} + Q_fQ_{dl}} \tag{2.26}
\]

He compared this to the overall impedance for the nested circuit, shown in Fig. 2.12a, where the double layer CPE is in parallel with the charge transfer resistance and the thin film elements. The overall impedance for the nested circuit in Fig. 2.12a after simplification is

\[
Z = R_s + \frac{R_{ct}R_fQ_{dl} + R_{ct}Q_fQ_{dl} + R_fQ_fQ_{dl}}{R_{ct}R_f + R_{ct}Q_f + R_fQ_{dl}\left(1+\frac{Q_f}{Q_{dl}}\right) + Q_fQ_{dl}} \tag{2.27}
\]
a. Nested circuit, \( R_s(Q_{dl}(R_{ct}(R_fQ_f))) \), with double layer CPE in parallel with the rest of the circuit elements.

b. Nested circuit, \( (C_{stray}(R_s(R_{ct}Q_{dl})(R_fQ_f))) \), stray capacitance in parallel with the rest of the circuit elements.

Figure 2.12 Additional equivalent circuits associated with electrodes containing surface films and including experimental artifacts.
It is now easy to see from equations 2.26 and 2.27 that the circuits shown in Fig. 2.11a and 2.12a are indistinguishable when $Q_f/Q_d \ll 1$. This is the case where the "current" flow through the double layer CPE is much smaller than through the rest of the circuit. One can see by comparing the circuit diagrams in Fig. 2.11a and 2.12a, that if there is no flow through the double layer CPE, that the circuits are the same.

A similar analysis can be applied to the circuits shown in figure 2.11a and 2.11b. Following the work of Silverman, an equation for the overall impedance of the equivalent circuits shown in figure 2.11a and 2.11b can be obtained. The overall impedance for the series circuit in figure 2.11a can be simplified to:

$$Z = R_s + \frac{R_{ct} R_f Q_d l + R_{ct} Q_f Q_d l + R_f Q_d l \left(1 + \frac{R_f}{R_{ct}}\right)}{R_{ct} R_f + R_{ct} Q_f + R_f Q_d l + Q_f Q_d l}$$  

The simplified expression for the nested circuit in figure 2.11b is:

$$Z = R_s + \frac{R_{ct} R_f Q_d l + R_{ct} Q_f Q_d l + R_f Q_d l}{R_{ct} R_f + R_{ct} Q_f \left(1 + \frac{R_f}{R_{ct}}\right) + R_f Q_d l + Q_f Q_d l}$$  

In this case, the only difference between eqn. 2.28 and 2.29 is the location of the term containing $(R_f/R_{ct})$. Thus the two
equivalent circuit models become indistinguishable, when the ratio \( R_f/R_{ct} \ll 1 \). This is the case where the charge transfer resistance is large with respect to the thin film resistance and by inspecting the two circuit diagrams one can see that if no current "flows" through the charge transfer resistance then the circuits are the same.

The circuit shown is figure 2.12b contains a stray capacitive element in parallel to the equivalent circuit shown in figure 2.11a. This is to account for the small, but finite amount of capacitive behavior due to the long wires necessary for working in the glove box and possible capacitance due to the potentiostat.

2.4.3 Non-Linear Least Squares Fitting

The EIS spectra were fit by an equivalent circuit, selected by the operator, using Boukamp's non-linear least squares fit program that runs on an IBM PC\(^6\) (other comparable programs are available\(^6\)). Initial values for the equivalent circuit elements are estimated by fitting semicircles and lines to the Nyquist plot of the EIS spectra. It is important to use reasonable values at the beginning of the fitting process or the fit will not converge. The program iteratively adjusts the values of the elements of an equivalent circuit until a reasonable fit to the data is obtained.
2.4.4 Validation of EIS spectra

An EIS spectra is considered to be valid data if the following criteria are met:

Causality: The response of the system is due only to the perturbation applied and does no contain significant components from spurious sources.

Linearity: The perturbation/response of the system is described by a set of linear differential laws. Practically, this condition requires that the impedance be independent of the magnitude of the perturbation.

Stability: The system must be stable in the sense that it returns to its original state after the perturbation is removed.

Continuity and finiteness: The impedance must be finite-valued and continuous over the frequency range $0 < \omega < \infty$. In particular, the impedance must tend to a constant, real value as $\omega \to 0$ and $\omega \to \infty$.

The condition of linearity may be tested by varying the magnitude of the potential perturbation. If the impedance response is unchanged by the change in the magnitude of the potential perturbation, then the response is linear. The condition of stability may be checked by observing whether the system returns to the initial point after the data has been collected. The condition of continuity and finiteness
may be evaluated by inspection of the spectra. To evaluate the condition of causality and the other three conditions, the Kramers-Kronig (K-K) transformation from physics may be used to evaluate the data.

The K-K transform allows the real part of the impedance spectra to be calculated from the imaginary part via the following equation:

$$Z' (\omega) - Z' (\infty) = \left( \frac{2}{\pi} \right) \int_{x=0}^{\infty} \frac{xZ'' (x) - \omega Z'' (\omega)}{x^2 - \omega^2} \, dx \quad (2.30)$$

and the imaginary part of the impedance spectra to be calculated from the real part via:

$$Z'' (\omega) = \left( \frac{2 \omega}{\pi} \right) \int_{x=0}^{\infty} \frac{Z' (x) - Z' (\omega)}{x^2 - \omega^2} \, dx \quad (2.31)$$

where $Z'$ and $Z''$ are the real and imaginary components of the impedance, respectively, at the angular frequencies $x$ (integrand) and $\omega$ (the "pole" frequency). One of the problems with using K-K transforms to validate real EIS spectra is that they are not obtained over the entire frequency range; however, the limits can be estimated or small deviations in the low frequency regime of the transform may be neglected, since the origin is due to the truncation of the impedance data at low frequencies.
Furthermore, since it has been demonstrated\textsuperscript{71} that the equivalent circuits involving passive elements (R, C, L) and the constant phase element (Q) obey the K-K relations, a good equivalent circuit fit with these elements to the EIS data indicates that the EIS data satisfies the conditions of the K-K transforms. Hence a good equivalent circuit fit indicates that the EIS data is valid.
CHAPTER 3: EXPERIMENTAL METHODS

3.1 Introduction

Corrosion is the result of complex electrochemical processes occurring at a metal surface. Thus, the study of the kinetics and phenomena occurring during the corrosion of Armco iron in methanol required the use of many different experimental techniques.

The kinetics of the corrosion process and changes in the electrical behavior of the interphase were studied by electrochemical means. The primary electrochemical technique used was electrochemical impedance spectroscopy, but potential polarization (cyclic voltammetry and linear potential polarization) was also used. Galvanic treatment of the electrodes was used to increase product formation.

There seemed to be two types of reaction products: solids at the electrode surface and products dissolved in the solution. The electrode surface was analyzed ex situ by XES, FTIR, Raman, XPS and SEM. The film was scraped off and the resulting powder was analyzed by XRD. Chemical analysis of the solution was done using atomic absorption spectroscopy, Karl Fischer titration, gas chromatography, mass spectrometry and combined gas chromatography/mass spectrometry.
3.2 Electrochemical Experiments

The impedance of an electrochemical cell is sensitive to the electrochemical environment and the electrode's surface geometry, composition and electron-band structure. The impedance of an electrode can be measured over a wide range of frequencies; this is referred to as the EIS spectra. These spectra often change with time for a given electrode due to film formation on the surface and changes in solute concentrations over time. In addition, due to microscopic differences in initial surface morphology, EIS spectra may differ from one electrode to the next, even though all the conditions (sample preparation, solution concentrations, temperature, reference electrode, pressure, etc.) are the same.

To improve reproducibility, special care was taken during the preparation for an experiment (details will be presented in latter sections). The solvent and any solute to be added were of high purity. The sample must be carefully polished and rinsed thoroughly. Polishing may substantially affect the electrochemical results, since it changes the electrode's effective surface area and initial surface morphology. The electrochemical cell must be well cleaned. In experiments by Banas, chlorine in parts per million levels was found to affect the corrosion of zinc in methanol.\(^{72}\)
3.2.1 The Glove Box

To minimize the leakage of water and oxygen into the electrochemical cell, many of the electrochemical experiments were conducted inside a glove box. The glove box, shown in a schematic form in figure 3.1, was a Mbraun MB 150B-G-I glove box with an argon atmosphere. It is equipped with an Mbraun Digital Oxygen Analyzer, Mbraun Moisture Analyzer, Mbraun Nitrogen Purification System MB 200N (not shown in figure) and a Leybold-Heraeus Trivac-B vacuum pump.

Initially, the oxygen and water trap systems worked quite well, although the nitrogen purification system was inoperable. When the trap systems were working, the oxygen level in the glove box remained below 10 ppm and water level below 1 ppm. However, the blower became inoperable during the course of the research and without the oxygen trap the level of oxygen in the glove box rose slowly over a period of four months stabilizing at 250 ppm. The water level remained below 1 ppm due to water absorption by hygroscopic salts being kept inside the glove box for a separate research project.
Figure 3.1 Schematic diagram of the Mbraun glove box. The dimensions are roughly 8 feet long, 2.5 feet deep and 5 feet tall. The blower and the water and oxygen traps, which are not shown in the diagram, are housed behind the control panel and accessed from the rear of the glove box. The nitrogen purification system, also not shown, sits just to the left of the glove box as a separate unit.
3.2.2 Solution and Sample Preparation

In the initial experiments, the samples were abraded using silicon carbide sandpaper down to 800 grit paper, rinsed with methanol and stored in a desiccator. Prior to each experiment, the sample was placed in a clean, dry sample holder and the sample and holder were kept in a desiccator at least overnight.

In later electrochemical experiments, the electrode was abraded with sequentially finer grade silicon carbide sandpaper to at least 800 grit, then polished to a mirror finish with 1.0, 0.30 and 0.05 μm alumina paste with sonication in reagent grade methanol for at least 2 minutes between steps. It was then either placed in a clean sample holder, sonicated in methanol or placed in a clean polystyrene jar and brought into the glove box via the small port after cycling the port between vacuum and argon several times.

The Armco iron samples were purchased as flat plates two inches by two inches by one quarter inch from Metal Samples Company and machined using lubrication to size. The finished samples were one inch in diameter and one eighth inch thick disks. The Armco iron samples were 99.874% pure containing, as reported by Metal Samples Co., the following impurities:
carbon, 0.03%; copper, 0.02%; manganese, 0.06%; phosphorous, 0.008%; and sulfur, 0.008%.

Two types of methanol were used as received in the experiments, anhydrous methanol from Aldrich with a water concentration of less than 50 ppm and Karl Fischer grade methanol from Fischer with a water concentration of less than 80 ppm. The lithium perchlorate (A.C.S. Reagent grade) was used as purchased from Aldrich. The tetrabutyl ammonium perchlorate (puriss grade) from Fluka was used as purchased. The phosphoric acid was A.C.S. reagent grade (85.9% acid balance water) from Baker and was used as purchased.

3.2.3 The Electrochemical Cell and Sample Holder

Two different types of electrochemical cells were developed for use in this study. One was a small volume cell roughly 6 inches high and 2.5 inches wide, shown in figure 3.2, which uses only 70 ml of solution. The small cell had three 14/20 female ground glass openings for the Luggin capillary and the compression fittings that seal the sample holder and counter electrode in place. It had two additional openings for a wire reference electrode and a septum for injecting the solution and/or purging the cell with gas. This design was quite compact and still allowed a one inch diameter sample to be used. It was compatible with the
Figure 3.2 Schematic (not to exact scale) of the small volume electrochemical cell.
sample holder that was designed and fabricated for these electrochemical experiments.

A larger volume cell roughly 6 inches high and 6 inches wide, shown in figure 3.3, was also developed. It had six openings, four 14/20 female ground glass openings for the Luggin capillary and the compression fittings that seal the two sample holders and an auxiliary counter electrode in place. The other two openings were for septa for access while the cell was sealed. This larger cell, developed for the galvanostatic treatment, where the anode and the cathode were both sample electrodes, used about 500 ml of solution.

The sample holder was made of Delrin, an acetal plastic. A diagram of the sample holder is shown in figure 3.4. Buna-N O-rings were used rather than Viton O-rings, since the methanol rapidly degrades Viton. The Buna-N O-rings were kept in methanol before being used until fresh methanol remained colorless, since the O-rings leached some substance into the methanol that turned it yellow. The sample holder held a one inch in diameter by one eighth inch sample; the entire front of the sample was exposed to the solution, while the back was sealed from the solution. This holder made it possible for both electrochemical experiments and XES experiments to be carried out on the same sample.
Figure 3.3  Schematic (not to scale) of the large electrochemical cell used primarily for galvanostatic treatment of the electrode. This cell is capable of holding two sample electrodes, an auxiliary counter electrode and a reference electrode via a Luggin capillary. One of the ports is not shown for clarity.
Figure 3.4 Schematic drawing of the Delrin sample holder. This figure showing a front view and a cut away side view is only roughly drawn to scale. The dimensions are 7 inches tall, 1.5 inches widest diameter and .75 inches thick.
3.2.3.1 Bench Top Electrochemical Experiments

The electrochemical cell was washed thoroughly, rinsed with distilled water and dried overnight in an oven, then it was cooled in a desiccator. On the day the experimental run was to begin, the electrochemical cell was assembled and sealed using silicone grease. The cell was then purged with nitrogen gas through one of the septa for at least half an hour. The methanol was then injected using a large glass syringe and, if LiClO₄ or H₃PO₄ were to be included in the solution, an appropriate amount of previously prepared solution was also injected. It was at this time that the reference electrode was inserted into the Luggin capillary.

3.2.3.2 Glove Box Electrochemical Experiments

The electrochemical cell was washed thoroughly, soaked overnight in distilled water, soaked overnight in nanopure (ion exchange purified, 17 to 18 MΩ) water and air dried. It was then assembled with silicone grease and placed in the large glove box entry port. The port was pumped down to vacuum (<1 mbar), filled with argon gas and left at least overnight. The port was pumped down to vacuum and refilled with argon gas again before bringing the electrochemical cell into the glove box.
3.2.4 The Reference Electrode and the Counter Electrode

Initially, a saturated calomel electrode (SCE) was used as a reference, since previously published work done in methanol used SCE reference electrodes. A SCE was a suitable reference electrode for polarization experiments in methanol containing large amounts of supporting electrolyte where minor fluctuations of the potential are not critical. However, using the SCE reference with the EIS technique, data below 10 mHz was unobtainable due to current fluctuations that overload the potentiostat. The cause of this is unknown, but may be due to an unstable junction between the aqueous SCE and the methanol solution.

The use of a platinum wire quasi-reference electrode proved quite useful and showed much better stability than the SCE reference. Impedance data was obtained in the millihertz range and the scatter of the low frequency data was greatly reduced. A gold wire reference electrode was also tested in an attempt to increase the reproducibility of the results and to increase cell stability. A gold wire quasi-reference was developed to be used with the electrochemical cell. While this was effective for gathering EIS spectra, the potential of the gold wire was not well defined and so...
the potential difference measured across the cell could not be compared from one experiment to the next.

A new reference electrode, shown in figure 3.5, was developed. This electrode used KCl-saturated methanol in place of the aqueous KCl in the SCE. It is referred to as the methanol saturated calomel electrode (MSCE). The MSCE exhibited superior behavior to the SCE, at least in terms of being able to obtain low frequency data. The potential of the MSCE was determined by comparing it to the potential of an SCE. Its potential was 15 mV negative of the SCE. It also had the advantage that any solution leakage across the junction would be of methanol not water.

3.2.5 Electrochemical Impedance Spectroscopy

The EIS spectra were acquired using a Schlumberger/EG&G system composed of a Schlumberger 1255 or 1260 frequency response analyzer, which has a frequency range of 0.00005-500,000 Hz, and a EG&G PAR 273 or 273A potentiostat. This system is driven by an IBM model 30 computer using the M388 impedance software developed by EG&G PAR. A schematic drawing of the system is shown in figure 3.6. The Schlumberger/EG&G system obtains the EIS spectra by synthesizing the wave form and applies it to the electrochemical cell through the potentiostat. The Schlumberger Frequency Response Analyzer measures the
Ground glass stoppers

Potassium chloride saturated methanol

14/20 ground glass male joint

Potassium chloride
Calomel
Liquid mercury
Tungsten wire
Vycor porous glass frit

Figure 3.5 Schematic drawing of the methanol saturated calomel reference electrode (MSCE). Calomel is a blend of Hg₂Cl₂ and liquid mercury.
Figure 3.6 Schematic of the Electrochemical Impedance set-up. The components of the electrochemical cell are shown but not labeled for clarity. Also, for many of the experiments the Faraday cage and the electrochemical cell were inside the glove box.
response and deconvolutes it using correlation techniques. The output is sent to the computer for storage and presentation.

In order to reduce the noise and lower the experimental scatter, a Faraday cage was built from copper screen. Since these experiments are very sensitive to electrical noise, a properly grounded Faraday cage is essential to obtaining low scatter data. In addition, all of the cables that attach to the electrochemical cell are insulated.

Even with Faraday cage and the MSCE, the potentiostat sometimes overloaded at frequencies below 10 mHz due to noise. This problem was overcome by attaching a 5 μF capacitor between the ground line of the electrometer and the working electrode. It was found that the capacitance must be low (< 10 μF) and at frequencies above 1 Hz, the attachment of a 5 μF capacitor give incorrect data.

3.2.5.1 Potential Dependent Measurements

The EIS spectra were obtained at fixed applied potentials going from cathodic to anodic biases. This method allowed the behavior of the various equivalent circuit model elements to be determined as a function of applied potential. The potential dependent behavior of the elements suggested which of the electrochemical processes each element corresponded to and, also suggested, when the elements did
not behave in the expected manner, that the model was incorrect.

3.2.5.2 Time Dependent Measurements

The EIS spectra were obtained at open circuit as a function of time. This gave information about the progress of the corrosion process over time. It was possible to carry out the two methods sequentially. First, the EIS spectrum was followed over time and subsequently the spectra were taken as a function of applied potential.

3.2.6 Galvanostatic Treatment

These experiments were carried out using the E.G.& G. PAR 273 or 273A potentiostat controlled by LabVIEW software running on a Macintosh computer, either a Quadra 950 or a Mac II. The control software was developed by Larry Schmidt in the Materials Research Laboratory at UH Manoa.

Galvanostatic treatment was carried out in order to increase the production of the corrosion products. This was necessary because the corrosion rates of the electrochemical systems investigated in this research project were quite slow. Without the galvanic treatment of the electrode systems, the concentrations of the reaction products were too low to measure by normal chemical analysis techniques.
Galvanostatic treatment consisted of forcing the electrochemical reactions at a fixed current by applying a sufficient potential between the working and the counter electrodes to maintain the desired current flow. A schematic of the set-up is shown in figure 3.7. The currents used for galvanostatic treatments were -20, -10, 1, 10 and 20 µA. The E.G.&G. PAR 273 and 273A potentiostats are capable of applying ±100 volts between the working and the counter electrode and ±10 volts between the working and the reference electrode. The current convention is the American convention, so a negative current means the working electrode is the anode and a positive current means the working electrode is the cathode.

To ensure that the anodic and cathodic reaction products produced during galvanostatic treatment were those that would be produced on an Armco iron surface, both the working and the counter electrodes were Armco iron samples. This was necessary because electrochemical reactions are dependent upon the composition of the electrode. Hence, if a glassy carbon counter electrode had been used, the half reaction occurring at the counter electrode could be different from what would occur at an Armco iron surface.
Figure 3.7 Schematic diagram of the Electrochemical set-up used for the Galvanostatic treatment of the electrodes. The components of the electrochemical cell are shown but not labeled for clarity. Also, for many of the experiments the Faraday cage and the electrochemical cell were inside the glove box.
3.3 Surface and Film Analysis

The Armco iron electrode surfaces were analyzed using five different techniques. The freshly polished Armco iron surface was analyzed using SEM with and without elemental detection and using XES. When the Armco iron electrodes were galvanostatically treated, a highly resistive yellow film was produced on the anodic electrode's surface and a sparse black film was produced on the cathodic electrode's surface. The yellow film formed on the anode was analyzed using SEM with and without elemental detection, Infra-Red Diffuse Reflectance Spectroscopy, Raman Spectroscopy, XES, XPS and XRD. The black cathodic film was analyzed using SEM with and without elemental detection and XES. Additionally, Armco iron electrodes which were used for EIS or potential polarization experiments were analyzed using SEM at the subsequent to the electrochemical experiments.

3.3.1 Scanning Electron Microscopy

Two different Scanning Electron Microscopes were used in this research project. The first SEM used in this project is housed in the Marine Sciences facilities at UH Manoa and was operated by their technician, Don Yancey. It is a Digital Scanning Electron Microscope (DSM 962) made by Zeiss Germany and was used to acquire the SEM images on some of the
galvanostatically treated Armco iron samples and on one freshly polished sample. This microscope is equipped with an Oxford Link Isis Elemental Detection System (EDS).

The EDS system is composed of a multichannel energy dispersive photon detector which measures the energy and intensity of the x-ray emission of the sample during electron bombardment. Initial elemental detection at low count rates and all images presented were acquired with 20 keV electron bombardment. Higher precision elemental detection was done at two different electron voltages (2 keV and 20 keV) with longer count times (until the carbon K emission counts exceeded 200) in an attempt to increase the surface sensitivity.

The second SEM used in this research is housed at the Center for Materials Research at Stanford University and was operated by their technician. The microscope was a Hitachi Model S-2500 equipped with a LaB6 electron gun and a maximum resolution of 35 Å. It was used to obtain images of three galvanostatically treated Armco iron electrodes.

3.3.2 Infra-Red Diffuse Reflectance Spectroscopy

A Nicolet 740 FT-IR Spectrometer equipped with a diffuse reflectance attachment was used by the author to obtain mid range IR spectra of the films which were galvanostatically
generated on the Armco iron surfaces. The background was run on a freshly polished untreated Armco iron sample.

3.3.3 Raman Spectroscopy

Raman Spectra were obtained using a Spex 1877 triple spectrometer located in the Hawaii Institute of Geophysics and operated by Dr. Shiv Sharma. The sample was excited with the 514.5-nm line of an Ar ion laser; typical laser powers ranged from 60 to 80 mW. The laser beam was reflected off the electrode surface and sent to the detector. The peak positions were calibrated using the carbon-oxygen peak position obtained from a standard calcite sample. The signal was of a low intensity so the spectra were acquired using ten to twenty minute count times.

3.3.4 X-ray Emission Spectroscopy

A 5 M grating spectrometer was used to obtain the XES spectra. This is a high resolution instrument developed by Andermann's group at University of Hawaii. The spectrometer can use either a variable energy electron gun or an X-Ray tube to excite the sample. The X-ray emission is measured using a thin window flow proportional counter.

The initial XES experiments on a one inch diameter disk sample were done with an electron gun at electron energies of
1, 1.5 and 2.5 kV and an instrumental resolution of 11.8 eV using 60 μm/60μm slit widths. The depth of penetration of the electron beam increases with increasing energy and so does the depth of the observation. The intensities of the Lα and Lβ emission peaks of iron were determined at their maxima for four Armco iron electrodes.

Later experiments were done using copper Lα photon excitation at an instrumental resolution of 2 eV. The filament was at 5 kV and 150 mA current. The carbon Kα emission was measured at 2 eV steps with a count time of ten minutes per step from an energy of 267 eV to 287 eV for four galvanostatically treated Armco iron electrodes.

### 3.3.5 X-ray Photoelectron Spectroscopy

The XPS was done on a Fisons Instruments S-Probe Surface Spectrometer located in the Center for Materials Research at Stanford University. This is a high spatial (50 microns) and energy (0.3 eV) resolution XPS with a monochromatized X-ray source. XPS spectra of a yellow film on an Armco iron anode generated by galvanostatic treatment. The spot size was 250 by 1000 microns and the resolution was 1.7 eV. The XPS spectra was obtained by a Stanford technician.
3.3.6 X-ray Diffraction

XRD was done on the powder resulting from scraping the surface of a galvanostatically treated Armco iron anode with an exacto knife. The powder was mounted on to a "zero-background" quartz glass slide. Analyses were made on a Scintag Pad V X-ray diffractometer with solid state Ge (germanium) detector using Cu K-alpha1 radiation housed in the Marine Sciences facilities at UH Manoa and was operated by Clark Sherman. The sample was analyzed over a range of 2 to 70 degrees 2-theta at a scan rate of 1 degree 2-theta per minute.

3.4 Chemical Analysis

3.4.1 Mass Spectrometry and Gas Chromatography/Mass Spectrometry

Analysis of liquid and gaseous samples were done in the Chemistry Department facilities at UH Manoa by the mass spectrometry technician, Mike Burger, using a VG Analytical 70SE dual focusing high resolution mass spectrometer. Initially, the samples of liquid methanol were injected through the heated liquids inlet normally reserved for PFK references. These methanol samples were injected 10 µL at a
time using several shots to flush the inlet each time. The liquid samples from galvanostatic treatment electrochemical cell were injected through the gas chromatography inlet onto a megabore methyl silicone column and then analyzed with the mass spectrometer. The gas samples were attached to the heated liquids inlet using a double ended needle and pulled in by vacuum.

An Armco iron electrode (after investigation by EIS for six months of submersion in methanol) was dried in the glove box, placed in a special holder and connected to the heated liquids inlet of the mass spectrometer via a double ended needle. The holder and the electrode were heated with a heat gun. When the vacuum on the special holder became excessive it was relieved by the injection of 1 ml of argon gas using a tubercular syringe. The inlet used was capable of a vacuum of approximately 20 mbar. Minimum pressure over the electrode reached a pressure on the order of 0.05 atm.

3.4.2 Gas-Solid Chromatography

The Gas-Solid Chromatography (GSC) experiments were run on a 5 ft x 1/8" solid phase Carboxen™-1000 packed column (Supelco, Inc.) using He carrier gas and a Thermal Conductivity Detector (TCD). Either μl quantities of solution were injected using a 10 μl glass micro-syringe or ml quantities of gas were injected using a 10 ml gas-tight
syringe directly onto the column. Peak separation was obtained at a column temperature of 165 °C and a He flow rate of 20 ml/min for both the gaseous and the liquid injections with hydrogen, argon/oxygen/nitrogen, water and finally methanol eluting sequentially at increasing retention times. The respective retention times were determined by injecting "standard" samples.

The "standard" samples were prepared as follows: Working inside the glove box, 10.0 ml of anhydrous methanol (the same methanol as used in the electrochemical experiments) was pipetted into each 40.0 ml borosilicate wide mouth vial and sealed with a silica lined septa. The vial was then removed from the glove box and either bubbled for two minutes with oxygen or hydrogen or 1.0 ml of nanopure water was injected.

Separation of hydrogen, argon/oxygen, carbon monoxide and carbon dioxide was obtained by lowering the column temperature to 65 °C and increasing the He flow rate to 30 ml/min. The retention times for hydrogen, argon/oxygen, carbon monoxide and carbon dioxide were determined by injecting 1 ml of the headspace from "standard" samples prepared with carbon monoxide or carbon dioxide additions to methanol onto the column. The retention times increased sequentially for hydrogen, argon/oxygen, carbon monoxide and carbon dioxide.
3.4.3 Atomic Absorption Spectroscopy

The Atomic Absorption data was acquired on a Perkin Elmer 3100 at a wavelength of 248.3 nm. The calibration was done using dilutions in reagent grade methanol of XUH-3A standard 2500 ppm iron in 10% Nitric acid. The standards were 1 ppm, 2.5 ppm, 5.0 ppm, 10 ppm and 12.5 ppm iron in methanol. The flame was run very lean due to the use of methanol, a fuel, as the solvent. It is interesting to note that, unlike aqueous solutions, a 1 ppm concentration of iron in methanol is already a faint yellow color.

3.4.4 Karl Fischer Titrations

The water content of the methanol has been evaluated using the Karl-Fischer titration method. Premixed, stable Karl-Fischer reagent was purchased from Fluka. The titrations were carried out in the ambient atmosphere, as were the calibrations. The titrations were done using a visual end-point (the solution turns brown).

In experiments performed outside of the glove box, the solution was removed from the sealed cell using a 50 ml glass syringe. A solution sample of 10 or 20 ml was then injected from the syringe into a 50 ml volumetric flask and titrated with the Karl-Fischer reagent to the visual end-point. In
experiments performed inside the glove box, a 20.0 ml sample was pipetted, using a 10.0 ml pipette, into a volumetric flask which was then sealed and removed from the glove box for water determination. The Karl-Fischer reagent was calibrated after each set of determinations by titrating a carefully weighed drop of water or by injection of 0.1 ml of a known mixture of water in methanol. In general, the reagent titrated between 4 and 5 mg of water per ml of reagent. For higher precision work the Karl-Fischer reagent was diluted two fold with Karl Fischer grade methanol; in this case, the reagent titrated between 2 and 3 mg of water per ml.

3.4.5 Preparation of Iron Powder in Methanol Solutions

The iron powder (J.T. Baker, reduced by hydrogen) was used as purchased. The iron powder was brought into the glove box. The samples were then prepared inside the glove box as follows: The 10 g of iron powder was placed inside a 40.0 ml borosilicate wide mouth vial, then 10.0 ml of anhydrous methanol (the same as used in the electrochemical experiments) or 5 mM TBAP methanol solution was pipetted into the vial and the vial was sealed with a silica lined septa. Four additional vials were also prepared as controls with only methanol. For the addition of oxygen or hydrogen, the
vial was removed from the glove box and bubbled for two minutes with either oxygen or hydrogen. For the samples containing water, 1.0 ml of nanopure water was injected using a disposable syringe.
4.1 Electrochemical Impedance Spectroscopy

The EIS spectra for Armco iron electrodes were acquired for several different methanol solution compositions. The corrosion behavior of Armco iron in "pure" methanol will be shown to be quite different from the results obtained when perchlorate salts were added to increase the solution conductivity. The effect of perchlorate salt additions was investigated at three concentrations, 5 mM, 50 mM and 100 mM. The effect of acid addition was studied at in 50 mM phosphoric acid methanol solution.

There are two modes in which the EIS experiments have been performed. One is to take the EIS spectra at fixed applied potentials going from cathodic to anodic biases. This method allows the behavior of the various equivalent circuit model elements to be determined as a function of applied potential. Presumably, the behavior of the elements determines which of the electrochemical processes each corresponds to and can also indicate that the model is incorrect when the elements do not behave as predicted by theory.

The second mode is to take EIS spectra at open circuit as a function of time. This gives information about the
progress of the corrosion process over time. It is possible to carry out the two methods sequentially. First, the EIS spectrum is followed over time and subsequently the spectra are taken as a function of applied potential.

4.1.1 Potential Dependent EIS

4.1.1.1 Armco Iron in 0, 50 and 100 mM Lithium Perchlorate Methanol Solutions

The results presented in this section were acquired using the benchtop protocol discussed in section 3.2.3.1 and the experimental method discussed in section 3.2.5.1. The counter electrode was a glassy carbon rod and the methanol was the anhydrous methanol purchased from Aldrich. When more than one EIS spectra was obtained at a given potential, the fit elements were averaged and it is this average which appears in the figures.

The EIS results for Armco iron in "pure" methanol, 50 mM LiClO₄ methanol solution, and 100 mM LiClO₄ methanol solution will show that the presence of LiClO₄ in the methanol alters not only the solution resistance, but the overall electrode reaction process. The solution composition for the five Armco iron electrochemical cells is shown in table 4.1. The changes in the electrode reaction process will be discussed in terms of the equivalent circuit model in figure 2.11b.
Table 4.1: Solution composition and initial potential for the electrochemical cells whose EIS data are presented in section 4.1.1.1.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Initial open circuit potential</th>
<th>weight percent water</th>
<th>Molarity of the LiClO₄ solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-91 mV</td>
<td>0.23</td>
<td>none added</td>
</tr>
<tr>
<td>II</td>
<td>-47 mV</td>
<td>0.36</td>
<td>none added</td>
</tr>
<tr>
<td>I</td>
<td>-50 mV</td>
<td>0.30</td>
<td>50 mM</td>
</tr>
<tr>
<td>II</td>
<td>-68 mV</td>
<td>0.42</td>
<td>50 mM</td>
</tr>
<tr>
<td>I</td>
<td>-46 mV</td>
<td>0.18</td>
<td>100 mM</td>
</tr>
</tbody>
</table>
As will be seen, each element in the equivalent circuit model was affected by the presence of LiClO$_4$ in the methanol solution.

The first element in the equivalent circuit model, shown in figure 2.11b, represents the solution resistance, $R_s$. As shown in figure 4.1, the solution resistance, as expected, was dramatically reduced by the presence of LiClO$_4$. The reduction in the solution resistance is the reason why LiClO$_4$ is added to so many of organic solutions used in corrosion experiments found in the literature. Some slight variation in the solution resistance for similar solution compositions was observed. These variations were small in comparison to the reduction of the solution resistance by two orders of magnitude due to the addition of LiClO$_4$ and can be attributed to small differences in the solution water content and cell configuration between experimental trials.

The second element in the equivalent circuit model, shown in figure 2.11b, represents the charge transfer resistance, $R_{ct}$. The equivalent circuit modeling values for the charge transfer resistance are shown in figure 4.2. This element should be proportional to the rate of the charge transfer reactions occurring at the electrode solution interface.
Figure 4.1 The values of $R_s$ obtained by fitting the EIS spectra for Armco iron in methanol solution containing 0, 50 or 100 mM LiClO$_4$ with the equivalent circuit, $R_s(R_{ct}Q_{dl})(R_fQ_f)$.
Figure 4.2 The values of $R_{ct}$ obtained by fitting the EIS spectra for Armco iron in methanol solution containing 0, 50 or 100 mM LiClO$_4$ with the equivalent circuit, $R_s (R_{ct} Q_{dl}) (R_f Q_f)$. 

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The data in figure 4.2 was fit to the following function:

$$R_{ct} = R_{ct}(corr) \exp\left(\frac{-1}{b_c} (V_{applied} - V_{oc})\right)$$  \hspace{1cm} (4.1)

where $R_{ct}(corr)$ is the charge transfer resistance at $V_{oc}$ and $b_c$ is the natural log "Tafel" slope which can be converted to a conventional Tafel slope by multiplying it by 2.303. Eqn. 4.1 results from dividing both sides of the natural log form of eqn. 2.11 by the overpotential and neglecting the anodic part. Table 4.2 contains the values obtained from fitting the data in figure 4.2 by eqn. 4.1.

The value of $R_{ct}(corr)$, in the absence of LiClO$_4$, was higher for Electrode II and comparable for Electrode I to the values obtained in the presence of LiClO$_4$. Furthermore, there seemed to be two different values for the cathodic Tafel slope which were independent of the presence of LiClO$_4$ in the solution. The average of the high values and the average for the low values for the cathodic Tafel slopes yield values of 0.288 V/dec and 0.180 V/dec, respectively. This would imply that the rate of the reaction is changing not as a function of LiClO$_4$, but as a function of some other uncontrolled variable quite possibly the concentration of oxygen in the solution. The concentration of water in the
Table 4.2 The results of the fit of the charge transfer resistance data for Armco iron in LiClO₄ methanol solutions, shown in figure 4.4, to the exponential function given in eqn. 4.1 assuming the open circuit potential is -100 mV versus MSCE.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Molarity of the LiClO₄ solution</th>
<th>R&lt;sub&gt;ct&lt;/sub&gt; at Voc = -100 mV (Ω x 10&lt;sup&gt;-4&lt;/sup&gt;)</th>
<th>1/b&lt;sub&gt;c&lt;/sub&gt; (V&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>R factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>none added</td>
<td>8.84</td>
<td>8.34</td>
<td>0.99</td>
</tr>
<tr>
<td>II</td>
<td>none added</td>
<td>58.7</td>
<td>13.4</td>
<td>0.99</td>
</tr>
<tr>
<td>I</td>
<td>50 mM</td>
<td>9.37</td>
<td>13.1</td>
<td>0.94</td>
</tr>
<tr>
<td>II</td>
<td>50 mM</td>
<td>2.46</td>
<td>7.67</td>
<td>1.0</td>
</tr>
<tr>
<td>I</td>
<td>100 mM</td>
<td>9.74</td>
<td>12.2</td>
<td>0.99</td>
</tr>
</tbody>
</table>
solution did not seem to correlate with the value of the cathodic Tafel slope.

By supplementing the data presented in table 4.2 with estimated values of the anodic Tafel slope, the corrosion current density was calculated using eqn. 2.13 and dividing by the nominal surface area (5.0273 cm²) and the corrosion rate was calculated using the standard formula:73

$$\text{Corrosion rate}(\text{mpy}) = \frac{0.13(j_{\text{corr}})(\frac{\text{MW}}{n})}{\rho}, \quad (4.2)$$

where $j_{\text{corr}}$ is the corrosion current density, MW is the molecular weight (MW = 55.85 g/mole), n is the number of electrons transferred (n = 2 electrons per mole, as discussed in section 6.4) and ρ is the density (ρ = 7.99 g/cm³).

The results are presented in table 4.3. The estimated values of the anodic Tafel slope were obtained as follows: 0.120 V/dec is a literature value from anodic polarization data in 100 mM LiClO₄, 0.552 V/dec is for Armco iron in 50 mM H₃PO₄ methanol solution as discussed in section 4.1.1.2 and ∞ V/dec is for the case of a limiting anodic current.

An inspection of the values listed in table 4.3 show that the corrosion current density and corrosion rate were dependent upon not only the solution composition, but varied from sample to sample. Furthermore, these values are
Table 4.3 The calculated corrosion current densities and corrosion rates for Armco iron in 0, 50 and 100 mM LiClO₄ methanol solutions.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Molarity of LiClO₄ solution</th>
<th>for Bₐ = 0.120 V/dec</th>
<th>for Bₐ = 0.552 V/dec</th>
<th>for Bₐ = ∞ V/dec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>jcorr jcorr jcorr</td>
<td>rate rate rate</td>
<td></td>
<td>rate rate rate</td>
</tr>
<tr>
<td></td>
<td>µA/cm² mpy µA/cm² mpy µA/cm² mpy</td>
<td></td>
<td></td>
<td>µA/cm² mpy µA/cm² mpy</td>
</tr>
<tr>
<td>I</td>
<td>0 mM</td>
<td>.0816 .0371</td>
<td>.180 .0816 .270</td>
<td>.122</td>
</tr>
<tr>
<td>II</td>
<td>0 mM</td>
<td>.0104 .00473</td>
<td>.0193 .00877 .0253</td>
<td>.0115</td>
</tr>
<tr>
<td>average for 0 mM</td>
<td>.0460 .0209 .0994 .0452 .148</td>
<td>.0669</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>50 mM</td>
<td>.0656 .0299</td>
<td>.123 .0560 .162</td>
<td>.0738</td>
</tr>
<tr>
<td>II</td>
<td>50 mM</td>
<td>.301 .137</td>
<td>.682 .310 1.06</td>
<td>.478</td>
</tr>
<tr>
<td>average for 50 mM</td>
<td>.183 .0981 .403 .183 .608</td>
<td>.276</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>100 mM</td>
<td>.0651 .0295</td>
<td>.124 .0564 .167</td>
<td>.0756</td>
</tr>
</tbody>
</table>
dependent upon the magnitude of the anodic Tafel slope used in the Stern-Geary equation to calculate the corrosion current. If the low value of the corrosion rate obtained for Armco iron in 0 mM LiClO₄ methanol solution is compared to the low value of the corrosion rate obtained for Armco iron in 50 mM LiClO₄ methanol solution, there is roughly a six-fold increase in the presence of LiClO₄. If the high value of the corrosion rate obtained for Armco iron in 0 mM LiClO₄ methanol solution is compared to the low value of the corrosion rate obtained for Armco iron in 50 mM LiClO₄ methanol solution, there is roughly a four-fold increase in the presence of LiClO₄.

The next equivalent circuit element is the constant phase element used to model the double layer capacitance, Q_{dl}. The fit values for this element of the equivalent circuit are shown in figure 4.3. The magnitude of the constant phase element increased with the addition of LiClO₄ to the methanol. This is as expected, since the increased presence of ions in solution leads to a compaction of the double layer and larger double layer capacitance. The magnitude of the double layer constant phase element was also dependent upon the overpotential and decreased as the potential approached the open circuit potential. This behavior was consistent with classical double layer theory as discussed in section 2.1.2.
Figure 4.3 The values of $Q_{d1}$ obtained by fitting the EIS spectra for Armco iron in methanol solution containing 0, 50 or 100 mM LiClO$_4$ with the equivalent circuit, $R_g (R_{ct} Q_{d1}) (R_f Q_f)$.
The fourth element, the second parallel resistance in the equivalent circuit, corresponds to the resistance of the film, \( R_f \), present on the surface of the electrode. Figure 4.4 indicates that this element is independent of the applied potential over the range studied. The magnitude of the film resistance is reduced by three orders of magnitude by the presence of \( \text{LiClO}_4 \). Since the resistance of a film was shown in section 2.3.1 to be proportional to the resistivity and thickness of the film, there are two simple explanations for this decrease in the film resistance element.

One explanation may be that the presence of \( \text{LiClO}_4 \) in the methanol solution makes the film less resistive. This might occur if the film were porous and the solution occupied the pores. In this case, the lower resistivity solution would make the film appear less resistive. The second explanation may be that the presence of \( \text{LiClO}_4 \) in the methanol decreases the film thickness. This could occur if the presence of the \( \text{LiClO}_4 \) in the solution increased the solubility of the film. It is most likely that there is some combination of these two processes occurring.

Using the resistivity of hematite \( (10^9 \text{ ohm-cm}^{75}) \) to estimate the resistivity of the film material, the thickness of the film can be estimated, in the presence of \( \text{LiClO}_4 \) and in its absence, using eqn. 2.23, the estimated film thicknesses are respectively, 500 Å and 250,000 Å. It should be noted; however that, these estimations do not consider the
Figure 4.4 The values of $R_f$ obtained by fitting the EIS spectra for Armco iron in methanol solution containing 0, 50 or 100 mM LiClO₄ with the equivalent circuit, $R_s (R_{ctQd1})(R_f Q_f)$. 

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possibility of the resistivity of the film changing with the addition of the LiClO₄ to the methanol. These simple calculations indicate that the changes in film resistance were most likely due to a combination of the film becoming thinner and less resistive, since a film could be visibly observed on the Armco iron electrodes which were immersed in methanol containing LiClO₄.

The final element in the equivalent circuit represents the constant phase element, Qₑ, in parallel with the film resistance. This element was found to increase by approximately two orders of magnitude due to the presence of LiClO₄ in the solutions. The values of the film CPE are shown in figure 4.5. From eqn. 2.21, it can be seen that the capacitance of a film is inversely proportional to the thickness of a capacitive film and directly proportional to the dielectric constant of the media. Thus, if the film was porous and the solution acting as the dielectric medium, then the capacitance would be expected to decrease in the presence of LiClO₄. This is because the presence of LiClO₄ in the methanol decreases the bulk solutions static dielectric constant from 30 to about 25. However, the capacitance increase implies that the thickness of the film is reduced by the presence of LiClO₄. This does not exclude the possibility of the resistivity of the film also decreasing though, since the change in the solutions dielectric constant is fairly small.
Figure 4.5 The values of $Q_f$ obtained by fitting the EIS spectra for Armco iron in methanol solution containing 0, 50 or 100 mM LiClO$_4$ with the equivalent circuit, $R_s(R_{ct}Q_{dl})(R_fQ_f)$. 
On the basis of the proceeding discussion, LiClO₄ does seem to affect the electrochemical behavior of Armco iron in methanol. Furthermore, its role the overall corrosion process does not appear to be limited to lowering the solution resistance. One of the most significant findings of this study is that the presence of LiClO₄ has been shown to affect both the thickness and nature of the thin film at the surface and the rate of reaction of the metal. The effect of LiClO₄ on the corrosion of Armco iron in methanol has been assumed to be negligible⁷⁷,⁷⁸.

4.1.1.2 Armco Iron in 50 mM Phosphoric Acid Methanol Solution

The system studied was Armco iron in a 50 mM phosphoric acid methanol solution. The solution consisted of 2.0 ml of 1.76 M H₃PO₄ in methanol added to 68.0 ml of anhydrous methanol (resulting in 50 mM H₃PO₄). The sample was abraded down to 800 grit silicon carbide paper and the electrochemical experiments were performed following the procedures outlined in sections 3.2.3.1 and 3.2.5.1.

The EIS data obtained on the Armco iron electrode in 50 mM phosphoric acid methanol solution has been broken into four parts to simplify the discussion and analysis. Part I is the first set of EIS spectra taken sequentially on days 2
and 3 at applied potentials of -400, -400, -300, -300, -200, -200, -100 and -100 mV vs. MSCE. Part II was taken on day 6 at the same applied voltages as Part I. Part III was taken on day 9 at applied voltages of -400, -400, -350, -350, -300, -250, -200 and -100 mV vs. MSCE. Part IV was taken (after leaving the cell at open circuit for 27 days) on day 36 at applied voltages of -500, -400, -300, -200, -100, 0, 100, 200 and 300 mV vs. MSCE.

The EIS spectra was fit with four equivalent circuits: the series circuit in figure 2.11a, \( R_s(R_{ct}Q_{d1})(R_fQ_f) \), the nested circuit in figure 2.11b, \( R_s(R_{ct}(Q_{d1}(R_fQ_f))) \), and to the these circuits using a capacitor in place of the film CPE, \( R_s(R_{ct}Q_{d1})(R_fC_f) \) and \( R_s(R_{ct}(Q_{d1}(R_fC_f))) \), respectively. Good fits to the EIS spectra are obtained for all four equivalent circuit models. A sample data set and the fit results are shown in figure 4.6 in a Nyquist plot and in figure 4.7 in a Bode plot.

Although there are only small differences in the fits, a careful inspection of the different circuit element's behavior as a function of potential enables an assignment of the most likely model. This is important, since as will be shown below, the values obtained for the equivalent circuit elements are dependent on the equivalent circuit used to fit the data.

First, fits of the four equivalent circuits to the EIS data were carefully analyzed to establish the ability of the
Figure 4.6 A Nyquist plot of a sample EIS spectra for Armco iron in 50 mM $\text{H}_3\text{PO}_4$ methanol solution and the fit results to nested and series equivalent circuits.
Figure 4.7 A Bode plot of a sample EIS spectra for Armco iron in 50 mM H₃PO₄ methanol solution and the fit results to nested and series equivalent circuits.
various circuits to model the data. Only the Part I data set will be shown here; however, all four sets were fit with the four equivalent circuits and analysis of Parts II, III and IV gave similar results to the analysis of Part I. After the best equivalent circuit had been established, the behavior of the system was analyzed as a function of time and polarization for the four data sets and compared to the results obtained in "pure" methanol.

A comparison of the values obtained for the solution resistance for Part I of the EIS data as fit with the four equivalent circuits is shown in figure 4.8. The values obtained for the solution resistance are fairly independent of the equivalent circuit used to model the data. This is as expected, since the solution resistance is additive to the rest of the circuit in all four cases. The apparent decrease in the solution resistance values with increasing potential was less than 5%, about 20 to 30 ohms. This was attributed to the dissolution of the electrode over the course of the experiments.

Unlike the solution resistance, the values for the charge transfer resistance, $R_{ct}$, shown in figure 4.9, were strongly dependent upon whether a nested or a series type of equivalent circuit was used to model the spectra. The values for $R_{ct}$ obtained from fits with the nested circuits were 40 to 50% larger than those obtained from fits to the series circuits. Because the overall corrosion rate is proportional
Figure 4.8 The values of $R_s$ obtained by fitting the EIS spectra obtained for Armco iron in 50 mM $H_3PO_4$ methanol solution with four different equivalent circuits.
Figure 4.9 The values of $R_{ct}$ obtained by fitting the EIS spectra obtained for Armco iron in 50 mM $H_3PO_4$ methanol solution with four different equivalent circuits.
to the charge transfer resistance, the data shown in figure 4.9 shows how important it is to establish which equivalent circuit model best describes the system so that an accurate rate of corrosion can be calculated.

The values of the double layer CPE, $Q_{dl}$, are shown in figure 4.10. Electrochemical double layer theory, as briefly discussed in Section 2.1.2, predicts that the double layer CPE should be dependent on the applied potential. The values of $Q_{dl}$ extracted with the series model showed a strong dependence upon potential; whereas, the values obtained from fits with the nested equivalent circuits were almost flat with potential. The fact that the values obtained using the series model better fit the theoretically predicted behavior suggests, that for this system, the series equivalent circuit is a better model of the electrochemistry than the nested one.

The values for the frequency exponent of the double layer CPE, shown in figure 4.11, were also dependent upon the choice of equivalent circuits and upon the applied potential. The meaning of the CPE exponent is not clear and there is at the present time no accepted theoretical explanation for its behavior.

Figure 4.12 contains the values for the film resistance, $R_f$, when the different equivalent circuits were fit to the spectra. When the data was fit by the nested circuit, the thin film resistance increased linearly with increasing
Figure 4.10 The values of $Q_{dl}$ obtained by fitting the EIS spectra obtained for Armco iron in 50 mM $H_3PO_4$ methanol solution with four different equivalent circuits.
Figure 4.11 The values of $n_{dl}$ obtained by fitting the EIS spectra obtained for Armco iron in 50 mM $\text{H}_3\text{PO}_4$ methanol solution with four different equivalent circuits.
Figure 4.12 The values of $R_f$ obtained by fitting the EIS spectra obtained for Armco iron in 50 mM $H_3PO_4$ methanol solution with four different equivalent circuits.
anodic potential; in contrast, the film resistance was constant when the series circuit was used to fit the spectra.

In parallel with the film resistance is the film capacitance or CPE. The values obtained for this element are presented in figure 4.13. These values were fairly constant as a function of potential (except for scatter, when a capacitor was used in place of the film CPE) and were not very sensitive to the configuration of the equivalent circuit. Theoretically, if the resistance of the film increases, then the capacitance would be expected to decrease. Thus, the values of \( R_f \) and \( Q_f/C_f \) obtained from fitting the nested circuits to the spectra do not agree with the theoretically predicted behavior.

The result presented in figures 4.7 thru 4.13 show that for the electrochemical system, Armco iron in 50 mM \( \text{H}_3\text{PO}_4 \) methanol solutions, fits using the series equivalent circuit shown in figure 2.11a, gave values for the various circuit elements which best match the behavior predicted by theory. On the other hand, the values obtained for \( R_f \), \( Q_f \) and \( Q_{dl} \), with fits using the nested equivalent circuit, shown in figure 2.11b, do not behave as a function of potential as predicted by theory. Thus, the series equivalent circuit may be the best model. It is also evident that the values obtained for the fits to the data were essentially unaffected by the use of a capacitor in place of the film CPE.
Figure 4.13 The values of $Q_f$ or $C_f$ obtained by fitting the EIS spectra obtained for Armco iron in 50 mM H$_3$PO$_4$ methanol solution with four different equivalent circuits.
Now that the best form of the equivalent circuit has been established as being the series circuit given in figure 2.11a, variations in the values obtained by fitting Parts I to IV of the EIS spectra taken as a function of potential for Armco iron in 50 mM H₃PO₄ methanol solution may be evaluated.

The values obtained for the solution resistance were fairly stable over the time of any one Part, as shown in figure 4.14, but decreased substantially over the course of the experiments from an initial high of 11,175 Ω in Part I to 800 Ω in Part IV. The overall decrease in solution resistance was not surprising, given that the metal was dissolving into the solution thus increasing the ionic strength of the solution.

The values for \( R_{ct} \) are shown in figure 4.15. The data shown was for polarization in the anodic direction where a decrease in \( R_{ct} \) indicates an increase in the rate of dissolution. The data in figure 4.15 was fit by the following function, assuming an open circuit potential of -400 mV:

\[
R_{ct} = R_{ct}(corr) \exp \left( \frac{1}{b_a} (V_{applied} - V_{oc}) \right) \tag{4.3}
\]

where \( R_{ct}(corr) \) is the charge transfer resistance at \( V_{oc} \) and \( b_a \) is the natural log "Tafel" slope which can be converted to a conventional Tafel slope by multiplying it by 2.303.
Figure 4.14  The values of $R_s$ obtained by fitting the EIS spectra for Armco iron in 50 mM $\text{H}_3\text{PO}_4$ methanol solution, Parts I-IV, with the equivalent circuit, $R_s(R_{ct}Q_{dl})(R_fQ_f)$. 

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Figure 4.15 The values of $R_{ct}$ obtained by fitting the EIS spectra for Armco iron in 50 mM $H_3PO_4$ methanol solution, Parts I-IV, with the equivalent circuit, $R_s(R_{ct}Q_{dl})(R_fQ_f)$. 

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Eqn. 4.3 was derived in a similar manner to eqn. 4.1 and is
the anodic branch of the natural logarithm form of the Tafel
equation expressed in terms of resistance. Table 4.4
contains the values obtained from fitting the data in figure
4.15 by eqn. 4.3. The value of the anodic Tafel slope
decreased from a value of 0.672 V/dec (Part I) to a value of
0.465 V/dec (Part IV). The cause of this decrease is not
currently understood.

By supplementing the data presented in table 4.4 with a
value for the cathodic Tafel slope of 0.200 V/dec from the
literature, the corrosion current density was calculated
using eqn. 2.13 and dividing by the nominal surface area
(5.0273 cm²) and the corrosion rate was calculated using eqn.
4.2 and similar parameter to those used in section 4.1.1.1.
The results are presented in table 4.5 and the average
corrosion rate for Armco iron in 50 mM methanol solution was
found to be 0.294 mpy.

The next element to consider is the double layer CPE.
As discussed in section 2.1.2, the double layer behavior is
expected to be potential dependent. Values of \( Q_{dl} \) are shown
in figure 4.16. The interday variability of the values of \( Q_{dl} \)
was small and the values of \( Q_{dl} \) for all four data sets showed
similar potential dependence. The values for the frequency
exponent of the double layer CPE are shown in figure 4.17.
These values were potential dependent and were of similar
size for all four data sets.
Table 4.4 The results of the fit by eqn. 4.3 of the charge transfer resistance data, shown in figure 4.15, for Armco iron in 50 mM H₃PO₄ methanol solution. Only the data in the linear region between -400 and -100 mV and an open circuit potential of -400 mV versus MSCE was assumed.

<table>
<thead>
<tr>
<th>Part</th>
<th>$R_{ct}$ at $V_{oc}=-400$ mV ($\Omega \times 10^{-4}$)</th>
<th>$1/b_a$ (V⁻¹)</th>
<th>$R$ factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.86</td>
<td>3.42</td>
<td>0.95</td>
</tr>
<tr>
<td>II</td>
<td>2.01</td>
<td>4.17</td>
<td>0.98</td>
</tr>
<tr>
<td>III</td>
<td>1.71</td>
<td>4.44</td>
<td>0.98</td>
</tr>
<tr>
<td>IV</td>
<td>2.37</td>
<td>4.95</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Table 4.5 The calculated corrosion current densities and corrosion rates for Armco iron in 50 mM H₃PO₄ methanol solution.

<table>
<thead>
<tr>
<th>Part</th>
<th>for $E_e = 0.200 \text{ V/dec}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$j_{corr}$ (μA/cm²)</td>
</tr>
<tr>
<td>I</td>
<td>.716</td>
</tr>
<tr>
<td>II</td>
<td>.630</td>
</tr>
<tr>
<td>III</td>
<td>.729</td>
</tr>
<tr>
<td>IV</td>
<td>.510</td>
</tr>
<tr>
<td>average</td>
<td>.647</td>
</tr>
</tbody>
</table>
Figure 4.16 The values of $Q_{dl}$ obtained by fitting the EIS spectra for Armco iron in 50 mM $H_3PO_4$ methanol solution, Parts I-IV, with the equivalent circuit, $R_s(R_{ct}Q_{dl})(R_fQ_f)$.
Figure 4.17 The values of frequency exponent for $Q_{dl}$ obtained by fitting the EIS spectra for Armco iron in 50 mM $H_3PO_4$ methanol solution, Parts I-IV, with the equivalent circuit, $R_s(R_{ct}Q_{dl})(R_fQ_f)$.
The next elements in the equivalent circuit model arise from the presence of a film at the surface. The values for the film resistance element are shown in figure 4.18. The film resistance is stable as a function of potential, but decreased substantially over the course of the experiments from a high of ~6500 $\Omega$ (Part I) to a low of ~3200 $\Omega$ (Part IV). The values of the film CPE are shown in figure 4.19. There is substantial scatter in the values for Part I and Part II. The film CPE also decrease with time from a high of ~1 $\mu$F (Part I) to a low of ~50 nF (Part IV). This is most likely due to changes in the film composition over the course of the experiments, since changes in film thickness (from film dissolution) would cause the film CPE to increase.

Finally, to illustrate the dramatic effect the addition of phosphoric acid has on the corrosion behavior of iron, a comparison of the values obtained, shown in figure 4.20, for the charge transfer resistance in the absence of supporting electrolyte (section 4.1.1.1) and in 50 mM phosphoric acid methanol solution (Part I) has been made. The acid shifts the open circuit potential by almost 300 mV in the negative direction and the charge transfer resistance at the respective open circuit potential are two orders of magnitude different. This suggest that at 50 mM concentrations of phosphoric acid, the corrosion rate might be increased by as much as a factor of 100.
Figure 4.18 The values of $R_f$ obtained by fitting the EIS spectra for Armco iron in 50 mM H$_3$PO$_4$ methanol solution, Parts I-IV, with the equivalent circuit, $R_s(R_{ct}Q_{dl})(R_fQ_f)$. 

- Part I (day 2 and 3)
- Part II (day 6)
- Part III (day 9)
- Part IV (day 26 and 27)
Figure 4.19 The values of $Q_f$ obtained by fitting the EIS spectra for Armco iron in 50 mM $\text{H}_3\text{PO}_4$ methanol solution, Parts I-IV, with the equivalent circuit, $R_s(R_{ct}Q_{dl})(R_fQ_f)$. 

- Part I (day 2 and 3)
- Part II (day 6)
- Part III (day 9)
- Part IV (day 26 and 27)
Figure 4.20 A comparison of the values for the charge transfer resistance in the absence of supporting electrolyte (section 4.1.1.1) and in 50 mM phosphoric acid methanol solution (Part I).
4.1.2 EIS Results for Armco Iron Exposed to 0 and 5 mM TBAP Methanol Solutions

EIS spectra at open circuit potential were acquired periodically for two or more weeks for five different Armco iron electrodes in methanol solutions, with tetrabutyl ammonium perchlorate (TBAP) added or with no additions, as outlined in section 3.2.5.2. All five electrodes were polished down to 0.050 μm Alumina as outlined in section 3.2.2. The solution compositions for each electrochemical cell is given in table 4.6. The spectra were fit with the series equivalent circuit shown in figure 2.11a.

The open circuit potential, shown in figure 4.21, decreases after the initial addition of the methanol solution to the cell, becoming fairly stable after about 3 days. The potential behavior appears to be sample dependent rather than solution dependent for these samples, since the open circuit potentials were substantially different for electrodes in identical solutions. In contrast, the values of the equivalent circuit modeling elements were dependent upon the solution composition.

The values of the solution resistance, shown in figure 4.22, was very stable in the cases where TBAP was added. The slight variation in the values for the two electrodes may be attributed to differences in the electrochemical cell.
Table 4.6 Solution composition and initial potential for the electrochemical cells whose EIS data are presented in section 4.1.2.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Initial open circuit potential</th>
<th>weight percent water</th>
<th>Molarity of the TBAP in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>174 mV</td>
<td>0.06</td>
<td>none added</td>
</tr>
<tr>
<td>II</td>
<td>-51 mV</td>
<td>0.08</td>
<td>none added</td>
</tr>
<tr>
<td>III</td>
<td>-51 mV</td>
<td>0.13</td>
<td>none added</td>
</tr>
<tr>
<td>I</td>
<td>-230 mV</td>
<td>0.07</td>
<td>5 mM</td>
</tr>
<tr>
<td>II</td>
<td>-158 mV</td>
<td>0.09</td>
<td>5 mM</td>
</tr>
</tbody>
</table>
Figure 4.21 Values of the open circuit potential measured over a two week period for five different Armco iron electrodes in 0 or 5 mM TBAP.
Figure 4.22 Values of the solution resistance measured over a two week period for five different Armco iron electrodes in 0 or 5 mM TBAP.
configuration. The effects of the small amounts of corrosion products that dissolve into the solution are hidden by the TBAP. For the cells with no electrolyte addition, the solution resistance began at a high value (~10,000 Ω) and decreased by an order of magnitude over the two week period to a low value of ~1000 Ω due to the ever increasing concentrations of ionic corrosion products in the solution.

The values of the charge transfer resistance, shown in 4.23, initially increased and then converged at about 20 kΩ for samples in the 5 mM TBAP solutions and at about 100 kohms for samples in pure methanol. These results suggest that previous work done on the corrosion of Armco iron in methanol, where perchlorate supporting electrolytes were used, may overestimate the corrosion rate by approximately one order of magnitude.

The values for the double layer CPE are presented in figure 4.24. As expected, the magnitude of the CPE increased with the addition of TBAP. This is due no doubt to the compaction of the double layer in the presence of the electrolyte ions in the solution as discussed in section 2.1.2. There is one case (II-no electrolyte added) in the absence of TBAP where the double layer CPE was of the same size as in the TBAP containing solutions; however, this value decreased on day 6 and dropped below the values obtained for the TBAP containing solutions.
Figure 4.23 Values of the charge transfer resistance measured over a two week period for five different Armco iron electrodes in 0 or 5 mM TBAP.
Figure 4.24 Values of the double layer CPE measured over a two week period for five different Armco iron electrodes in 0 or 5 mM TBAP.
The values of the surface film resistance are shown in figure 4.25. The samples in pure methanol solutions had film resistances which were quite scattered from a low value of 400 Ω to a high value of 800 kΩ with an average value of around 1 kΩ. Electrodes in the 5 mM TBAP solution had surface film resistances which were much less scattered and decreased slowly over the two week period from a high of 200 Ω to a low of 90 Ω.

The values of the film CPE are shown in figure 4.26. The values of the film CPE for the samples in methanol containing TBAP was more stable and larger than those obtained in the absence of TBAP. However, this element exhibited a large amount of scatter, making it difficult to analyze possible changes in the film CPE effected by the presence of TBAP.

The exponent of the frequency of the film CPE was unity in the TBAP solutions, but ranged between 0.85 and 1.0 in pure methanol. This could be due to the quality of the data obtained in the different solutions or could reflect a difference in the chemistry of surface film that develops in the different solutions.
Figure 4.25 Values of the film resistance measured over a two week period for five different Armco iron electrodes in 0 or 5 mM TBAP.
Figure 4.26 Values of the film CPE measured over a two week period for five different Armco iron electrodes in 0 or 5 mM TBAP.
4.2 Galvanostatic Treatment

To increase the concentration of corrosion products in the solution and on the surface of the Armco iron electrodes, Armco iron electrodes were galvanostatic treated in methanol solutions. The equipment is described in detail in section 3.2.6 and the treatment current, total charge and type of chemical analysis carried out on the resultant solutions is presented for each galvanostatic electrochemical cell in table 4.7. Table 4.8 presents specific information on each galvanostatically treated Armco iron electrode. Included in the table 4.8 is the reference name of the electrode, whether it was the working or the counter electrode in the galvanostatic cell, what it looked like at the end of the treatment, the type(s) of surface analysis performed on it and the film resistance, if measured.

An inspection of table 4.8, shows that several of the galvanostatically treated Armco iron anodes, Anode III, Anode IV and Anode IV, developed very resistive yellow surface films as a result of being galvanostatically treated. The highly resistive anodes developed very smooth surface films as shown by the SEM images in figures 5.7 and 5.12. These surface films were composed of iron, carbon and oxygen and represent a new type of passivating film never before reported.
When EIS spectra were taken on the Cathodic electrodes after galvanostatic treatment, they gave very unusual spectra that could not be fit by the usual equivalent circuits, such as those in figures 2.11 and 2.12. The reason why such unusual EIS spectra were obtained for the Cathodic electrodes is not clear and an attempt to validate the data by testing it with the Kramers-Kronig transformation was unsuccessful. The Kramers-Kronig transform of the data indicated that it did not properly transform and was not valid data. These unusual spectra were, however, reproducible and were observed for more than one cathode.
Table 4.7 The treatment current, total charge passed and whether chemical analysis was carried out on the solution for the electrochemical cells used in the galvanostatic treatment.

<table>
<thead>
<tr>
<th>Electrochemical cell</th>
<th>Treatment current (µA)</th>
<th>Total charge passed (C)</th>
<th>Chemical analysis of solution?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galv I</td>
<td>10**</td>
<td>23.01</td>
<td>GC/MS</td>
</tr>
<tr>
<td>Galv II</td>
<td>10</td>
<td>5.758</td>
<td>no</td>
</tr>
<tr>
<td>Galv III</td>
<td>-10</td>
<td>12.096</td>
<td>no</td>
</tr>
<tr>
<td>Galv IIIb</td>
<td>10</td>
<td>1.834</td>
<td>no</td>
</tr>
<tr>
<td>Galv IV</td>
<td>-10</td>
<td>5.496</td>
<td>no</td>
</tr>
<tr>
<td>Galv IVb</td>
<td>-10</td>
<td>9.916</td>
<td>no</td>
</tr>
<tr>
<td>Galv V</td>
<td>-10</td>
<td>6.180</td>
<td>AAS</td>
</tr>
<tr>
<td>Galv VI</td>
<td>-10</td>
<td>10.31</td>
<td>AAS &amp; GC</td>
</tr>
<tr>
<td>Galv VII</td>
<td>20</td>
<td>13.90</td>
<td>AAS</td>
</tr>
<tr>
<td>Galv VIII*</td>
<td>-20</td>
<td>8.112</td>
<td>no</td>
</tr>
</tbody>
</table>

*This electrochemical cell was purged with oxygen gas and not run inside the glove box.

**Galv I was initially treated at a current of 1 µA for three weeks.
Table 4.8 Information on the galvanostatically treated Armco iron electrodes. The specifics of the galvanostatic treatment are given in table 4.7.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Working or counter</th>
<th>Visible inspection of surface</th>
<th>Surface analysis performed</th>
<th>Electrode film resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode I</td>
<td>counter</td>
<td>small spots</td>
<td>XES</td>
<td>100 kΩ</td>
</tr>
<tr>
<td>Cathode I</td>
<td>working</td>
<td>dark brown</td>
<td>XES</td>
<td>10 kΩ</td>
</tr>
<tr>
<td>Anode II</td>
<td>counter</td>
<td>yellow film</td>
<td>SEM w/EDS XES</td>
<td>15 kΩ</td>
</tr>
<tr>
<td>Cathode II</td>
<td>working</td>
<td>gray film</td>
<td>SEM w/EDS XES Raman</td>
<td>not determined</td>
</tr>
<tr>
<td>Anode III</td>
<td>working</td>
<td>yellow film</td>
<td>SEM w/EDS</td>
<td>70 MΩ</td>
</tr>
<tr>
<td>Cathode III</td>
<td>counter</td>
<td>dark spots</td>
<td>SEM w/EDS</td>
<td>not determined</td>
</tr>
<tr>
<td>Cathode IIIb</td>
<td>working</td>
<td>black coating</td>
<td>SEM w/EDS</td>
<td>not determined</td>
</tr>
<tr>
<td>Anode IV</td>
<td>working</td>
<td>yellow/blue film</td>
<td>SEM</td>
<td>300 kΩ</td>
</tr>
<tr>
<td>Cathode IV*</td>
<td>counter</td>
<td>black coating</td>
<td>SEM</td>
<td>10 kΩ</td>
</tr>
<tr>
<td>Anode IVb</td>
<td>working</td>
<td>yellow/blue film w/pits</td>
<td>SEM XPS</td>
<td>not determined</td>
</tr>
<tr>
<td>Anode V</td>
<td>working</td>
<td>darker</td>
<td>none</td>
<td>not determined</td>
</tr>
<tr>
<td>Cathode V</td>
<td>counter</td>
<td>none</td>
<td>none</td>
<td>not determined</td>
</tr>
<tr>
<td>Anode VI</td>
<td>working</td>
<td>yellow/blue film</td>
<td>Raman</td>
<td>3 MΩ</td>
</tr>
<tr>
<td>Cathode VI</td>
<td>counter</td>
<td>black coating</td>
<td>none</td>
<td>70 kΩ</td>
</tr>
<tr>
<td>Anode VII</td>
<td>counter</td>
<td>yellow film</td>
<td>Raman FTIR</td>
<td>100 kΩ</td>
</tr>
<tr>
<td>Cathode VII</td>
<td>working</td>
<td>dark coating</td>
<td>FTIR</td>
<td>not determined</td>
</tr>
<tr>
<td>Anode VIII</td>
<td>working</td>
<td>yellow blue</td>
<td>none</td>
<td>150 Ω</td>
</tr>
</tbody>
</table>

*used in both Galv IV and Galv IVb—total charge = 14.916C
CHAPTER 5: FILM ANALYSIS RESULTS AND DISCUSSION

5.1 Introduction

When Armco iron electrodes were galvanostatically treated in methanol at current densities of 2 μA/cm² to 4 μA/cm² as discussed in section 4.2, the electrodes developed relatively thick surface films. The anode developed a yellow film which in some cases became highly resistive and the cathode developed a dark coating or dark deposits on its surface. To elucidate the reactions which produced these thick surface films, their composition and morphology was studied, as discussed below, using several different techniques.

5.2 X-Ray Emission Spectroscopy

Amongst many other studies, X-ray Emission Spectroscopy (XES) has been used by Andermann's group to investigate the ambient corrosion of Cu, Ni, and Fe⁸⁰,⁸¹. This technique is well suited for investigating the chemical composition and bonding of the near surface region of metal surfaces. It is more compatible with electrochemical measurements, because, unlike most surface science and thin film techniques, it does
not require ultra-high vacuum and it also probes, non-consumptively, more than the first 25 to 50 Å of the surface.

5.2.1 Carbon Kα emission spectra for
Galvanostatically treated Armco Iron electrodes

The XES instrument, described in section 2.3.4, used in these studies is a high resolution instrument and the peaks in figure 5.1 shows some of the structure of the carbon K emission data (valence electrons filling the 1s carbon core hole) acquired using copper Lα photon excitation on two galvanostatically treated one inch disk Armco iron electrodes, Anode I and Cathode I. Instrumental difficulties precluded the acquisition of even higher resolution XES spectra. As discussed in detail in section 4.2, the Anode I and Cathode I were created by passing a 10 μA current between the two Armco iron electrodes while they were submerged in anhydrous methanol. An Armco iron electrode (freshly polished and sonicated in methanol) gave 5 counts/minute at 277 eV. This then was considered the background signal. The spectra revealed that both surfaces contained significant amounts of carbon on them and that the valence levels of the carbon in the anode might have differed from those in the cathode.
Figure 5.1 Carbon K emission XES data for galvanostatically treated Armco iron samples (Anode I and Cathode I). The total charge passed between the electrodes was 4.95 C and the methanol solution was yellow at the end of the treatment. A clean Armco iron sample gave a carbon signal of 5 counts/minute at 277 eV. The cathode exhibited a dark black coating and the anode exhibited a yellow film.
The lines shown in figure 5.1 correspond to Gaussian peaks being fit to the data. The results of the Gaussian peak fits to the two emission spectra are presented in table 5.1. Both spectra seemed to deconvolute into two peaks. Although the visual inspection of the emission spectra of the anode showed the presence of a possible third peak centered about 271 eV, attempts to include a third peak in the fit were not successful.

5.2.2 Depth profile of the chemical modification of Armco iron electrodes

The fact that some type of chemical modification of the surface had occurred was supported by x-ray emission results. The degree of chemical modification has been shown to be proportional to the Fe Lβ/Lα intensity ratio, with a higher ratio indicating chemical modification\textsuperscript{15}. Furthermore, by varying the energy of the incoming electron beam, the depth of penetration may be changed; so that, the chemical modification as a function of depth can be measured.

The intensity of the Fe Lβ and Fe Lα x-ray emission peaks were measured at the peak maxima for four Armco iron samples abraded down to 800 grit silicon carbide sandpaper and subsequently subjected to different treatments. The "methanol exposed sample" was submerged in methanol for one month. The "ambient sample" was kept in a desiccator for one month.
Table 5.1 Gaussian fit parameters for the carbon Kα X-ray emission spectra shown in figure 5.1.

<table>
<thead>
<tr>
<th>parameter</th>
<th>Armco iron anode</th>
<th>Armco iron cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>base line</td>
<td>4.59 counts/min</td>
<td>3.96 counts/min</td>
</tr>
<tr>
<td>peak height</td>
<td>4.33 counts/min</td>
<td>32.68 counts/min</td>
</tr>
<tr>
<td>peak position</td>
<td>274.98 eV</td>
<td>276.74 eV</td>
</tr>
<tr>
<td>base line</td>
<td>0.68 counts/min</td>
<td>2.89 counts/min</td>
</tr>
<tr>
<td>peak height</td>
<td>23.85 counts/min</td>
<td>9.69 counts/min</td>
</tr>
<tr>
<td>peak position</td>
<td>277.45 eV</td>
<td>280.79 eV</td>
</tr>
<tr>
<td>base line</td>
<td>3.35 counts/min</td>
<td>1.97 counts/min</td>
</tr>
<tr>
<td>R factor</td>
<td>0.991</td>
<td>0.994</td>
</tr>
</tbody>
</table>
month. The "corroded sample" was anodically biased (up to 2 V versus the MSCE) in methanol for several days and developed a gray surface film. The "cathodic sample" was biased cathodically (down to -1 V versus the MSCE) in methanol.

The X-ray emission results in figure 5.2 are shown without error bars for simplicity; however, the error when using 1.0 and 1.5 kV kinetic energy excitation electrons was quite large (3 to 10 %) due to poor counting statistics. The apparent differences in the ratios at 1.0 kV and 1.5 kV were not statistically significant. The error (< 1%) was much smaller for 2.5 kV kinetic energy excitation electrons and the difference between the corroded sample and the other three samples was significant.

The Fe L\sb{\beta}/L\sb{\alpha} ratios, shown in figure 5.2, indicated that both the "methanol exposed sample" and the "ambient sample" had the same level of oxidation near the surface. Also, evident for the samples other than the "corroded sample" in figure 5.2 was the decreasing modification with depth. The "corroded sample" showed a higher Fe L\sb{\beta}/L\sb{\alpha} ratio than the other samples particularly at the depth penetrated to by the 2.5 kV electrons.

Since the exact density and chemical composition of the deposits on the surface of the Armco iron electrodes was not known, the penetration depth of the electron beam could not be accurately calculated. Based upon prior XES experiments
Figure 5.2 XES $L_\beta/L_\alpha$ intensity ratios for four differently treated Armco iron samples. All sample were abraded to 800 grit Si/C abrasive paper. The "ambient sample" was stored in a desiccator for one month. The "methanol exposed sample" was submerged in methanol at open circuit for one month. The "corroded sample" was subjected to anodic polarization and the "reduced sample" was subjected to cathodic polarization.
The penetration depths were estimated to be, for the 1.0, 1.5 and 2.5 kV electrons, 100, 150 and 400 Å, respectively.

5.3 Scanning Electron Microscopy

The reaction rates of the corrosion process are believed to be perturbed by the presence of grain boundaries and defect sites in the surface. Corrosion occurring at specific sites on the surface can lead to pitting of the surface rather than a general corrosive attack. The chemistry of pits has been shown to vary substantially from the bulk solution often becoming quite acidic due to the oxidation products being constrained by the pit.

If pitting occurs, the results obtained from EIS experiments must be interpreted carefully, since the measured impedance averages the behavior of the entire surface. If the dissolution reaction is several orders of magnitude faster in pits which occupy only a small fraction of the surface, the calculated rates of reaction will be erroneous. To better characterize the mechanism of attack, a scanning electron microscope (SEM) was used to inspect the surfaces after the corrosion experiments.

SEM can also be used in conjunction with elemental detection systems (EDS) and the chemical composition of electrode surface can be semi-quantitatively measured. This
was done for several galvanostatically treated Armco iron electrodes. Using the SEM in conjunction with EDS, it was possible to view different regions of the electrode surface and determine the local chemical composition semi-quantitatively.

### 5.3.1 SEM with EDS of Galvanostatically Treated Armco Iron Electrodes

Besides changes in the solution after passing a current of 10 μA between two Armco iron samples immersed in methanol for one to three weeks, the surfaces of the electrodes changed. The anode remained highly reflective, but turned a salmon pink to bright yellow color due to the deposition of solid reaction products at the surface. In two cases, this film became highly resistive, so resistive that the potentiostat (that can apply a one hundred volt potential) could not pass a 10 μA current between the two electrodes. The cathode became opaque and developed dark gray to black deposits on the surface, but did not become highly resistive. The composition of these surface films and deposits is an important clue to how corrosion occurs at an iron surface. Thus, attempts were made to characterize these films and deposits.

The exact galvanostatic treatment each of the electrodes, discussed in sections 5.3.2 and 5.3.3, received...
is in section 4.3. When low precision EDS was used to evaluate the elemental composition of various surface regions, the semi-quantitative results are shown in parentheses after the element. Higher precision EDS was done to better quantify the relative amounts of iron, carbon and oxygen. The X-ray emission spectra were measured until the carbon counts exceeded 200 counts. The x-ray emission peaks were then fit with Gaussian functions and the counts per second determined. The counts per second determined at higher total counts gave a better estimate of the relative amounts of iron, carbon and oxygen present in the area of interest.

5.3.1.1 Untreated Armco Iron Electrode

Figure 5.3 shows an SEM image of the surface of an Armco iron electrode that was polished and then submerged in methanol for three days. Arrow A indicates an inclusion in the surface that was composed of iron (~54%), chromium (~1%), manganese (~21%), oxygen (~23%) and carbon (<1%). The presence of this spot on the untreated electrode indicates that the presence of these inclusions on the cathode and anode surfaces, to be discussed in the next two sections, was not due to the electrochemical treatment. Arrow D is pointing at what appears to be a grain boundary.
Figure 5.3  A SEM image of the surface of an untreated Armco iron electrode. The arrows indicate the various regions of interest. Arrow A indicates an inclusion. Arrow B indicates a grain boundary and arrow C indicates the general surface. Arrow C indicates the clean surface that contained primarily iron (~102%) and a small amount of carbon (~2%).
5.3.1.2 Galvanostatically Treated Armco Iron Cathodes

An SEM image of the surface of a galvanostatically treated Armco iron cathode (Cathode III) is shown in figure 5.4. Visual inspection of the surface revealed small dark spots distributed on the electrode surface. The deposit indicated by arrow A in figure 5.4 consists of primarily iron (~47%), oxygen (~38%) and carbon (~12%), with small amounts of sulfur (~2%) and chlorine (<1%). Arrow B indicates an inclusion in the surface that contains mostly iron (~54%), chromium (~1%), manganese (~19%), oxygen (~23%) and carbon (~2%). This feature was seen in all the electrode surfaces studied and, as was shown in section 5.3.1.1, was present in the untreated surface. Arrow C indicates what will be called the off deposit region and this area contained primarily iron (~99%) with small amounts of carbon (<1%) and oxygen (<1%). Arrow D indicates the edge of the cathodic deposit and this area contained primarily iron (~97%) with small amounts of carbon (~3%).

Unlike Cathode III, most of the galvanostatically treated cathode samples developed a dark poorly adhered film over most of the surface. An SEM image of Cathode IIIb, which developed a thin coating of this type of film, is shown
Figure 5.4 A SEM image of the surface of a galvanostatically treated Armco iron electrode (Cathode III). The arrows indicate the various regions of interest. Arrow A (on deposit) indicates a cathodic deposit. Arrow B indicates an inclusion. Arrow C (off deposit) indicates the general surface away from the deposit region and arrow D indicates the edge of the deposit region.
in figure 5.5. There are small fairly uniform in size crystals evident in the image one of which is pointed to by arrow A. These crystals are roughly 10-20 μm in diameter and composed primarily of iron (~50%), oxygen (~27%) and carbon (~10%), with small amounts of sulfur (~4%), chlorine (~4%), zinc (~2%) and copper (~1%). They appear strikingly similar in shape to some of the crystals of haematite synthesized by Reeves and Mann\textsuperscript{83}. Arrow B indicates an off deposit region which was primarily iron (~90%) and carbon (~6%), with small amounts of sulfur (~2%), zinc (~1%) and copper (~1%).

The higher precision EDS data in figure 5.6 presents a slightly different picture of the cathodic surfaces, than the semi-quantitative results obtained at lower counts. Using the ratio of the counts per second to approximate the relative amount of an element in the scan area, the composition of the two cathodic deposits can be estimated. The ratio of iron to oxygen to carbon for Cathode III on deposit is roughly 3:9:1 and off deposit is roughly 58:2:1. The ratio of iron to oxygen to carbon for Cathode IIIb on crystal is roughly 9:38:1 and off deposit is roughly 24:3:2.

Both the semi-quantitative results and the higher precision analysis of x-ray emissions at longer count times showed the cathodic deposits to be composed primarily of iron, oxygen and carbon. The large amounts of oxygen in the deposits and the lack of an equal amount of carbon imply that
Figure 5.5 A SEM image of the surface of a galvanostatically treated Armco iron electrode (Cathode IIIb). Cathode IIIb was covered lightly with a dark gray film and the arrows indicate the various regions of interest. Arrow A (on crystal) indicates a cathodically deposited crystal and arrow B (off crystal) indicates the general surface away from the cathodically deposited crystals.
Figure 5.6 A bar graph of the x-ray emission counts per second for Cathode III and Cathode IIIb for different regions of interest as shown in figures 5.4 and 5.5.
a source of oxygen other than the methanol solvent is contributing to these cathodic deposits. The two most likely candidates are dissolved oxygen and water both of which can react with iron ions in the solution to give a dark brown to black iron oxide precipitate.

5.3.1.3 Galvanostatically Treated Armco Iron Anodes

The galvanostatically treated Armco iron anodes developed a yellow film which in several cases became highly resistive. A SEM image of the surface of Anode III is shown in figure 5.7. Anode III developed a highly resistive film. Arrow A indicates a portion of the smooth surface film which is primarily composed of iron (~97%) and carbon (~3%). Arrow B indicates an inclusion which contains mostly iron (~61%), chromium (<1%), manganese (~14%), oxygen (~21%) and carbon (~3%).

A SEM image of the inclusion indicated by arrow B in figure 5.7 is shown in figure 5.8. Arrow A indicates the inclusion and arrow B indicates the edge of the inclusion where small amounts of aluminum were detected. This is from the aluminum oxide used to polish the electrode samples.

A SEM image of the surface of Anode II is shown in figure 5.9. This electrode did not develop a large resistance during the electrochemical experiments and one look at the image in figure 5.9 explains why. The film
Figure 5.7  A SEM image of the galvanostatically treated Armco iron anode (Anode III) surface. The arrows indicate the various regions of interest. Arrow A indicates the general surface which is covered by the yellow film. Arrow B indicates an inclusion.
Figure 5.8 A close-up SEM image of the inclusion indicated by arrow B in figure 5.7 on the galvanostatically treated Armco iron anode (Anode III) surface indicating with arrows the various regions of interest. Arrow A indicates the general surface of the inclusion and arrow B indicates the edge of the inclusion where small amounts of aluminum oxide were detected.
Figure 5.9 A SEM image of the galvanostatically treated Armco iron anode (Anode II) surface. The arrows indicate the various regions of interest. Arrow A indicates a pit. Arrow B indicates an inclusion. Arrow C indicates the general surface which is covered by the yellow film and arrow D indicates some type of deposit which contains trace amounts of silicon and chlorine in addition to iron, oxygen and carbon.
contains numerous pits, one of which is indicated by arrow A.

The elemental analysis of the dark spot indicated by arrow A shows only iron to be present. Arrow B indicates the ever present inclusion which contains mostly iron (~55%), chromium (~1%), manganese (~18%), oxygen (~24%) and carbon (~2%). Arrow C indicates a portion of the smooth surface film which is primarily composed of iron (~97%) and carbon (~4%) and arrow D indicates a feature that was only seen on this electrode. The deposit indicated by arrow D was composed primarily of iron (~63%), oxygen (~28%) and carbon (~7%), with small amounts of chlorine (<1%) and silicon (<1%).

The higher precision EDS data from 2 kV and 20 kV electron bombardment is shown in figure 5.10 for the yellow film on the surface of Anode III. The 20 kV electrons penetrate deeper into the surface than the 2 kV electron, thus the differences in the counts per second indicate possible changes in the film composition with depth.

Using the ratio of the counts per second to approximate the relative amount of an element in the scan area, the composition of the film can be estimated. The ratio of iron to oxygen to carbon for Anode III measured for 2 kV electron bombardment is roughly 3:7:7 and roughly 41:5:2. Once again, the higher precision data indicates a different composition. The high relative amount of iron in the 20 kV data indicates that at this electron energy the entire thickness of the film is being probed. The carbon to oxygen ratios suggest some
Figure 5.10 A bar graph of the x-ray emission counts per second for Anode III for different electron bombardment energies.
type of iron compound which contains roughly equal amounts of carbon and oxygen.

5.3.2 SEM without EDS of Galvanostatically Treated Armco Iron Electrodes

SEM images were taken of three galvanostatically treated Armco iron electrodes (Anode IV, Anode IVb and Cathode IV) at the Center for Materials Research at Stanford University. The details of the galvanostatic treatment of each electrode are discussed in section 4.3.

An SEM image of the surface of Cathode IV, which had a thick dark layer covering its surface, is shown in figure 5.11. It is clear in the image that this coating is probably quite porous from the presence of cracks and from the roughness of the surface. Arrow A indicates a crack in the surface coating and arrow B indicates a protruding deposit. Much like the crystals seen in figure 5.5, the deposits on the surface of Cathode IV are round. The light color of the deposit indicates that it contains significant amounts of lighter elements. The dark color of the cracks indicates a high iron content.

The two anodes did not develop highly resistive films and when the SEM images are viewed it is clear why. An SEM image of Anode IV which had a yellow pink film is shown in figure 5.12. Arrow A indicates a region where the film
Figure 5.11 A SEM image of Cathode IV which had a thick dark layer covering its surface. The arrows indicate the various regions of interest. Arrow A indicates a crack in the surface coating and arrow B indicates a protruding round shaped deposit.
Figure 5.12 A SEM image of Anode IV which had a yellow pink film. Arrow A indicates a region where the film appears to be intact. Arrow B shows the film lifted off the surface of the electrode and arrow C shows a region where dissolution of the iron has occurred underneath the film.
appears to be intact. Arrow B shows the film lifted off the surface of the electrode and arrow C shows a region where dissolution of the iron has occurred underneath the film.

The SEM image of Anode IVb in figure 5.13 shows that, while this electrode developed a smooth film over most of the surface, the film is not continuous. Arrow A points to a large snake shaped corrosion feature. This feature most likely developed along a defect in the electrode's surface. Arrow B indicates the general surface film which was quite smooth and arrow C indicates a rather large inclusion. A higher magnification image, shown in figure 5.14, of the deposit pointed to by arrow A in figure 5.13 shows that it is cracked as indicated by arrow A. Also, there appears to be a deep crack along the edge of an inclusion which is indicated by arrow B.

5.4 Fourier Transform Infra-Red Diffuse Reflectance Spectroscopy

Fourier Transform Infra-red Diffuse Reflectance Spectroscopy (FTIRDRS) was used to characterize the surface films found on two galvanostatically treated Armco iron electrodes, Anode VII and Cathode VII. The specific treatment these electrodes received is given in section 4.3. The spectra obtained gave weak signals necessitating count
Figure 5.13 A SEM image of a galvanostatically treated Armco iron anode, Anode IVb. This electrode developed a smooth film over most of the surface, but the film is not continuous. The arrows indicate features of interest. Arrow A points to a large snake shaped corrosion feature. Arrow B indicates the general surface film which was quite smooth and arrow C indicates a rather large inclusion.
Figure 5.14  A higher magnification SEM image of the deposit on Anode IVb, pointed to by arrow A in figure 5.12. The image shows that the deposit is cracked as indicated by arrow A. There also appears to be a deep crack along the edge of an inclusion which is indicated by arrow B.
times of 20 minutes to measure defined peaks; however, some very useful information was obtained.

The FTIRDRS background spectra which was run on a freshly polished Armco iron electrode is shown in figure 5.15. This spectra was fairly noisy especially between 1400-1900 cm\(^{-1}\) and between 3500-3900 cm\(^{-1}\) where the IR stretches of air are located. Also there are two peaks evident between 2300 and 2400 cm\(^{-1}\) which are from the carbon dioxide stretching. Thus any data in these three region is not reliable.

The FTIRDRS spectra for the surface film on Anode VII is shown in figure 5.16. Peaks are seen at 2950 and 2800 cm\(^{-1}\) (shown in greater detail in figure 5.17) which are assigned to CH\(^3\) stretches. A peak is also seen at 1050 cm\(^{-1}\) which is assigned to O-CH\(^3\) stretching. The O-C stretch for liquid methanol has been observed\(^8\) at 1029 cm\(^{-1}\) and the O-C stretches for alkyl-metal methoxides have been reported\(^9\) in the range from 992 cm\(^{-1}\) to 1104 cm\(^{-1}\). The peaks between 2300 and 2400 cm\(^{-1}\) are assigned to incomplete background subtraction for carbon dioxide, since no detection of CO\(_2\) stretching was seen in the Raman work discussed in the next section. This FTIRDRS spectra is a remarkable good match to the one FTIR spectra for ferric oxymethoxide found in the literature\(^10\) where IR peaks were found at 2950, 2800 and 1050 cm\(^{-1}\).
Figure 5.15 FTIRDRS background spectra which was run on a freshly polished Armco iron electrode. This spectra is fairly noisy between 1400-1900 cm\(^{-1}\) and between 3500-3900 cm\(^{-1}\) where the IR stretches of air are located. The two peaks evident between 2300 and 2400 cm\(^{-1}\) are assigned to the carbon dioxide stretching of air.
Figure 5.16 FTIRDRS spectra for the surface film on Anode VII. Peaks are seen at 2950 and 2800 cm⁻¹ (shown in greater detail in figure 5.16) which are assigned to CH₃ stretches. A peak is also seen at 1050 cm⁻¹ which is assigned to O-CH₃ stretching.
Figure 5.17 Expansion of the IR region from 3300 to 2100 cm\(^{-1}\) for the FTIRDRS spectra shown in figure 5.16. Peaks are seen at 2950 and 2800 cm\(^{-1}\) which are assigned to CH\(_3\) stretches.
The FTIRDRS spectra on Cathode VII is shown in figure 5.18. This spectra does not have any significant peaks above 1500 cm\textsuperscript{-1} and so does not contain any CH\textsubscript{3} in its surface film. An expansion of the region below 1500 cm\textsuperscript{-1} is shown in figure 5.19. Only poor signal-to-noise could be achieved due to the small amount of sample available; however, several weak peaks are discernible in this region of the IR band. There are five possible peaks in this region at 705, 850, 950, 1060 and 1190 cm\textsuperscript{-1}. An inspection of the IR spectra for iron oxides and iron oxyhydroxides\textsuperscript{87} show IR absorption peaks in this region. This overlap suggests that the coating on the surface of Cathode VII is some type of iron oxide.

5.5 Raman Spectroscopy

The Raman spectra were obtained for the yellow surface films found on two galvanostatically treated Armco iron electrodes, Anode II and Anode VII. The spectra obtained for the surface film of Anode II is shown in figure 5.20. The peaks obtained were weak and the spectra is noisy. There are many possible peaks in the spectra, but only the most prominent features will be discussed. The most prominent peaks are at 170, 230, 680 (broad), 840 and 1020 (broad) cm\textsuperscript{-1}.

The spectra obtained from the powder resulting from scraping the surface of Anode VII is shown in figure 5.21. This spectra has two fairly sharp peaks at 327 and 350 cm\textsuperscript{-1}.
Figure 5.18 FTIRDRS spectra of the surface coating on Cathode VII. This spectra does not have any significant peaks above 1500 cm\(^{-1}\) and so does not contain any CH\(_3\) in its surface film. There are five possible peaks at 705, 850, 950, 1060 and 1190 cm\(^{-1}\).
Figure 5.19  An expansion of the region below 1500 cm$^{-1}$ for the FTIRDRS spectra shown in figure 5.18. There are five possible peaks in this region at 705, 850, 950, 1060 and 1190 cm$^{-1}$.
Figure 5.20  The Raman spectra obtained for the surface film of Anode II. The most prominent peaks are at 170, 230, 680 (broad), 840 and 1020 (broad) cm$^{-1}$.
Figure 5.21 The spectra obtained from the powder resulting from scraping the surface of Anode VII. This spectra has two fairly sharp peaks at 327 and 350 cm\(^{-1}\) and two broad peaks centered at 687 and 993 cm\(^{-1}\).
and two broad peaks centered at 687 and 993 cm\textsuperscript{-1}. An attempt was made to increase the signal by changing the energy of the laser beam; however, this resulted in a lowering of the signal intensity. The Raman band positions for various iron oxides and oxyhydroxides were tabulated by Johnston\textsuperscript{88} and also by Oblonsky and Devine\textsuperscript{89} in papers studying the aqueous corrosion of iron.

The broad peaks at 680 and 687 can be assigned to Fe-O stretching and are seen in the Raman spectra of \( \alpha \)-FeOOH, \( \gamma \)-FeOOH, \( \delta \)-FeOOH, \( \gamma \)-Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4}. The peaks near 1000 can be assigned to O-CH\textsubscript{3} stretching and the peaks at 230, 327 and 350 are similar in position to Raman bands observed for \( \alpha \)-FeOOH, \( \gamma \)-FeOOH, \( \alpha \)-Fe\textsubscript{2}O\textsubscript{3}, \( \gamma \)-Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4}. This suggests that the anodic films are composed of an iron oxyhydroxide like compound.

5.6 X-ray Photoelectron Spectroscopy

The X-ray Photoelectron Spectra was measured for a galvanostatically treated Armco iron electrode, Anode IVb. The details of the galvanostatic treatment of the electrode are in section 4.3. The anodic electrode had a visible yellow/pink film on its surface, but had not become highly resistive. SEM images of this surface are shown in figure 5.13. The SEM image at x150 magnification reveals a smooth
film over much of the electrode surface with a large trail of what appears to be a different product running across it. A closer look (at 3000 magnification, shown in figure 5.14) shows that the trail has cracks which penetrate into the iron substrate. These cracks account for the fact that the film never became highly resistive.

The XPS spectra is shown in figure 5.22. It shows only peaks for carbon, oxygen and iron. The corrected binding energies, relative areas and atomic percents are given in table 5.2. The amounts of carbon and oxygen are quite high, 59% and 35%, respectively. There are roughly two oxygens for every carbon according to this data. The amount of iron is low, only 6%. This implies a compound with an approximate formula of FeC_{10}O_{6} with the possibility of hydrogens also being part of the compound, since XPS does no detect the presence of hydrogen.

Another very interesting aspect of this data is in the iron XPS peaks. There is a 1.5 eV change in the splitting between the Fe 2p1/2 and Fe 2p3/2 from 13.0 eV to 14.5 eV and the binding energies of the Fe 2p1/2 electrons at 727.0 eV and Fe 2p3/2 electrons at 712.5.0 eV are shifted to higher energies than the literature values^{90} for iron of 720.0 eV and 707.0 eV, respectively. The so called "chemical shift" with oxidation state is a well known phenomena in XPS^{91}. This shows that the iron is in a highly oxidized state.
Figure 5.22 XPS spectra obtained on a galvanostatically treated Armco iron anode (Anode IVb).
Table 5.2 Summary of XPS data obtained on a galvanostatically treated Armco iron anode.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Corrected binding energy</th>
<th>Relative peak area</th>
<th>Atom % from relative area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 2p$_{1/2}$</td>
<td>727.0</td>
<td>714</td>
<td></td>
</tr>
<tr>
<td>Fe 2p$_{3/2}$</td>
<td>712.5</td>
<td>632</td>
<td>6</td>
</tr>
<tr>
<td>O 1s</td>
<td>531.6</td>
<td>3718</td>
<td>35</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.6</td>
<td>6225</td>
<td>59</td>
</tr>
<tr>
<td>Fe 3s</td>
<td>93.7</td>
<td>1013</td>
<td></td>
</tr>
<tr>
<td>Fe 3p</td>
<td>55.7</td>
<td>829</td>
<td></td>
</tr>
<tr>
<td>O 2s</td>
<td>22.6</td>
<td>2889</td>
<td></td>
</tr>
<tr>
<td>O 2p</td>
<td>6.2</td>
<td>24187</td>
<td></td>
</tr>
</tbody>
</table>
5.7 X-ray Diffraction

The XRD data was not conclusive. A diffraction pattern was measured on the powder resulting from scraping the yellow film off a galvanostatically treated Armco iron anode, Anode II. The resulting powder was less than 1 mg, but an attempt was made to obtain a spectra. The results are shown in figure 5.23. There were only two well defined peaks in the pattern, one with 2-theta of 44.6° and the other with 2-theta of 31.6°. The peak at 44.6° corresponded to a d spacing of 2.03 Å and was attributed to the iron substrate. The peak at 31.6° corresponded to a d spacing of 2.83 Å and was of an unknown origin.
Figure 5.23 XRD spectra obtained from the powder resulting from scraping the surface of Anode II.
CHAPTER 6: SOLUTION ANALYSIS RESULTS AND DISCUSSION

6.1 Introduction

There are numerous possible oxidation and reduction reactions that can be postulated using iron, methanol, water and oxygen. The result presented in this chapter will allow some of the possible reactions to be excluded and support others. In order to have large enough quantities of corrosion products to measure analytically, Armco Iron electrodes were treated galvanostatically.

The galvanostatic treatment, discussed in detail in section 4.2, resulted in films being formed on the Armco iron electrode surfaces and their analysis was discussed in chapter five. The galvanostatic treatment also turned the methanol solutions yellow. The chemical composition of the resulting solution was investigated using Gas Chromatography, Atomic Absorption Spectroscopy (AAS) and Gas Chromatography/Mass Spectrometry (GC/MS).

Since the oxidation and reduction products resulting from the galvanostatic treatment of Armco iron electrodes might be different from non-forced corrosion products, solutions resulting from iron powder soaking in methanol solutions for several months, was also analyzed. Iron powder was used to provide a large surface area for corrosion to
occur on using a small amount of iron. The preparation of the iron powder/methanol solution mixtures is detailed in section 3.4.5.

6.2 Possible Oxidation-Reduction Reactions

During the corrosion of Armco iron in methanol, there are many possible anodic and cathodic half reactions that could be occurring at the electrode surface. In trying to determine what the oxidation and reduction half-reactions are in the Armco iron system, the first thing to figure out is what types of products may be produced in the system. In the following two sections a list of possible half reactions for a system containing iron, methanol, water and oxygen is presented.

6.2.1 Possible Oxidation Half Reactions

\[
\begin{align*}
\text{Fe} (s) & \rightarrow \text{Fe}^{2+} + 2e^- \\
\text{Fe} (s) & \rightarrow \text{Fe}^{3+} + 3e^- \\
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + 1e^- \\
\text{CH}_3\text{OH} & \rightarrow (\text{CH}_3\text{O})_{\text{ads}} + \text{H}^+ + 1e^- \\
\text{CH}_3\text{OH} & \rightarrow \text{CH}_2\text{O} + 2\text{H}^+ + 2e^- \\
\text{CH}_3\text{OH} & \rightarrow (\text{CHO})_{\text{ads}} + 3\text{H}^+ + 3e^- \\
\text{CH}_3\text{OH} & \rightarrow \text{CO} + 4\text{H}^+ + 4e^- \\
\text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 & \rightarrow \text{CO}_2 + 4\text{H}^+ + 4e^- 
\end{align*}
\]
\[ \text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{CO}_3^{2-} + 4\text{H}^+ + 4\text{e}^- \quad (6.9) \]

\[ \text{H}_2\text{O} \rightarrow (\text{OH})_{\text{ads}} + \text{H}^+ + \text{1e}^- \quad (6.10) \]

\[ \text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad (6.11) \]

\[ \text{Fe}(s) + \text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{FeCO}_3(s) + 4\text{H}^+ + 4\text{e}^- \quad (6.12) \]

\[ \text{Fe}(s) + 2\text{CH}_3\text{OH} \rightarrow \text{Fe(OCH}_3)_2(s) + 2\text{H}^+ + 2\text{e}^- \quad (6.13) \]

\[ \text{Fe}(s) + \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{Fe(OCH}_3)(\text{OH})(s) + 2\text{H}^+ + 2\text{e}^- \quad (6.14) \]

\[ \text{Fe}(s) + 3\text{CH}_3\text{OH} \rightarrow \text{Fe(OCH}_3)_3(s) + 3\text{H}^+ + 3\text{e}^- \quad (6.15) \]

\[ \text{Fe}(s) + 2\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{Fe(OCH}_3)_2(\text{OH})(s) + 3\text{H}^+ + 3\text{e}^- \quad (6.16) \]

\[ \text{Fe}(s) + \text{CH}_3\text{OH} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OCH}_3)(\text{OH})_2(s) + 3\text{H}^+ + 3\text{e}^- \quad (6.17) \]

\[ \text{Fe}(s) + \text{CH}_3\text{OH} + 1/2\text{O}_2 \rightarrow \text{FeO(OCH}_3)(s) + \text{H}^+ + \text{1e}^- \quad (6.18) \]

\[ \text{Fe}(s) + \text{H}_2\text{O} + 1/2\text{O}_2 \rightarrow \text{FeO(OH)}(s) + \text{H}^+ + \text{1e}^- \quad (6.19) \]

\[ \text{Fe}(s) + \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{FeO(OCH}_3)(s) + 3\text{H}^+ + 3\text{e}^- \quad (6.20) \]

\[ \text{Fe}(s) + 2\text{H}_2\text{O} \rightarrow \text{FeO(OH)}(s) + 3\text{H}^+ + 3\text{e}^- \quad (6.21) \]

### 6.2.2 Possible Reduction Half Reactions

\[ \text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}(s) \quad (6.22) \]

\[ \text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}(s) \quad (6.23) \]

\[ \text{Fe}^{3+} + \text{1e}^- \rightarrow \text{Fe}^{2+} \quad (6.24) \]

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (6.25) \]

\[ 2\text{H}^+ + 1/2\text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O} \quad (6.26) \]

\[ 2\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{OH}^- \quad (6.27) \]

\[ 2\text{Fe}^{2+} + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{FeO}(s) \quad (6.28) \]

\[ 2\text{Fe}^{2+} + 3/2\text{O}_2 + 4\text{e}^- \rightarrow \text{Fe}_2\text{O}_3(s) \quad (6.29) \]

\[ 2\text{Fe}^{3+} + 3/2\text{O}_2 + 6\text{e}^- \rightarrow \text{Fe}_2\text{O}_3(s) \quad (6.30) \]

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6.3 Gas-Solid Chromatography

6.3.1 Gas-Solid Chromatography of the Solutions Resulting from the Galvanostatic Treatment of Armco Iron Electrodes in Methanol

The Gas-Solid Chromatography (GSC) chromatogram obtained (column temp.: 165 °C, He flow rate: 20 ml/min) for a 2 µl injection of a solution sample from a galvanostatic treatment electrochemical cell, Galv II, onto a GSC column is shown in figure 6.1. The three peaks present in the spectra corresponded to argon, water and methanol. The chromatogram in figure 6.1 was typical for an injection of solution samples onto a GSC column. No peaks other than methanol, water and argon/oxygen were observed by GSC.

The GSC chromatograms obtained (column temp: 65 °C, He flow rate: 30 ml/min) for 1 ml gaseous injections of the Galv VI headspace (a), a gas sample of the glove box atmosphere (b), headspace gas from a carbon monoxide spiked methanol "standard" sample (c) and an injection of a mixture of carbon dioxide and argon (d), are shown in figure 6.2. These GSC chromatograms indicated that the Galv VI sample did not
Figure 6.1  GSC chromatogram obtained (column temp.: 165 °C, He flow rate: 20 ml/min) for a 1 µl injection of a solution sample from a galvanostatic treatment electrochemical cell, Galv II.
Figure 6.2 The GSC chromatograms obtained (column temp: 65 °C, He flow rate: 30 ml/min) for 1 ml gaseous injections of the Galv VI headspace (a), a gas sample of the glove box atmosphere (b), headspace gas from a carbon monoxide spiked methanol "standard" sample (c) and an injection of a mixture of carbon dioxide and argon (d).
contain significant amounts of carbon monoxide or carbon dioxide.

The GSC chromatograms obtained (column temp: 65 °C, He flow rate: 30 ml/min) for 2 ml gaseous injections of the Galv II headspace (a) and a hydrogen spiked "standard" sample (b), are shown in figure 6.3. These chromatograms indicated that the Galv II sample did not contain significant amounts of hydrogen.

6.3.2 Gas Chromatography of the Solutions Resulting from Iron Powder Soaking in Methanol Solutions

In order to raise the concentrations of corrosion products without galvanostatically treating Armco iron electrodes, iron powder was mixed with methanol solutions (preparation described in section 3.4.5) and allowed to sit for several months. The exact compositions of each iron powder/methanol solution vial are listed in table 6.1. Duplicates of each vial were prepared and vials 1-10 were sent to Dr. Smotkin at Illinois Institute of Technology. Visual inspection of the vials after they had sat for several months revealed that an orange/brown substance and a black substance had been formed. The methanol solutions in the vials were colorless.
Figure 6.3 The GSC chromatograms obtained (column temp: 65 °C, He flow rate: 30 ml/min) for 2 ml gaseous injections of the Galv II headspace (a) and a hydrogen spiked "standard" sample (b).
Table 6.1 Composition of iron powder and methanol solution mixture for gas chromatography evaluation of possible corrosion products in the solution.

<table>
<thead>
<tr>
<th>vial number</th>
<th>Weight of iron powder (g)</th>
<th>Weight of methanol (g)</th>
<th>Additions to the vials</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.0510</td>
<td>7.8879</td>
<td>5 mM TBAP</td>
</tr>
<tr>
<td>2</td>
<td>10.0246</td>
<td>7.8649</td>
<td>None</td>
</tr>
<tr>
<td>3</td>
<td>10.0248</td>
<td>7.8647</td>
<td>None</td>
</tr>
<tr>
<td>4</td>
<td>10.0117</td>
<td>7.9880</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>5</td>
<td>10.0518</td>
<td>7.7744</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>6</td>
<td>10.0377</td>
<td>7.7833</td>
<td>Oxygen gas</td>
</tr>
<tr>
<td>7</td>
<td>10.0142</td>
<td>7.8121</td>
<td>Oxygen gas</td>
</tr>
<tr>
<td>8</td>
<td>10.0216</td>
<td>7.8941</td>
<td>1 ml water</td>
</tr>
<tr>
<td>9</td>
<td>0.00000</td>
<td>7.8671</td>
<td>None</td>
</tr>
<tr>
<td>10</td>
<td>0.00000</td>
<td>7.8005</td>
<td>None</td>
</tr>
<tr>
<td>11</td>
<td>10.0210</td>
<td>7.8057</td>
<td>5 mM TBAP</td>
</tr>
<tr>
<td>12</td>
<td>10.0030</td>
<td>7.9087</td>
<td>None</td>
</tr>
<tr>
<td>13</td>
<td>10.0240</td>
<td>7.7690</td>
<td>None</td>
</tr>
<tr>
<td>14</td>
<td>10.0328</td>
<td>7.8541</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>15</td>
<td>10.0419</td>
<td>7.8698</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>16</td>
<td>10.0254</td>
<td>7.8485</td>
<td>Oxygen gas</td>
</tr>
<tr>
<td>17</td>
<td>10.0392</td>
<td>7.8286</td>
<td>Oxygen gas</td>
</tr>
<tr>
<td>18</td>
<td>10.0148</td>
<td>7.8460</td>
<td>1 ml water</td>
</tr>
<tr>
<td>19</td>
<td>0.00000</td>
<td>7.8462</td>
<td>None</td>
</tr>
<tr>
<td>20</td>
<td>0.00000</td>
<td>7.8537</td>
<td>None</td>
</tr>
</tbody>
</table>
GSC chromatograms obtained for 1 ml injections of the headspace gas from vials 11-20 showed no evidence of any other substance besides methanol, water and oxygen/argon/nitrogen (not resolved) being present in the solutions. The results obtained by Dr. Smotkin's research assistant on the ten vials sent to them also showed no evidence of any other substance besides methanol, water and oxygen/argon/nitrogen (not resolved) being present in the solutions.

6.4 Gas Chromatography/Mass Spectroscopy

Samples of liquid methanol, removed from two electrochemical cells after the EIS experiments were finished and samples of fresh methanol, were injected through the heated liquids inlet normally reserved for PFK references. The methanol samples were injected 10 μl at a time using several shots to flush the inlet each time. The background subtracted mass spectra for the clean methanol is shown in figure 6.4. There were no significant peaks above mass 50 and the spectra shows masses for methanol, oxygen, water and nitrogen. A background subtracted mass spectra obtained for the methanol solution removed from an electrochemical cell is shown in figure 6.5. The mass spectra for the methanol removed from the electrochemical cell shows mass peaks corresponding to carbon dioxide, argon, oxygen, methanol, nitrogen and...
Figure 6.4 The background subtracted mass spectra for the clean methanol. There were no significant peaks above mass 50 and the spectra shows masses for methanol, oxygen, water and nitrogen.
Figure 6.5 A background subtracted mass spectra obtained for the methanol solution removed from an electrochemical cell. There were no significant peaks above mass 50 and the spectra shows masses for methanol, oxygen, water and nitrogen.
water. The presence of carbon dioxide in the spectrum is not conclusive evidence for its presence in the solution, since the amounts of oxygen and nitrogen are high and suggest air leakage.

Both gas and liquid samples were collected from Galv I, during the galvanostatic treatment of two Armco iron electrodes in methanol. The electrodes were treated using the galvanostatic treatment described in section 3.2.6 at a current of 1 μA for three weeks. At this point, the headspace gas was analyzed by mass spectrometry and only methanol and air contamination was found in the headspace gas sample. Subsequently, the current was increased to 10 μA and left for 20 days.

Back of the envelop calculations show that for a total of four electrons (low estimate) transferred and a solution volume of 300 ml, the total galvanostatic treatment should lead to a product concentration of about 0.16 mM or enough to see analytically. Liquid samples from the galvanostatic electrochemical cell were injected through the gas chromatography inlet onto a megabore methyl silicone column and then analyzed with the mass spectrometer. Nothing significant was detected in the solution removed from the galvanostatic electrochemical cell. The second gas sample was attached to the heated liquids inlet using a double ended needle and pulled in by vacuum. The gas sample appeared to contain significant amounts of carbon monoxide and carbon
dioxide, but these gases were also observed in the glove box atmosphere sample.

An Armco iron electrode (after investigation by EIS for six months of submersion in methanol) was dried and placed in a special holder in the glove box, then connected to the heated liquids inlet via a double ended needle. Gas samples were pulled in by vacuum and when the vacuum became excessive it was relieved by the injection of 1 ml of argon gas using a tubercular syringe. The inlet used was capable of a vacuum of approximately 20 mbar. Minimum pressure over the electrode probably reached a pressure on the order of 0.05 atm.

The mass spectra for an initial sample of the gas in the special holder is shown in figure 6.6. This spectra contains mass peaks corresponding to carbon dioxide, argon, hydrogen chloride, oxygen, methanol, nitrogen and water. Again, the presence of the oxygen and nitrogen in the spectra casts doubts on whether the carbon dioxide was in the gas sample or was due to air leakage.

The special holder and the electrode were then warmed slowly with a heat gun and a mass spectra for this treatment is presented in figure 6.7. This spectra contains mass peaks corresponding to carbon dioxide, argon, oxygen, methanol, nitrogen and water. The mass peaks for hydrogen chloride are not in the spectra. Heating of the holder was continued to just above the level where it was too hot to touch the glass.
Figure 6.6 The mass spectra for an initial sample of the gas in the special holder containing an Armco iron electrode. This spectra contains mass peaks corresponding to carbon dioxide, argon, hydrogen chloride, oxygen, methanol, nitrogen and water.
Figure 6.7 The mass spectra for slow warming of the electrode sample and holder. This spectra contains mass peaks corresponding to carbon dioxide, argon, oxygen, methanol, nitrogen and water.
bottom. The mass spectra obtained under these conditions is presented in figure 6.8. This spectra is almost identical to the one obtained at low warming.

Finally, the special holder was flushed with an injection of argon gas and the mass spectra obtained is shown in figure 6.9. Once again no new mass peaks are seen. The hydrogen chloride peaks are more intense, but that is the only significant change.

6.5 Atomic Absorption Spectroscopy

Since the methanol solutions in the galvanostatic electrochemical cells turned yellow, it was apparent that under these conditions substantial amounts of iron were dissolving into the solution. To quantify this dissolution process and determine whether the iron was dissolving as Fe\(^{2+}\) or Fe\(^{3+}\), solution samples taken over the course of three different galvanostatic treatments, Galv V, Galv VI and Galv VII were analyzed by Atomic Absorption Spectroscopy. The specifics of the galvanostatic treatments are presented in section 4.2. Assuming the reactions in eqn. 6.1 and 6.2 are the only oxidation reactions occurring, the concentrations resulting from the iron dissolution to Fe\(^{2+}\) or Fe\(^{3+}\) can be readily calculated. The results of these calculations will be presented with the AAS data for comparison.
Figure 6.8 The mass spectra for heavy warming of the electrode sample and holder. This spectra contains mass peaks corresponding to carbon dioxide, argon, oxygen, methanol, nitrogen and water.
Figure 6.9 The mass spectra obtained when the special holder was flushed with an injection of argon gas. Once again no new mass peaks are seen.
It is noteworthy that when preparing the standards for the Atomic Absorption Spectroscopy that the methanol solution is visibly yellow colored at iron concentrations of 1 ppm. This suggests that with the proper equipment it might be possible to follow the dissolution of iron in methanol by Ultra-violet Visible Spectroscopy.

The AAS results for the samples taken from Galv V are presented in figure 6.10. The experimentally determined iron concentrations increase almost linearly with the total charge passed through the electrochemical cell. The values for the calculated iron solution concentrations are higher than the measured values for both cases and the difference between the measured and calculated concentration increases for iron dissolving as Fe$^{2+}$.

The AAS results for the solution samples taken from Galv VI are presented in figure 6.11. Once again the experimentally determined concentrations increase almost linearly with the total charge passed through the electrochemical cell. At charge values less than 15 C the concentrations calculated for dissolution as Fe$^{3+}$ almost match the experimental data perfectly. However, the difference between the measured and calculated concentrations increases at higher total charge passed especially for iron dissolving as Fe$^{2+}$.

The AAS results for the solution samples taken from Galv VII are presented in figure 6.12. Again the experimentally
Figure 6.10 AAS results for solution samples taken from Galv V.
Figure 6.11 AAS results for solution samples taken from Galv VI.
Figure 6.12 AAS results for solution samples taken from Galv VII
determined concentrations increase linearly with the total charge passed through the electrochemical cell. Once a total charge of 10 C has been passed through the electrochemical cell, the concentrations calculated for dissolution as Fe\textsuperscript{3+} drops below the experimental data. However, the difference between the measured and calculated concentrations for iron dissolving as Fe\textsuperscript{2+} increases at higher total charge passed.

The amount of iron "missing" from the solution can be calculated by taking the difference between the calculated Fe\textsuperscript{2+} or Fe\textsuperscript{3+} concentrations and the measured value. This data is shown in figure 6.13. Where does the iron go? Well, a look at table 4.6 shows that there are visible surface films on all the electrodes from galvanostatic treatment cells, Galv V, Galv VI and Galv VII. Assuming a value of 100 g/mol for the average molecular weight of the solid corrosion products, the amount of corrosion products can be estimated for the three different galvanostatic cells using either the Fe\textsuperscript{2+} results or the Fe\textsuperscript{3+} results, respectively: Galv V, 1.3 mg or 0.2 mg, Galv VI, 8.2 mg or 0.4 mg and Galv VII, 2.2 mg or negative value. Since the films are visible on the surfaces and weighed at least 1 mg (for Galv VII) when scraped off, the iron is probably dissolving into solution as Fe\textsuperscript{2+}. 

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Figure 6.13 The amount of iron "missing" from the solutions in the galvanostatic cells investigated.
CHAPTER 7: CONCLUSIONS

7.1 Electrochemical

Perhaps the most important electrochemical conclusion reached is that perchlorate salts are not very good supporting electrolytes to use in corrosion experiments conducted in organic solutions. The idea put forth in the literature\textsuperscript{93}, that if an ion does not absorb on a surface or effect reaction kinetics in aqueous systems, it will not absorb or effect the reaction kinetics in organic solutions, is absurd. The surface absorption properties of ions are related in part to their solvation in solution and the solvation properties of organic solution can be quite different from the solvation properties of water.

Secondly, a careful analysis of the equivalent circuit fit values, for EIS spectra acquired as a function of applied potential on Armco iron in 50 mM phosphoric acid, shows that care must be taken when using equivalent circuits to model the corrosion behavior of electrochemical systems. The analysis of the circuit element values as a function of potential allows the model which most closely matches theoretical predictions to be used for evaluating the impedance data. Furthermore, the dramatic effect of acid on the electrochemical behavior of the iron electrode is shown. The open circuit potential shifts almost 300 mV in the
negative direction, a result which matches those of the literature. The charge transfer resistance is shown to be substantially lower over much of the potential range studied.

The EIS data taken as a function of time indicate that after a period of equilibration lasting roughly two to three days, the electrochemical behavior becomes fairly stable. This means that in studies of the corrosion behavior of Armco iron in methanol data need only be acquired over a two day period to predict the corrosion rate and behavior of the electrochemical system.

Finally, the galvanostatic treatment of Armco iron electrodes in methanol lead to the discovery of a highly resistive yellow film. This film is very exciting, since if it could be generated reproducibly, it could have substantial utility in the prevention of the corrosion of iron or perhaps have interesting materials properties.

7.2 Film Analysis

Analysis of the galvanostatically treated Armco iron electrode surfaces by XES, SEM, SEM with EDS, FTIRDRS, Raman, XPS and XRD yielded much useful information regarding the chemical composition of the anodic and cathodic films. It is crucial to understand the nature of films formed on the electrode surfaces during corrosion, since they play such an important role in preventing the rapid dissolution of base
metals, such as iron. It is important to note that the oxidation of iron is thermodynamically favored, so that corrosion prevention must rely on reducing the kinetics to limit iron's corrosion rate.

XES spectra showed that the films contained carbon and that the bonding of the carbon in the anodic film was different from the bonding in the cathodic film. XES Fe Lβ/Lα ratios taken using variable energy electron bombardment showed difference in the chemical modification with depth. This data confirms the findings of the Keio University Chemistry Department that a thin film is present on air polished iron electrodes.

The SEM images taken at Stanford University explained why the two galvanostatically treated Armco iron electrodes sent there for analysis had not become highly resistive when undergoing galvanostatic treatment. These images showed flaws in the yellow surface film, pits through the film in the case of Anode IVb and porous corrosion deposits formed on select areas of the electrode surface.

The SEM images taken in conjunction with EDS measurements proved to be extremely helpful in putting together a picture of what is occurring during the galvanostatic treatment. Firstly, the extremely high resistivity of the film on Anode III makes a great deal of sense when the SEM is viewed. This film was remarkably smooth and we were unable to locate any pits or substantial
defects. The EDS results for the anodic films showed then to be composed of iron, carbon and oxygen, with the oxygen to carbon ratio being somewhere around 1 to 1 or 2 to 1. Care must be taken when interpreting the EDS results, since even at higher counts this method of elemental analysis is only semi-quantitative.

The SEM images for the galvanostatically treated cathode showed deposits on a fairly clean iron surface. The suggests that the cathodic reactions are occurring at select sites on the electrode surfaces. EDS of the cathodic deposits showed them to be composed primarily of iron and oxygen with smaller amounts of carbon. This suggests that the cathodic deposits are composed of some type of iron oxide.

FTIRDRS performed on galvanostatically treated Armco iron electrodes gave weak but useful signals. The anodic film exhibited IR absorption which suggested the presence of iron methoxy bonding in the yellow anodic film. In contrast, the FTIRDRS results for the cathodic deposits did not indicate the presence of methoxy, but rather gave further support to the idea that the cathodic deposits are some form of iron oxide.

Raman Spectroscopy was not very useful giving very weak peaks which did not correspond for different galvostatically treated electrodes. The few peaks that were seen for the anodic surfaces are most likely due to iron oxygen bonding.
XPS spectra taken on a galvanostatically treated Armco iron electrode also showed the yellow film to be composed of iron, oxygen and carbon with a rough oxygen to carbon ratio of 1 to 2. Furthermore, the large chemical shift in the Fe $2p_{1/2}$ binding energy of 7 eV suggest that the iron is in a highly oxidized state or an electron deficient valence electron structural state.

XRD data on the powder scraped from a galvanostatically treated anode showed one diffraction peak ($d=2.028 \text{ Å}$) that may be attributed to the film. Since only one diffraction pattern for an iron oxymethoxide could be located in the literature, the structure of the film compound could not be established.

To summarize, the overall conclusion that can be reached from the surface film analysis, is that the anodic films are most likely composed of an iron methoxide or iron oxymethoxide compound. The cathodic deposits appear to be composed of some type of iron oxide or oxyhydroxide with some carbon content of unknown origin.

7.3 Chemical Analysis

All attempts to find possible oxidation or reduction products of methanol in the solution resulting from galvanostatic treatment of the Armco iron electrode gave essentially negative results. Calculations of the
concentrations which would be produced if the methanol were being oxidized or reduced to a soluble or gaseous product indicate that the concentrations would be high enough to detect. This allows most alternate reactions to be excluded from consideration when formulating a reaction scheme for the corrosion process.

A result proved to be very useful and showed very conclusively that under galvanostatic treatment the Armco iron electrode dissolves into the solution. A comparison of the measured iron concentrations to the concentrations predicted by the amount to charge passed across the interface indicates that the iron is dissolving as ferrous ions. This result is in concurrence with results in the literature\textsuperscript{96}.

### 7.4 Overall Reaction Scheme

Combining the chemical results with the film analysis the author would like to propose the following plausible overall reaction scheme. The production of iron oxide or iron oxyhydroxide at the galvanostatically treated cathodes suggest that one or more of the following reactions may be occurring:

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2\text{Fe}^{2+} + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{FeO}(s) \tag{7.1}
\]
\[
2\text{Fe}^{2+} + 3/2\text{O}_2 + 4\text{e}^- \rightarrow \text{Fe}_2\text{O}_3(s) \tag{7.2}
\]
\[
2\text{Fe}^{3+} + 3/2\text{O}_2 + 6\text{e}^- \rightarrow \text{Fe}_2\text{O}_3(s) \tag{7.3}
\]
$$3\text{Fe}^{2+} + 2\text{O}_2 + 6\text{e}^- \rightarrow \text{Fe}_3\text{O}_4(s) \quad (7.4)$$

$$3\text{Fe}^{3+} + 2\text{O}_2 + 9\text{e}^- \rightarrow \text{Fe}_3\text{O}_4(s) \quad (7.5)$$

$$\text{Fe}^{2+} + \text{O}_2 + \text{CH}_3\text{OH} + 3\text{e}^- \rightarrow \text{FeOOH}(s) + \text{CH}_3\text{O}^- \quad (7.6)$$

$$\text{Fe}^{3+} + \text{O}_2 + \text{CH}_3\text{OH} + 4\text{e}^- \rightarrow \text{FeOOH}(s) + \text{CH}_3\text{O}^- \quad (7.7)$$

However, the AA data indicates that the iron in solution is in the 2+ oxidation state, therefore reactions 7.3, 7.5 and 7.7 must be eliminated.

The primary oxidation reaction as demonstrated by the AA data is:

$$\text{Fe}(s) \rightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (7.8)$$

but this does not explain the anodic film. The anodic films were yellow in color and stable in air, excluding the possibility of ferrous methoxide which is green and unstable in oxygen^{97}. Leaving two possible compounds as candidates for the anodic surface film: ferric methoxide and ferric oxymethoxide. The reactions which can yield these two compounds are:

$$\text{Fe}(s) + 3\text{CH}_3\text{OH} \rightarrow \text{Fe(OCH}_3)_3(s) + 3\text{H}^+ + 3\text{e}^- \quad (7.9)$$

$$\text{Fe}(s) + \text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \rightarrow \text{FeO(OCH}_3)(s) + \text{H}^+ + \text{e}^- \quad (7.10)$$

$$\text{Fe}(s) + \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{FeO(OCH}_3)(s) + 3\text{H}^+ + 3\text{e}^- \quad (7.11)$$

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Considering the instability of ferric hydroxide$^{98}$, it seems highly unlikely that ferric methoxide would be stable and reaction 7.9 can be eliminated from consideration. Therefore, the most likely candidate for the anodic film is ferric oxymethoxide.
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