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THE INHIBITION OF ELECTRON-TRANSFER PROCESSES ON ALUMINUM ALLOY VIA CHROMATE ION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
The Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
William J. Clark Jr., B.S

The Ohio State University
2002

Dissertation Committee:
Professor Richard L. McCreery, Adviser
Professor Prabir K. Dutta
Professor Gerald S. Frankel

Approved by

RT McCrery
Adviser
Department of Chemistry
ABSTRACT

Localized corrosion of aluminum alloys is problematic. The susceptibility to such corrosion is linked to the existence of intermetallic phases that generate galvanic couples on the alloy surface. Corrosion inhibition is accomplished by the use of inhibitors containing chromate ions (Cr\textsuperscript{VI}) to form chromate conversion coatings on the alloy surface. The action of chromate ion is superior but due to the toxicity of chromate an impetus exists for its replacement with more benign alternatives. However, the mechanism of chromate inhibition is not well understood.

To gain insight into the inhibition mechanism of chromate, a separation of corrosion reactions approach was taken. Galvanic couples of pure metals and aluminum alloy 2024-T3 in various combinations were used to approximate the local corrosion processes taking place on the alloy surface. The samples were separated into separate chambers to allow for independent control of environmental conditions at the anode and cathode and the current between the electrode was measured with a zero-resistance ammeter. Cr\textsuperscript{VI} was shown to strongly inhibit cathodic reactions both in solution and as a pretreatment, indicating persistence of the effect. Addition of chromate resulted in a current transient attributed to Cr\textsuperscript{VI} reduction to Cr\textsuperscript{III} prior to inhibition. Solution-phase chromate exhibited anodic inhibition of passive current but not at potentials positive of breakdown as explained with mixed potential theory.
Interaction of chromate with electrode surfaces was examined with voltammetry. Chromate was shown to inhibit many reduction processes on several electrode materials, including systems that require adsorption and outer sphere systems. This is achieved by the reduction of Cr$^{VI}$ to Cr$^{III}$ and subsequent immobilization on the electrode surface. The surface layer is in near-monolayer quantities and the reduction reaction occurs at potentials well positive of in-field conditions experienced by aluminum alloy 2024-T3.

Replacements for chromate ion based inhibition were examined using information gained about the inhibition mechanism of chromate as a guide. Diethyldithiocarbamate and diazonium salt modification of various electrode surfaces was performed and examined by Raman spectroscopy. Voltammetry and galvanic couples were used to evaluate the replacement candidates. Specific interaction with intermetallic sites on AA 2024-T3 was observed.
Dedicated to Kellie Clark - my partner in life
ACKNOWLEDGMENTS

Reaching my goal of obtaining a Ph. D. could not have been accomplished without the inspiration, encouragement, and prodding of numerous people along the way. As such, many thanks are in need of giving and are yet unable in this short space.

First, I should thank the anonymous philosophy professor who spoke about learning for learning's sake at my wife's OSU orientation in 1995. I think a spark may have been kindled that day that became a flame about 2 years later when I decided to head to graduate school after 10 years away from academia.

My adviser, Richard McCreery, has been a joy to work with. I am always amazed at both the depth and breadth of his knowledge. His style of advising, presence without pressure, allows the student to grow and explore ideas without the worry of traveling too far down unfruitful research paths.

The members of the McCreery group also were instrumental in my journey towards my goals. Each person I have encountered - from those who have gone before me (T. C. Kuo, H. H. Yang, Stacy DuVall, Jeremy Ramsey, Kristin Frost, Lin Xia, Bill McGovern, and Srikanth Ranganathan), to my classmates (Ilson Steidel and Jingya Wu), to those who arrived later (Belinda Hurley, Y. Y. Hu, Franklin Anariba, Aletha Nowak, Brian Snyder, Laura Eichorst, Takashi Itoh, and Ali Solak) - has influenced my science in some way.
I think you learn most from those just preceding you. With that in mind I especially want to acknowledge Jeremy Ramsey and Srikanth Ranganathan. Our many casual science conversations in the lab both answered questions and generated more. I hope I have been as helpful for those newer group members. The McCreery group has always been good science and good fun.

Despite the help from all those listed above my goals would not have been possible without family to share my joy and frustrations. My in-laws (Ken and Sherry Fluty) and grand in-laws (Virginia and Ralph Ferryman) have been more like a second set of parents and grandparents. Thank you for always being there to help out and for your interest in my goals. My parents (Trudy and Bill Clark) have always encouraged my learning through the years. Thanks to Mom for taking me to your laboratory when I was little. Thanks to Dad for telling me to study and not “do like he did” in school. You have always been there when I needed you. I couldn’t ask for better parents.

I save the last and greatest acknowledgement for my wife, Kellie. Without her, none of this would have ever been accomplished because I would have been too afraid to take the risk. Her enthusiasm and extroverted personality have let me experience life in a way that would not have been possible had we not met. Thank you for believing in me when I probably didn’t believe in myself. I hope I can repay you for all the sacrifices you have made to let me pursue this goal. I will try my best. I love you more than anything.
VITA

October 28, 1965 ................................................. Born - Nelsonville, Ohio

1987 ........................................................................ B.S. Chemical Engineering,
Ohio University
Athens, Ohio

1987-1995 ............................................................. Engineer, Research and Technical Service
Chi-Vit Corporation
Urbana, Ohio

1995-1997 ............................................................. Chemical Supervisor
Abrasive Technology, Inc.
Westerville, Ohio

1997-present ......................................................... Graduate Teaching and Research Assistant
The Ohio State University

PUBLICATIONS

1. W. J. Clark, R. L. McCreery “Inhibition of Corrosion-Related Reduction
(9), B379.

Approach to Investigating Chromate Effects on Aluminum Alloy 2024-T3”

3. R. Bommaraju, T. Jackson, J. Lucas, G. Skoczylas, B. Clark “Design,
development, and application of mold powder to reduce slivers”. *Iron Steelmaker*

FIELDS OF STUDY

Major Field: Chemistry
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CHAPTER 1

INTRODUCTION

A 2002 report sponsored by CC Technologies, the Federal Highway Administration, and NACE International (the National Association of Corrosion Engineers) estimated that the cost of corrosion in the United States is $276 billion per year.¹ This staggering number was calculated based upon an extensive study that considered direct costs (including design, manufacturing, construction, and management) and indirect costs (costs not incurred by the owners or operators of a product) for a wide range of sectors including utilities, transportation, infrastructure, government, and manufacturing. Some subsets of these areas are directly affected by the investigations herein. The corrosion costs to aircraft in the transportation sector is listed as $2.2 billion per year. The corrosion costs for defense in the government sector is $20.0 billion per year. $121.4 billion per year was deemed the cost for corrosion control methods. This amount was noted to be over 1% of the Gross Domestic Product of the United States. The cost of corrosion has steadily increased over the years with previous estimates of $5.4 billion in 1949, $10 billion in 1966, $70 billion in 1976, and $126 billion in 1982.²³

³ The cost of corrosion inhibitors alone has increased from $600 million in 1982 to $1.1 billion in 1998.¹
Aside from the cost of corrosion the dangers of corrosion to humans are evident by accidents that have occurred that were due solely or in part to corrosion. The Silver Bridge collapse in 1967 at Point Pleasant, West Virginia killed 46 people. Over a 40 year time period stress corrosion and corrosion fatigue caused a critical failure to a suspension chain mounting although technology at the time could not have detected the developing flaw. In 1988, an Aloha Airlines Boeing 737 lost part of its fuselage, killing a flight attendant. Cracks attributed to corrosion were found upon investigation of the accident. A series of explosions in Guadalajara, Mexico, in April 1992 that killed 215 people were attributed to a corroded gasoline pipeline leaking into a sewer.

The study of corrosion and its control is an interdisciplinary science that involves such fields as materials science; chemistry; and electrical, civil, chemical, and mechanical engineering. Corrosion is commonly found on visible items such as cars, pipes, and buildings but also is an important problem in less visible areas like hip replacements in the medical field and the microelectronics industry. Each case of corrosion has similar electrochemical backgrounds but manifestation can arise in ways numerous enough to warrant separate classifications of corrosion types.

The investigations contained herein are concerned specifically with corrosion of an aluminum alloy, which predominantly manifests itself as localized events that can result in cracking of the alloy. Aluminum alloy 2024-T3 is the particular substrate studied, as it is one of the most corrosion-prone of the aluminum alloys and is used structurally in aircraft. Currently, a method of corrosion control for aluminum alloys utilizes formation of chromate-based conversion coatings and painting with chromate-
containing primers. Although inhibition with chromate compounds is very effective, exhibiting a property that allows areas scratched clean of any coating to be protected by surrounding coating material, chromate compounds are known carcinogens. As such, an impetus exists to replace chromate-based inhibition methods with more benign alternatives.\textsuperscript{11}

In order to replicate the superior performance of chromate-based corrosion inhibition a logical approach is to select alternates that mechanistically inhibit corrosion in a similar manner. Unfortunately, the inhibition mechanism of chromate compounds is not historically well-known. Only during the last decade has research begun to delve heavily into this area, prompted by the desire for chromate replacements.

The research described herein looks specifically at the mechanism of solution phase chromate (hexavalent chromium, $\text{Cr}^{VI}$) towards corrosion inhibition of AA 2024-T3 and application of the information obtained towards selection of possible replacements. Each chapter will present an introductory discussion of relevant topics including pertinent information already discovered regarding chromate inhibition mechanisms. The balance of this chapter will discuss (1) an overview of electrochemical phenomena with an emphasis towards corrosion, (2) a short review of forms of corrosion, (3) more detail about aluminum alloys (particularly AA 2024-T3) and corrosion inhibition with chromate compounds, and (4) a review of Raman spectroscopy, a technique which is particularly well-suited for identification of compounds relevant to corrosion.
Solution-phase voltammetry and its relation to corrosion

Corrosion is defined as the "destructive result of chemical reaction between a metal or metal alloy and its environment".\textsuperscript{3 \textcopyright 5} The reactions that take place nearly always involve a transfer of electrons from one species to another. Thus corrosion is an electrochemical process (or reaction). Electrochemical reactions (redox reactions) require both reduction and oxidation to occur as free electrons require high energy and unusual experimental conditions to produce, such as liquid ammonia solvent.\textsuperscript{12} Redox reactions can take place between a number of species. The reaction

\[
\text{Fe(NO}_3\text{)}_2\text{(aq)} + \text{Ce(NO}_3\text{)}_4\text{(aq)} \rightarrow \text{Fe(NO}_3\text{)}_3\text{(aq)} + \text{Ce(NO}_3\text{)}_3\text{(aq)}
\]  

is a redox reaction because Fe loses electrons (is oxidized) and Ce gains electrons (is reduced). Considering only the species with changes in oxidation state results in

\[
\text{Fe}^{2+} + \text{Ce}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+}
\]  

which can also be formally separated into two half-reactions that show the loss and gain of electrons.

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^{-}
\]  
\[
\text{Ce}^{4+} + e^{-} \rightarrow \text{Ce}^{3+}
\]
If the reactions are separated into separate chambers to keep the solutions from bulk mixing (i.e. with a glass frit that allows ion migration), but electrically connected (let us say by a wire), electrons will flow through the wire from the chamber containing Fe\(^{2+}\) to the chamber containing Ce\(^{4+}\). This current can be measured and the cell is referred to as a galvanic (or voltaic) cell. The wire collects, transports, and distributes the electrons.

The portion of the wire in contact with the solution is termed the electrode. For now, assume that the electrode does not interact with the species being reduced or oxidized except to transfer electrons.

As with all reactions, half-reactions follow the laws of thermodynamic equilibria. However, the inclusion of electrons complicates matters. Potential is the quantity of work required to bring a point-charge from infinity to a point in an electric field. The reduction potential (in volts, V) of a half-reaction is defined as a quantity of work required to bring an electron from infinite distance and combine with a species (e.g. Ce\(^{4+}\)) to reduce it (e.g. Ce\(^{3+}\)). As a convention, the energy of an electron increases as the potential becomes more negative. As the energy of an electron in an electrode is increased (potential moved negative), it will eventually reach a point where its energy in the electrode will be higher than if it is combined with a species in solution. Since thermodynamics favors the lowest energy state, the electron will transfer from the electrode to the solution species. Every reduction reaction has a unique potential. However, the reduction potential of a single half-reaction is difficult to define since infinite separation is difficult.
Two half-reactions necessarily have different reduction potentials. Therefore, the potential difference (or electron energy difference) serves as a driving force for redox reactions. If the electron in species A has a higher energy than it would if it were residing in species B there is an impetus for the oxidation of A and reduction of B. This difference in driving force can be measured experimentally. If the reaction is allowed to occur, one can show that the $\Delta G^0$ (the Gibb’s Free Energy change) for the reaction is related to the difference in the potential of the half-reactions, or the cell potential ($E^0$),

$$
\Delta G^0 = -nF E^0_{\text{rxn}} \quad (\text{and}) \quad \Delta G = -nF E^0_{\text{rxn}}
$$

(1.5)

where $n$ is the number of electrons transferred and $F$ is Faraday's constant (96485 C/equivalent). The superscript $^0$ denotes that the system is at standard temperature and pressure and all species are at unit activity. The equilibrium constant of the reaction ($K_{\text{rxn}}$) can be related to $E^0_{\text{rxn}}$ as

$$
RT \ln K_{\text{rxn}} = -\Delta G^0 = -nF E^0_{\text{rxn}}
$$

(1.6)

Tables have been constructed based on these differences in potential. Basic lists of reduction reactions can be found in any general chemistry text and extensive lists in more detailed compilations. Generally, one reaction is defined to be zero potential and all others are referenced to it. In most modern cases, the defined zero potential half-reaction is the reduction of hydrogen.
The normal hydrogen electrode (NHE) is the representation of this reaction and is described in basic and advanced chemistry texts. Returning to equations 1.3 and 1.4 (now writing them both as reduction reactions) and adding published reduction potential values yields:

$$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad E^0 = 0.770 \text{ V (vs. NHE)} \quad (1.8)$$

$$\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+} \quad E^0 = 1.440 \text{ V (vs. NHE)} \quad (1.9)$$

The difference between the potentials ($E_{\text{rxn}}$), 0.67 V, is the driving force for reaction 1.2. The half-reaction with the more positive potential accepts an electron from the half-reaction with the more negative potential.

Concerning corrosion, the number of relevant half-reactions is smaller. Generally, the oxidation reactions involve the oxidation of the metal or alloy being investigated and thus have potentials that are relatively negative. Reduction reactions are limited in the world of aqueous corrosion (the focus of this study) to the reduction of oxygen, hydrogen ions, or water. Metal ions can serve as the reductant (or oxidizing agent) but those cases are specialized and will be mentioned only as needed. Table 1.1 lists the reduction potentials of several relevant corrosion half-reactions.
Table 1.1: Selected reduction potentials for various half-reactions useful in studying corrosion, under standard state conditions.\textsuperscript{15} pp 699-701

Two examples of these reduction reactions serve to illustrate the driving forces for corrosion. The aluminum half-reaction has a reduction potential of -1.706 V and that for the oxygen half-reaction is 1.229 V. By placing oxygen and aluminum metal together there is a driving force of 2.395 V for the reaction (Al oxidation - O\textsubscript{2} reduction) to occur. On the other hand placing gold metal and oxygen together results in no reaction, as the gold ion only exists at more positive potentials than 1.68 V.

The potentials listed in Table 1.1 are defined as standard reduction potentials and are usually denoted by $E^0$ with the definition that the system is at standard temperature and pressure and the oxidized and reduced species are at unit activity ($\alpha = 1$). The

<table>
<thead>
<tr>
<th>Reduction reaction</th>
<th>$E^0$ (V) vs NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}^+ + e^- = \text{Au}$</td>
<td>1.68</td>
</tr>
<tr>
<td>$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$</td>
<td>1.33</td>
</tr>
<tr>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O}$</td>
<td>1.229</td>
</tr>
<tr>
<td>$\text{Pt}^{2+} + 2e^- = \text{Pt}$</td>
<td>1.2</td>
</tr>
<tr>
<td>$\text{Ag}^+ + e^- = \text{Ag}$</td>
<td>0.7996</td>
</tr>
<tr>
<td>$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^-$</td>
<td>0.401</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2e^- = \text{Cu}$</td>
<td>0.3402</td>
</tr>
<tr>
<td>$2\text{H}^+ + 2e^- = \text{H}_2$</td>
<td>0.000</td>
</tr>
<tr>
<td>$\text{Fe}^{3+} + 2e^- = \text{Fe}$</td>
<td>-0.409</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-$</td>
<td>-0.8277</td>
</tr>
<tr>
<td>$\text{Mn}^{2+} + 2e^- = \text{Mn}$</td>
<td>-1.209</td>
</tr>
<tr>
<td>$\text{Al}^{3+} + 3e^- = \text{Al}$</td>
<td>-1.706</td>
</tr>
<tr>
<td>$\text{Mg}^{2+} + 2e^- = \text{Mg}$</td>
<td>-2.375</td>
</tr>
</tbody>
</table>
measured potential, \( E \), is perturbed by deviations from this and is defined by the Nernst equation obtainable from the thermodynamic free energy relationship.

\[
\Delta G = \Delta G^\circ + RT \ln \frac{\alpha_{\text{red}}^b}{\alpha_{\text{ox}}^a} \tag{1.10}
\]

Inserting Equation 1.5 and rearranging gives

\[
E = E^\circ + \frac{RT}{nF} \ln \frac{\alpha_{\text{ox}}^a}{\alpha_{\text{red}}^b} \tag{1.11}
\]

This is true for the generic reaction

\[
a(\text{Ox}) + n(e^-) \rightarrow b(\text{Red}) \tag{1.12}
\]

where \( \alpha \) is the activity and \( a \) and \( b \) are coefficients of the constituents of the half-reaction. If other species (that do not change oxidation state) are involved in the reaction, they too must be included in the Nernst equation - products in the denominator and reactants in the numerator. The most common additional species are \( \text{H}^+ \) or \( \text{OH}^- \), which means that \( \text{pH} \) can have a major effect on the reduction potential for systems involving \( \text{H}^+ \) (or \( \text{OH}^- \)). The two listings for the reduction of oxygen in Table 1.1 show the dramatic effect that \( \text{pH} \) can have. The activity of the species is usually replaced by concentration ([]) and the
activity coefficients ($\gamma$) are combined with $E^0$ to give the formal potential ($E^{\circ}$). The resulting common form of the Nernst equation is

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

(1.13)

A more extensive development of the Nernst equation and the thermodynamics of electrochemical reactions is presented by Bard and Faulkner.\textsuperscript{15} pp. 44-85

A significant difference between voltammetry and corrosion arises when experimental control is considered. The difference is not fundamental but is manifested in the responses of voltammetric and corrosion systems to perturbations. As predicted by the Nernst equation (Eq. 1.13) the potential of a system is determined by several variables. If a variable changes, the system deviates from equilibrium. The response of the system to a perturbation is to try to change the species concentrations. To do this oxidation and reduction must occur which results in a current (electron flow).

Voltammetry is a technique where potential is controlled and the system is studied by observing the current response. Corrosion is in effect uncontrolled voltammetry in the sense that the environment adjusts the variables and the system attempts to return to equilibrium. Most often, this is accomplished by a metal giving up electrons (in other words - corroding!). The remainder of this section will describe pertinent electrochemical concepts in a voltammetric manner (i.e. current response to controlled potential changes). Generally, in electrochemical experiments only one half-reaction is
studied. The oxidation and reduction processes discussed are merely forward and backward reactions of the same process. Often the electrode material is not considered to affect the properties of the analyte. The same concepts apply to corrosion although the variables are not controlled by the experimenter but set by the corroding environment. Both (or more) half-reactions are important and occur in parallel. In addition, the electrode is an intimate part of the process because it is generally the species being oxidized. The next section of this chapter considers corrosion electrochemistry more specifically.

Thermodynamics alone do not adequately predict the response of electrochemical systems to perturbations in potential. Equations 1.11 - 1.13 assume equilibrium is reached instantaneously and that changes in conditions are infinitesimal compared to the whole system. Thus, a change in the potential of a system will cause an instantaneous shift in the concentrations of Ox and Red in Equation 1.12. A measurement of the current (electron motion) under this presumption would theoretically yield a current of infinite magnitude for zero time passed. In reality, charge transfer kinetics or mass transport limit the current. The transfer of electrons into (or out of) an atom (molecule) is governed by kinetics. A finite current can be measured for a finite time as the system returns to equilibrium. As an example, the previously discussed potential difference between oxygen and aluminum implies a large driving force for the reaction. However, it is a fact that items such as aluminum ladders (instead of piles of aluminum oxide) exist despite this difference in potential. If potential differences in half-reactions were the only factor governing the driving force for a reaction, humankind would likely not exist. Most
biological molecules have reduction potentials lower than oxygen.\textsuperscript{16,17} If the reactions proceeded rapidly according to thermodynamic considerations these molecules would be irreversibly oxidized.

The kinetics of electron transfer are developed from the same concepts as kinetics for homogeneous chemical reactions (not involving electron transfer). The reduction reaction

\[ \text{Ox} + ne^- \rightarrow \text{Red} \tag{1.14} \]

is better written as

\[ \text{Ox} + e^- \underset{k_b}{\xrightarrow{k_f}} \text{Red} \tag{1.15} \]

showing that the reaction has forward and backward rate constants that govern kinetics of the reaction. The system is usually considered to conform to Arrhenius-like behavior. That is

\[ k = A'e^{-\Delta G^\ddagger/RT} \tag{1.16} \]
where $k$ is a rate constant, $A'$ is a frequency factor, $\Delta G^i$ is the free energy of activation (related to Arrhenius’ original activation energy $E_A$), and $R$ and $T$ are as defined earlier. $\Delta G^i$ for forward and reverse reactions is shown graphically in Figure 1.1. It is the free energy difference between the products or reactants of a reaction and the activated complex, expressed as $\Delta G^+_b$ and $\Delta G^-_b$, respectively. The free energy of the reaction, $\Delta G^0_{\text{rxn}}$, is the difference between $G_{\text{products}}$ and $G_{\text{reactants}}$ (also the difference between $\Delta G^+_b$ and $\Delta G^-_b$). In an electrochemical reaction, the energy of the system can be controlled by changing the energy of the electron. Figure 1.2 shows this graphically for a system which changes to favor the forward (reduction) reaction. The energy of the electron is increased by moving from $E^0$ to $E^0-E$. The change in free energy for the $(\text{Ox} + e^-)$ as a result is expressed as $-nF\Delta E$ as presented in Equation 1.6. This term can be expressed fractionally as $\alpha(-nF\Delta E)$ and $(1-\alpha)(-nF\Delta E)$ and represents the decrease in activation barrier ($\Delta G^0_{\text{f}} - \Delta G^+_b$) for the forward reaction $(\text{Ox} + e^- \rightarrow \text{Red})$ and an increase in the activation barrier ($\Delta G^0_{\text{b}} - \Delta G^-_b$) for the reverse reaction $(\text{Red} \rightarrow \text{Ox} + e^-)$. $\alpha$ is the transfer coefficient (different from $\alpha$ used earlier for activity) and is defined below. Since the barrier for reduction becomes smaller, the reaction proceeds to produce the reduced species. The forward and reverse directions of Equation 1.15 can be combined into one kinetic expression that expresses both reactions’ contribution to the overall measured current. This expression is known as the Butler-Volmer equation.

\[
i = i_0 \left[ e^{-a_n F} - e^{(1-\alpha)a_n F} \right]
\]  

(1.17)
Figure 1.1: Schematic of free energy changes during a reaction.
Figure 1.2: Effect of changing electron energy on the free energies of activation of forward and reverse electron-transfer reactions. In this case the electron energy is increased from $E^0$ to $E^0 - E$. Decreased $\Delta G_f^*$ and increased $\Delta G_b^*$ result.
where \( \eta \) is the overpotential (or distance away from the equilibrium potential, \( E - E^0 \)), \( f \) is \( F/RT \), \( \alpha \) is the transfer coefficient which relates to the angle of intersection of the free energy of products and reactants on a reaction coordinate curve, and \( i_0 \) is the exchange current. The exponential terms of the equation represent the forward and reverse reactions. By inspection, it is noted that as the overpotential, \( \eta \), increases in either positive or negative direction, one of the terms becomes negligible compared to the other.

The exchange current, \( i_0 \), contains the standard rate constant for the reaction, \( k^0 \), which expresses the kinetics of the electron transfer process. \( k^0 \) is a function of the rate constant for either the forward or reverse reactions, \( k_f \) or \( k_b \). The relations 1.18 - 1.20 follow

\[
k_f = k^0 e^{-\alpha f(E - E^0)} \quad (1.18)
\]

\[
k_b = k^0 e^{(1 - \alpha) f(E - E^0)} \quad (1.19)
\]

\[
i_0 = nFAk^2C_{Ox}^{(1-\alpha)}C_{Red}^{\alpha} \quad (1.20)
\]

with \( C_{Ox}^{(1-\alpha)} \) and \( C_{Red}^{\alpha} \) being the bulk concentrations of the oxidized and reduced species.

The exchange current \( (i_0) \) is the residual current that exists even when the system is at equilibrium. In other words, it is the magnitude of the equal forward (reduction) and reverse (oxidation) currents. It cannot be directly measured because the net current is zero at equilibrium. Figure 1.3 (a through d) graphically shows Equation 1.17 for a system and illustrates the effect of varying \( i_0 \) (as a result of decreasing \( k^0 \)). The net
Figure 1.3: Plots of the Butler-Volmer equation demonstrating the effects of different exchange currents ($i_0$). a) $i_0 = 10 \mu A$. b) $i_0 = 1 \mu A$. c) $i_0 = 0.1 \mu A$. d) $i_0 = 0.01 \mu A$. Plots a through d show both net current and forward and reverse reaction contributions to net current. Plot e shows the area near $E^0$ with net current for differing $i_0$ plotted together. For the reaction $\text{Ox} + e^- \rightarrow \text{Red}$ with $E^0 = 0 \text{ V}$. 

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(Figure 1.3 continued)

\[ i_0 = 0.1 \mu A \]

\[ i_0 = 0.01 \mu A \]

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(Figure 1.3 continued)
current is shown along with the forward and reverse reaction currents for four different $i_0$ magnitudes. As observed, once the system moves slightly away from equilibrium one of the two components dominates. The exchange current is a direct reflection of the kinetics of an electrochemical system. Larger exchange currents result in small overpotentials needed to cause the reaction to go one way or the other. In fact, as $i_0$ approaches infinity the system approaches thermodynamic control and, without other factors, the current would be infinite as the potential is moved from equilibrium as described earlier. Conversely, small exchange currents require larger overpotentials to create significant rates of the forward or backward reactions. Figure 1.3(e) shows net currents for all four $i_0$ magnitudes near $E^0$ illustrating the change in slope with changing $i_0$.

The exchange current can be obtained by the use of Tafel plots. Rearranging the Butler-Volmer equation and plotting $\log|i|$ vs. $\eta$ will give a theoretically symmetrical plot (if $\alpha = 0.5$) as shown in Figure 1.4. The two slopes of the linear portions of the curve have slopes equal to $\alpha nF/2.3$ and $(1-\alpha)nF/2.3$ and if extrapolated they intersect at $\eta = 0$ at $\log|i_0|$.

Finally, mass transport plays a significant role in the current response as overpotentials become larger. With only kinetic control (Equation 1.17), the current exponentially approaches infinity as the overpotential is increased. In reality, Equation 1.17 does not completely describe the system response. The species concentrations at the surface of the electrode are only equal to the bulk solution concentration at equilibrium.
Figure 1.4: Tafel plot showing behavior of net current for the reaction $\text{Ox} + e^- \rightarrow \text{Red}$. Determination of exchange current ($i_0$) is shown.
for the case of soluble Ox and Red species. As soon as the system deviates from equilibrium the concentrations of species at the surface change as they are oxidized or reduced. When the potential of the system is moved negative of equilibrium Ox species are converted to Red according to Equation 1.17. Soon the surface of the electrode would be enriched with Red species. Current would quickly stop because there would be no more Ox at the surface to accept electrons. Mass transport (diffusion, convection, and migration) allows species to move towards and away from the electrode surface. Mass transport can replenish the surface of the electrode to keep the surface and bulk concentrations constant only within a limited range from the equilibrium potential. As overpotential is increased further the current will tend to level at a value called the limiting current, $i_l$. Species are reduced (or oxidized) as fast as they reach the electrode. The current is more accurately given by

$$i = i_s \left[ \frac{C_{Ox}(0,t)}{C_{Ox}} e^{-\alpha \text{inf}} - \frac{C_{Red}(0,t)}{C_{Red}} e^{\alpha \text{inf}} \right]$$

(1.21)

where $C_{Ox}(0,t)$ and $C_{Red}(0,t)$ are the concentrations of oxidized and reduced species at the surface of the electrode ($x = 0$) at time $t$. It is generally accepted that the simpler version of the expression (Eq. 1.17) is valid only to current magnitudes about 10% of the limiting current magnitude.
Corrosion and its relation to solution-phase voltammetry

As stated previously, corrosion is an uncontrolled electrochemistry experiment in the sense that the conditions are set by the environment rather than a human experimenter. The same concepts apply to corrosion that apply to solution-phase voltammetry but a few phenomena are applied mainly to corrosion. The first is the application of electron transfer kinetics to corrosion observations. The exchange current is applicable in corrosion systems in the same manner as described above. Another observation in corrosion with some metals is passivity. This is represented in Figure 1.5 for a generic system represented by

\[ M^{n+} + n e^- \rightarrow M \]  

(1.22)

As the potential is moved positive of equilibrium, the current increases as expected indicating the oxidation of \( M \). As the potential is moved move positive, however, the current dramatically decreases. This occurs because of the formation of a thin oxide film (passive film) on the surface of the electrode, which is in many cases only nanometers thick. This lower current remains constant until a more positive value is reached that has enough overpotential to break down the film or drive another oxidation reaction. Some metal cations are water-soluble, in which case passivity is not observed. Passivity is noted in many metals and is a primary reason that corrosion does not entirely consume engineering metals in field applications. Addition of chromium as an alloying element to form stainless steels results in passive film formation that resists corrosion.Iron in
Figure 1.5: Demonstration of passivity.
concentrated nitric acid is also protected by a passive layer.\textsuperscript{18} Anodizing treatments that form thick oxide layers are common especially on aluminum products such as cookware. Many metals in their oxidized states have limited solubility and a precipitated film forms, adhering strongly to the metal surface creating a thick protective film. This film eventually restricts the access of oxidizers to the metal surface thus effectively changing the \( k^0 \) for the system as it grows thicker. If the oxide precipitate does not adhere strongly it will not restrict access for oxidizers and corrosion will continue. The most common example of this process is rusting of iron where Fe is oxidized to \( \text{Fe}^{2+} \), which is soluble. The \( \text{Fe}^{2+} \) is further oxidized to \( \text{Fe}^{3+} \), which precipitates on the surface (as \( \text{Fe}_2\text{O}_3 - n\text{H}_2\text{O} \)).\textsuperscript{19, p. 929}

An important concept in corrosion is mixed potential. This idea was originated by Wagner and Traud in 1938 and has been used extensively since.\textsuperscript{20} The concept is based upon the potential and current for a corrosion system being dictated by the independent current-voltage response of the individual reactions taking place. The individual reactions are assumed to have no interdependence although reports cite limitations to this assumption.\textsuperscript{21, 22} Mixed potential theory is depicted graphically in Figure 1.6 to describe the conditions of corrosion for an arbitrary metal M (with \( E^0 = -0.25 \text{ V} \)) using oxygen reduction (assigned with \( E^0 = -0.1 \text{ V} \) for illustration) as the driving force. The top graph depicts the crossing of the oxygen reduction branch with the metal oxidation branch. At this point, the net current is zero because the oxidation current is equal to the reduction current. The potential at which this occurs is called the corrosion potential (\( E_{\text{corr}} \)) or the open circuit potential (\( E_{\text{oc}} \)). The corrosion current (\( i_{\text{corr}} \)) is
Figure 1.6: Demonstration of mixed potential theory using polarization curves for individual redox reactions of oxygen and a metal. $E^0$ and $i_0$ for the reactions are arbitrarily assigned. Top plot shows determination of $E_{corr}$ and $i_{corr}$. Bottom plot shows effect of reducing kinetics of the oxygen reaction on the system.
analagous to the exchange current discussed earlier. However, it does not represent the rates of the forward and reverse reactions as for a half-reaction at equilibrium. It represents the quantity of metal that is oxidizing (corroding) - and how much oxygen is being reduced. Changes in the kinetics of either the oxygen or metal half-reactions can have dramatic effects on $E_{\text{corr}}$ and $i_{\text{corr}}$ as illustrated in the bottom graph. The exchange current for oxygen has been reduced by one order of magnitude, possibly due to an inhibitor or passive film. Also, oxygen reduction kinetics may vary substantially with the identity of the metal.\(^3\) Comparison with the top graph shows the $E_{\text{corr}}$ to be shifted about 0.025 V negative and $i_{\text{corr}}$ to be decreased by about a factor of 3 as a result of reduced oxygen reduction kinetics.

Some notes on nomenclature are needed here. In corrosion, and to a lesser extent in classical electrochemistry, reactions are termed anodic (oxidation) and cathodic (reduction) reflecting the electrode at which the oxidation (anode) and reduction (cathode) reactions take place in a separated system. From now the terms anodic and oxidation (cathodic and reduction) will be interchanged freely. The terms active and noble are also used to describe metals (or regions) that are more or less readily oxidized, respectively. Active metals oxidize freely and have more negative reduction potentials. Noble metals tend to oxidize slowly or not at all and have more positive reduction potentials. The conventions for presenting current-potential graphs vary with discipline also. Corrosion scientists often present potential data on the y-axis (with positive potentials top and negative potentials bottom) and current data on the x-axis (often logarithmically). In chemistry, the study of voltammetry originally used mercury
electrodes that tend to oxidize if the potential is moved positive of about 0.200 V (vs. NHE). As a result, voltammetric graphs were initially plotted with current on the y-axis (with increasing reduction currents upward) and potential on the x-axis (with more negative potentials to the right). That convention remains widely in use in chemistry and will be followed in this manuscript. As a note, the convention used in Europe is similar to the chemistry convention used in the United States but positive and negative values are reversed.

The current-potential response of a system can be studied in the region around $E_{\text{corr}}$ to gain insight into the corrosion mechanism. A polarization curve is a controlled potential scan while monitoring current. The polarization experiments using a system as in Figure 1.6 would result in a curve that would appear similar to a Tafel curve but with the asymptotic portion centered around $E_{\text{corr}}$. By observing the shape of the two legs of the curve, decisions can be made about such things as whether the metal is in a passive region or if the oxygen reduction is limited by kinetics or mass transport. Another common technique to evaluate kinetics is to measure the polarization resistance ($R_p$) of the system. This is similar to a measurement in solution-phase voltammetry known as charge transfer resistance ($R_{CT}$). In this experiment, the system is scanned slowly near $E_{\text{corr}}$ (or $E^0$ for voltammetry). The current-potential dependence here is nearly linear as illustrated in Figure 1.3. The $R_p$ (and $R_{CT}$) are equal to the inverse slope of this line. The expression
\[ R_{CT} = \frac{RT}{n F i_0} \]  

contains \( i_{corr} \) (or \( i_0 \)) in the denominator, thus kinetic parameters can be obtained. \( \alpha \) drops out of the expression for \( R_{CT} \) for measurements around \( E^0 \). For \( R_p \) the expression is similar but more complex because two separate reactions have fundamentally different \( \alpha \) values. Also commonly used is electrochemical impedance spectroscopy (EIS). This technique performs a similar experiment of perturbing the potential slightly around \( E_{corr} \) but by imposing a variable frequency alternating potential. Similar information can be gained from this technique, but will not be discussed here.

A commonly used reference source in corrosion is the potential-pH diagram (or Pourbaix diagram). They will not be fully developed here but they have been constructed for a great number of metal systems.\(^3\) A Pourbaix diagram for chromium is presented in Chapter 3 (Figure 3.17). In general, they are thermodynamic diagrams that relate varying oxidation state and compounds (both soluble and insoluble) with changes in potential and pH. Pourbaix diagrams are a convenient way to predict the tendencies of a metal to be in oxidized or reduced form, in much the same way as reduction potential tables, with the added variable of pH effects.

**Forms of corrosion**

The electrochemistry of corrosion has been discussed with relation to kinetic and thermodynamic properties that govern electron transfer. The reactions manifest

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themselves in nature in many ways. A few relevant forms will be discussed here with a mention of others.

Uniform or general corrosion, as the name implies, is an oxidation of the overall surface of a metal, and the dissolution of the surface proceeds in a consistent manner. Based on corrosion current ($i_{\text{corr}}$) measurements, the amount of corrosion over time can be estimated (i.e. in $\mu$m/year). Design of materials can be modified to consider the corrosion rate. Consequently, this form of corrosion is better understood than other forms as experimental observations are reflective of the entire system.

Galvanic corrosion occurs when two dissimilar metals come into contact. When the metals make electrical contact the potential of the system must come to one value. $E_{\text{oc}}$ of the system stabilizes at a point between the open circuit potential of either metal. The reasons can be explained using mixed potential theory. The system is more complex than uniform corrosion as there are now two metals to consider along with the cathodic reaction. However, keeping in mind that at open circuit the net current is zero, we predict that one of the metals (the more active) will oxidize faster and the other (more noble) will act as a preferential site for a reduction reaction. Since the more noble metal is held at a potential more negative than its open circuit under uncoupled conditions, it likely has a more pristine surface (less oxides) than under non-coupled conditions. Oxygen reduction in particular is catalyzed on bare metals via adsorption, so galvanic corrosion can proceed at high rates. In addition, since no oxide builds up on the noble metal as in uniform corrosion the cathodic reaction can continue more or less unabated. The area ratio of anode to cathode is important in galvanic corrosion as well.
As the cathode size increases, it can support faster reduction and its exchange current (not current density) increases. Area changes lead to similar results as the kinetic effects illustrated in Figure 1.6. Increased exchange current for oxygen causes the open circuit potential to shift positive and the corrosion current to increase. Galvanic corrosion has been studied extensively, with recent reports in areas as varied as surgical implants, semiconductors, concrete reinforcement, and dentistry along with the more traditional areas such as plumbing and construction. Interestingly, the properties of galvanic corrosion are also used to prevent corrosion via cathodic protection. The material to be protected is coupled to a more active metal (called the sacrificial anode), its potential is shifted negative, and its oxidation rate is decreased. The sacrificial anode corrodes and eventually must be replaced.

Localized corrosion occurs on the surface of a single metal but involves specific sites rather than general corrosion. An important type of localized corrosion is pitting corrosion. Corrosion of this type is characterized by pits, or depressed dissolved areas on the surface of the metal. Figure 1.7 shows a diagram of a corroding pit. The pit may have a small opening leading to a larger void under the surface. Corrosion of this type is troublesome as it can lead to cracking of the metal and premature failure. Generally, reduction reactions occur around the pit as oxidation proceeds inside the pit. The pH inside the pit can become quite acidic as the dissolved metal ions combine with water to liberate $H^+$. In advanced stages, the pit may be self-sustaining with $H^+$ reduction acting as the cathodic reaction. Characterization of pitting using nominal corrosion current ($i_{corr}$) can be misleading. Since the corrosion currents are localized, the local current
Figure 1.7: Diagram of a corroding pit on the surface of a metal. Oxidation and pH drop is indicated in the pit. Reduction processes take place around the pit periphery. Adapted from Jones.3 p. 214
density (A/cm²) in a pit can be very high, causing rapid dissolution. Current densities in pits have been measured as high as 1000 A/cm².32 Metals that have passive layers are especially susceptible to pits if local breakdown of the layer occurs. Figure 1.5 shows a rapid increase in current when a critical potential positive of the passive region is reached. This is generally referred to as the stable pitting potential (E_{pit}). If the potential is scanned negative after exceeding this value the current will remain at high values even when potentials negative of E_{pit} are reached. Eventually the potential reaches a negative enough value that the surface repassivates. The mechanism of pitting initiation is unclear although it is thought to be related to local increases in surface concentration of aggressive anions such as chloride.33-35 Alloys with multiple solid phases generally exhibit localized corrosion since the different phases can generate galvanic couples. More will be presented regarding this process in the next section. Several reviews of pitting corrosion have appeared since 1990, including discussions of pitting mechanism and measurement techniques.36-45

Other forms of corrosion exist that are less relevant to the topic presented herein. Crevice corrosion is a type of localized corrosion that occurs in the confined area where surfaces are in contact, such as a washer and a bolt. Environmentally induced cracking can occur at sites where stresses are present in a corroding environment. Intergranular corrosion occurs at defects along grain boundaries, where corrosion resistance may be lower. Dealloying is the selective dissolution of an active element from an alloy, leaving the more noble element behind. Erosion-corrosion is the increased corrosion caused by high velocities of corrosive fluid.
Aluminum Alloy 2024-T3

Aluminum alloys are used widely, in part because of density, cost, and stability. Pure aluminum has the disadvantage of low strength when compared to many other metals but it also has the advantage of low density. By adding alloying elements to aluminum, the strength is increased while the lower density is maintained. Table 1.1 lists various aluminum alloys by their designation number series, with the major alloying element and applications.

<table>
<thead>
<tr>
<th>Alloy series designation</th>
<th>Major alloying element</th>
<th>Some uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>none (&lt;1% other elements)</td>
<td>Chemical equipment, decorative trim aircraft structure</td>
</tr>
<tr>
<td>2000</td>
<td>Copper (~5%)</td>
<td>aircraft structure</td>
</tr>
<tr>
<td>3000</td>
<td>Manganese (~1.2%)</td>
<td>cooking utensils, roofing signs</td>
</tr>
<tr>
<td>4000</td>
<td>Silicon (~12%)</td>
<td>Brazing and welding</td>
</tr>
<tr>
<td>5000</td>
<td>Magnesium (0.3-5%)</td>
<td>Ornamental trim, boats, gun mounts</td>
</tr>
<tr>
<td>6000</td>
<td>Magnesium/silicon</td>
<td>buildings, bridges, welded construction</td>
</tr>
<tr>
<td>7000</td>
<td>Zinc (3-8%) and magnesium</td>
<td>aircraft structure</td>
</tr>
</tbody>
</table>

Table 1.2: Aluminum alloy series classification. Adapted from Apblett.46 p. 667

Unfortunately, alloying aluminum increases its susceptibility to corrosion. The 2000 and 7000 series are most prone to corrosive attack. These alloys are the highest in copper content, which is used for strength. One of the most prone to attack is Aluminum Alloy (AA) 2024-T3 used structurally in aircraft. The T3 designation is related to the heat treatment the alloy undergoes to strengthen it. The nominal composition of AA
2024-T3 is 4.4% Cu, 0.6% Mn, 1.5% Mg with the balance aluminum. Uniform corrosion is not generally a problem with pure aluminum, as in the range of about pH 4-8 a thin layer of aluminum oxide covers the surface and provides a barrier to water and chloride ions. However, alloys are characterized by the occurrence of secondary phase precipitates. These phases can be either insoluble impurities in aluminum or compounds that form and precipitate upon heat treatment. For AA 2024-T3 the phases have been characterized into four major types, with stoichiometries of Al₃CuMg, Al₆(Cu,Fe,Mn), Al₇Cu₂Fe, and (Al,Cu)₆Mn. The designations Al₆(Cu,Fe,Mn) and (Al,Cu)₆Mn indicate that the stoichiometry is Al₆X (where X is Cu, Fe, or Mn) or X₆Mn (where X is Al or Cu in any combination summing 6). The majority (~75%) of these particles are the first two types. About 4% of the surface of the alloy is occupied by secondary phase particles. The presence of these secondary phases, sometimes called intermetallic particles, establishes galvanic couples within the alloy. When the secondary phase precipitates form, they can, depending upon the formation mechanism, deplete the immediate area around them of copper. The galvanic couples lead to localized pitting corrosion in the areas of the intermetallic particles.

Figure 1.8 presents micrographs of a sample of AA 2024-T3 that has been polished with 0.05 μm aqueous alumina slurry with various magnifications and after 48 h corrosion in 0.1 M NaCl. The 100x magnification [Figure 1.8(c)] clearly shows the presence of intermetallic phases. Al₆(Cu,Fe,Mn) particles are visually noted by their large irregular shape as characterized previously. The primary phase (noted as the matrix phase) has a composition that is near the nominal composition. The intermetallic
Figure 1.8: Optical micrographs of AA 2024-T3. Top micrograph is polished to 0.05 μm with an alumina slurry. Bottom micrograph is after 48 h in 0.1 M NaCl showing hydroxide precipitate and pitting. (a) 10x magnification. (b) 50x magnification. (c) 100x magnification. See text concerning assignment of intermetallic phases.
Figure 1.8 continued

(b) Polished AA 2024-T3 50x magnification

After 48 h in 0.1 M NaCl hydroxide precipitate

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Matrix - has near nominal composition

Possible $\text{Al}_2\text{CuMg}$ type intermetallic

$\text{Al}_6(\text{Cu,Fe,Mn})$ type intermetallic

Polished AA 2024-T3 100x magnification

After 48 h in 0.1 M NaCl hydroxide precipitate
noted as "possible Al$_2$CuMg" is denoted as such due to its uncertain assignment. The Al$_2$CuMg phase tends to be round as observed here but is generally smaller in size.\textsuperscript{51, 53}

As will be discussed in Chapter 2 the Al$_2$CuMg phase is active compared to the matrix and other intermetallic phases. Polishing in water can cause corrosion of this particle and may result in the observation of a larger surface feature. To be more general the site may be described as a probable active intermetallic that has undergone some corrosion as a result of aqueous polishing. For the remainder of this manuscript this surface feature of AA 2024-T3 will be designated "possible Al$_2$CuMg" when discussed. The badly corroded surface with pits and hydroxide precipitate is clearly observed after exposure to corrosive electrolyte.

**Inhibition of AA 2024-T3 corrosion via chromate compounds**

AA 2024-T3 is highly susceptible to localized corrosion as discussed above. Despite this, it remains an alloy that is used in aircraft and other critical structural systems. Practical applications are permitted by the use of corrosion inhibitors based on chromate compounds. Specifically, the surface of AA 2024-T3 (and other aluminum alloys) is treated to form a chromate conversion coating (CCC) and then covered with a primer containing chromate prior to painting.

The CCC is formed by immersing the aluminum alloy in acidic solution containing Cr$^{VI}$, fluoride, and accelerants such as ferricyanide. A common formulation is Alodine$^{TM}$ 1200S from Henkel Corporation (Madison Heights, MI) which was used in the investigations herein when a CCC was desired. The fluoride and low pH act to
dissolve the passive oxide layer from the surface. Bare aluminum then reacts with \( \text{Cr}^{\text{VI}} \) reducing it to \( \text{Cr}^{\text{III}} \) which begins to polymerize as the concentration of \( \text{Cr}^{\text{III}} \) increases. More \( \text{Cr}^{\text{VI}} \) then adsorbs to the \( \text{Cr}^{\text{III}} \) sol-gel and is immobilized.\(^{54,55}\) The \( \text{Cr}^{\text{VI}} \) can be adsorbed and released from the \( \text{Cr}^{\text{III}} \) backbone with changes in pH and concentration.\(^{56}\) These properties help explain the self-healing properties of CCC's that have been shown where exposed surfaces are protected if CCC coatings are in close proximity.\(^{57-60}\)

Chromate conversion coatings provide excellent protection from corrosion but there is an impetus for replacement of \( \text{Cr}^{\text{VI}} \) compounds as inhibitors. \( \text{Cr}^{\text{VI}} \) has been shown to be toxic, and has been proposed to be both a carcinogen and a mutagen.\(^{61-64}\) A particularly dangerous route of exposure is inhalation. The toxicity apparently occurs as \( \text{Cr}^{\text{VI}} \) is easily transported through cell and nuclear membranes. Once inside a cell, reduction to \( \text{Cr}^{\text{V}}, \text{Cr}^{\text{IV}}, \) and \( \text{Cr}^{\text{III}} \) trap the chromium inside the cell as they are not able to diffuse out.\(^{65}\) \( \text{Cr}^{\text{III}} \) complexes with DNA strands to cause breaks and crosslinks. \( \text{Cr}^{\text{V}} \) has been linked to physiological conditions such as bronchitis, pneumonia, and gastrointestinal, hepatic, and renal problems.

**Raman Spectroscopy**

In the study of corrosion one often desires to know the chemical identity of a metal alloy or a species on the surface (e.g. hydroxide precipitate) or in solution near the metal surface (e.g. an inhibitor). Surface techniques commonly used include X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Energy...
Dispersive X-Ray Spectroscopy (EDS) and Wavelength Dispersive X-Ray Spectrometry (WDS). These probes are quite sensitive and can be focused microscopically onto a surface to characterize inhomogeneities, thus providing valuable spatial definition. The intermetallic phase particles in AA 2024-T3 have been characterized with EDS and WDS.\(^{48}\) The information obtained is generally elemental rather than molecular in nature as the use of high-energy electrons perturbs inner-shell electrons of atoms, although oxidation state can sometimes be obtained and used to infer bonding. Forms of mass spectrometry such as Secondary Ion Mass Spectrometry (SIMS) are also employed, using high energy ion beams to detach atoms and molecules from a surface which are directed into a mass analyzer. Molecular information (mass number) is obtainable but the ion beam can also cause degradation of the surface. In addition, these surface techniques are not amenable to in-situ study of surfaces in corrosive solution.

Vibrational spectroscopy probes the bonding of molecules through interactions of radiation of lower frequency than the electron beams used as described above. Since bonding is probed, identification of different molecules with the same elemental constituents is possible. Surface species, either corrosion inhibitors or corrosion products, are likely candidates for investigation. Vibrational spectroscopy also tends to be quite amenable to solution-phase investigations and thus is attractive as an in-situ technique. Vibrational techniques also have been adapted for microscopic analysis, offering the possibility of spatial resolution of surface interactions. However, unlike the surface techniques described above, vibrational spectroscopy is not a good choice for determining elemental composition. A discussion of vibrational spectroscopy with a
focus on the Raman effect and some examples of use in corrosion-related investigations follows.

One of the fundamental properties of a molecule is motion. Every molecule has $3n$ degrees of freedom with respect to motion where $n$ is the number of atoms in the molecule. This motion consists of translational, rotational, and vibrational components. Translations are movement of the molecule along a line or displacement from point to point. Every molecule has three translations corresponding with $x$, $y$, and $z$ coordinates. Rotations are angular displacements around the center of mass of a molecule. Molecules generally have three rotations around the $x$, $y$, and $z$ axes. The exception is for a linear molecule since two of the axes of rotation are identical. These molecules have two rotations. The remainder of the degrees of freedom is taken by molecular vibrations. These are oscillations between nuclei in a molecule. The oscillations may be a complex mixing of stretches, bends, and twists between two or more nuclei. A particular vibration is characterized by its oscillation frequency. By subtraction of rotations and translations, there are $3n-6$ vibrational degrees of freedom ($3n-5$ for linear molecules). The water and carbon dioxide molecules have 3 and 4 vibrations as depicted in Figure 1.9. Obviously, the number of vibrations increases quickly with increasing number of atoms in a molecule. Consider that a simple sugar molecule, glucose ($C_6H_{12}O_6$), has 66 different vibrations. The more complex sucrose ($C_{12}H_{22}O_{11}$) has 129 different vibrations! Some of the vibrations may be identical due to the symmetry of the molecule (said to be degenerate) but the numbers are still large.
Figure 1.9: Vibrations for CO$_2$ and H$_2$O molecules. + and - indicated in and out of page plane motion. Adapted from Skoog, et al. 66 pp. 388-389

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Vibrational spectroscopy uses electromagnetic radiation to probe the vibrations of a molecule. The most common technique used to study the vibrations of molecules is infrared absorption (IR) spectroscopy. This technique is well established and is based on the absorption of radiation in the infrared region of the electromagnetic spectrum (10^-13000 cm^-1). If the molecule undergoes a change in dipole moment because of a particular vibration, it can absorb radiation having the same frequency as the vibration.

Raman spectroscopy is also a form of vibrational spectroscopy. As light passes a molecule some of it can be scattered. This process is not an absorption process but an interaction of an incident electromagnetic field with the electron cloud of the molecule. If the molecule is polarizable, the incident radiation induces an oscillating dipole in the molecule that has the same frequency as the incident radiation. The oscillating dipole emits this radiation from its own field in all directions. This is known as Rayleigh scattering. C. V. Raman first discovered in 1928 that some of the scattered light had frequencies that were different from the incident frequency. This arises due to the vibrations of the molecule. If a vibration alters the polarizability of a molecule (not dipole moment as for IR spectroscopy), the field of the oscillating dipole can change as well, and the scattered light is shifted in frequency. The difference in frequency between the incident light and the scattered light is known as the Raman shift (normally expressed as cm^-1). The shift in frequency may be to longer or shorter wavelengths, known as Stokes and anti-Stokes shifts, respectively. The full expression for scattering is
\[ P = \alpha E_0 \cos 2\pi v_0 t + E_0 Q'_i \left( \frac{\delta \alpha}{\delta Q'^0_j} \right) \cos 2\pi (v_0 + v_j) + \cos 2\pi (v_0 - v_j) \]  

(1.24)

| Rayleigh | anti-Stokes | Stokes |

where \( P \) is the polarization (or intensity of scattered light), \( \alpha \) is the polarizability, \( E_0 \) is the incident electric field, \( v_0 \) is the frequency of the incident radiation, \( Q'_i \) represents a vibration (or normal mode), and \( v_j \) is the frequency of the vibration. The parts of the equation that relate to the three discussed forms of scattering are indicated. Graphically, the scattering process is shown in Figure 1.10 and is compared with IR and electronic absorption processes.

In general, the intensity of the scattered light is much lower than the intensity of incident light. Additionally, of the scattered light, the Raman scattering intensity is much lower than the Rayleigh scattering intensity. The anti-Stokes shifts are much weaker than Stokes shifts because they arise from molecules that are in excited vibrational energy levels (only appreciable at higher temperatures). As a comparison, the probability of a molecule to scatter shifted frequencies is about \( 10^{-10} \) as likely to occur as the absorption of a photon in an IR spectroscopy.\(^{69} p. 3 \) Even if a molecule has vibrations that change the polarizability the observed Raman effect may be very weak or very strong. It is related to the magnitude of the \( \frac{\delta \alpha}{\delta Q'_j} \) term of the scattering equation and is called the Raman cross section (\( \sigma_j \)).
Figure 1.10: Illustration of Raman effect using energy level diagrams. Compared with Rayleigh scattering and electronic and infrared absorptions.

a scattering from molecules in the ground state illuminated with radiation of frequency $v_0$.

b scattering from molecules in a vibrationally excited state illuminated with radiation of frequency $v_0$. 

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With the low probabilities of the Raman effect, one might wonder why it is useful at all since it measures vibrational frequencies as does IR absorption spectroscopy. Some properties of the Raman effect make it attractive, particularly for studying aqueous corrosion. First, Raman scattering takes place regardless of the wavelength of incident radiation and is proportional to the intensity of the incident radiation. Thus, the advent of lasers allowing very high intensities was fortuitous for Raman spectroscopists. Second, the Raman cross-section (thus the intensity of scattering) is related to frequency of incident radiation as a $v^4$ function. Lower wavelengths greatly increase the observed intensity. Third, the selection rule for the Raman effect is a change in polarizability, not a change in dipole moment as for IR. Molecules often have vibrational frequencies that change either but not both of these properties, due to symmetry. Thus, some bands are observable with Raman that are not with IR. Fourth, as a result of the selection rules, water has very strong IR absorption but weak Raman scattering. Raman spectra can easily be taken with minimal interference from water. This opens a wide window for the use of Raman in applications where IR is limited by water absorption.

One of the major interferences for observing Raman scattered light is fluorescence. As shorter wavelengths of incident radiation are used (to increase scattering intensity) electronic transitions may occur that result in fluorescence. The intensity of fluorescence is often $10^5$ to $10^8$ times that of Raman scattering and thus can easily drown out the Raman shifted photons. A number of higher-wavelength lasers have been developed (including diode lasers and infrared lasers) that reduce fluorescence.
although at the cost of reduced observed intensity due to the $v^4$ loss of intensity discussed earlier.

Other technological advancements that have aided in advancing Raman spectroscopy include the development of charge-coupled device (CCD) detectors that are highly sensitive and permit multiwavelength detection rather than scanning.\textsuperscript{70, 71} High quality laser rejection filters that effectively filter the Rayleigh scattered light are available. In addition, the ever-increasing capabilities of personal computers make large amounts of data collection and manipulation possible.

In addition to the above descriptions, Raman intensities may be increased by other factors. These are so-called resonance Raman and surface enhanced Raman. Resonance Raman takes place when the incident radiation has wavelengths near electronic transitions for a molecule. The Raman cross-section increases as the electronic transition is neared.\textsuperscript{72, 73} Often, resonance Raman will selectively enhance particular vibrations without enhancing others.\textsuperscript{74} Surface enhanced Raman is a complex process that permits intensity enhancement of up to $10^6$. It was first reported in 1974 and involves the increase in Raman intensity for molecules bonded or near selected metal surfaces.\textsuperscript{75} The intensity increase is a result of both electric field enhancement and chemical enhancement and has been discussed extensively in the literature.\textsuperscript{76-81}

Instrumentation for Raman spectroscopy is conceptually rather simple. A schematic of a Raman spectrometer is shown in Figure 1.11. The laser beam is focused onto the sample to increase its power density and maximize the intensity of the Raman scattering. The fact that Raman scattering occurs in all directions allows many options
Figure 1.11: Schematic of a Raman spectrometer
for spectral collection. Liquid and solid (or surface) samples are all easily adapted to most spectrometers. Most Raman spectrometers use 180° collection optics. The focused incident light from the laser source strikes the sample and the scattered light returns along the same axis. Since the laser beam is focused and the Raman scattered light is collected through the same lens alignment of the spectrometer is considerably easier. The collected light is filtered with a band rejection filter to remove the Rayleigh scattering frequencies and dispersed onto a CCD detector via a grating in the spectrograph. Raman microscopy is also used with the laser beam being focused through a microscope objective. The general optics are similar but the overall setup is considerably more complex to steer the laser and scattered light through the system. The tightly focused laser can be used to probe samples at multiple depths or to focus on specific objects on a surface.

Raman spectroscopy has been used effectively to study corrosion products formed on the surface of metals. Chromate films have been particularly amenable to study by Raman spectroscopy as differences in the bonding of CrVI are distinguishable. Vibrational band differences between AlodineTM 1200S solution based CrVI and chromate conversion coating film species observed with Raman allowed the assignment of the CrIII-O-CrVI mixed oxide species to the CCC. This assignment provided information related to CCC structure and the binding and release of CrVI into solution which is related to the self-healing properties of CCC’s. The accumulation of CrVI at corroding pits in AA 2024-T3 was demonstrated using Raman microscopy in corrosive aqueous solution. Raman spectral features differentiated the CrVI in solution within a pit from CrVI.
adsorbed to aluminum hydroxide corrosion precipitate within the pit. Small differences in intensities of three spectral bands of synthetic Al$^{\text{III}}$.O-Cr$^{\text{VI}}$ with pH were used estimate the pH at which adsorption occurred. Solution-phase speciation of Cr$^{\text{VI}}$ (as HCrO$_4^-$, CrO$_4^{2-}$, and Cr$_2$O$_7^{2-}$) based upon pH and concentration was achieved as the three Cr$^{\text{VI}}$ species have distinct bonding and symmetry thus differences in Raman response.$^{86}$

The versatility of Raman spectroscopy should prove valuable in the evaluation of possible replacements for chromate compounds. Both confirmation of identity and spatial detection on heterogeneous alloy surfaces should be possible. Many candidates for replacements of chromate are organic molecules. Many organic compounds tend to be polarizable (a requirement for Raman scattering) and have quite large Raman cross sections that aid in identifying interactions via Raman spectroscopy.

**Overview of Research**

The research presented in this dissertation probed the inhibition mechanism of chromate in the context of corrosion of aluminum alloy 2024-T3. Information was gathered with electrochemical and spectroscopic techniques. The data acquired, however, extends beyond the mechanism for protection of AA 2024-T3 to the understanding of properties of chromate ion interaction with surfaces and effects on electron transfer. This information aids in the selection and evaluation of possible compounds to replace chromate-based inhibitors.

Chapter 2 presents an examination of cathodic and anodic effects of chromate ion based inhibition using a separated-reaction approach. It expands on research presented
Galvanic couples were studied in the context of intermetallic galvanic couples occurring on the surface of AA 2024-T3 by using a zero-resistance ammeter. Pure metals were substituted as models for the anodic and cathodic sites on AA 2024-T3 and observations are explained with mixed potential theory. The approach was extended to other systems to gain insight about the chromate inhibition mechanism and demonstrate the validity of the technique.

Chapter 3 is concerned with the actions of chromate as a cathodic inhibitor. Voltammetric measurement techniques (both diffusive and convective) were used to characterize the mechanism and properties of chromate interaction with various electrodes including copper, glassy carbon, and platinum. The effect of chromate on non-corrosion related electron transfer processes was examined to aid the understanding of its superior actions as an inhibitor.

Chapter 4 applies information gained from the actions of chromate ion inhibition to the evaluation of two classes of organic compound, dithiocarbamates and diazonium salts, as possible inhibitors. The compounds' interactions with both AA 2024-T3 and model samples were examined via Raman spectroscopy. Finally, the species were evaluated electrochemically with methods used to evaluate chromate in earlier chapters.

An appendix is included that discusses initial observations of conductance switching of diazonium salt modified electrodes.
CHAPTER 2

APPLICATION OF GALVANIC COUPLING TO THE STUDY OF CORROSION INHIBITION PROCESSES OF CHROMATE ON ALUMINUM ALLOY 2024-T3 VIA A SEPARATION OF REACTIONS APPROACH

INTRODUCTION

Aluminum alloy 2024-T3 (AA2024-T3) has been well documented to be highly susceptible to corrosion, particularly localized pitting corrosion and intergranular corrosion. As discussed in chapter 1 AA2024-T3 has a nominal composition of 3.8-4.9% Cu, 1.2-1.8% Mg, 0.3-0.9% Mn, 0.5% Fe, 0.5% Si, 0.25% Zn, 0.1% Cr, 0.05% Ti with the balance being aluminum. However, it is an inhomogeneous alloy containing several distinct solid phases that form upon production. These secondary-phase intermetallic particles are compositionally higher in alloying elements as compared to the alloy matrix (having the nominal composition). Explanations for increased corrosion susceptibility for AA2024-T3 center on the existence of these particles. Intermetallic particles greater than 0.2 μm in diameter have been characterized into four groups, accounting for about 85% of particle types, classified as Al₂CuMg (S-phase), Al₆(Cu,Mn,Fe), Al₃Cu₂Fe, and
Figure 2.1 shows a micrograph of AA2024-T3 polished to 0.05 μm with alumina. Al$_2$CuMg (S-phase) and Al$_6$(Cu,Mn,Fe) phases are shown and are defined visually as discussed in Chapter 1 (Figure 1.8). The open circuit potentials of many of these intermetallic particles have been compiled and are positive (or become positive after de-alloying - explained below) versus the alloy matrix phase. Subsequently, local galvanic couples occur with the intermetallic sites becoming cathodes. This may explain the observation of pitting of the alloy matrix around these intermetallic particles. Al$_2$CuMg particles have open circuit potential values negative of the alloy matrix and thus are initially anodic. Recent advances have revealed that these S-phase particles de-alloy by dissolution of the Mg and Al portion of their composition. This leaves primarily a copper sponge-like residue. Another study using Scanning Kelvin Probe Force Microscopy found the Al$_2$CuMg particles to be more noble (open circuit potential more positive) than the matrix in the as-polished condition due to a surface film. Film damage (either by scratching or prolonged exposure to chloride) caused the potential of the particles to become active (open circuit potential more negative) relative to the alloy matrix and dissolution of the particles ensued. Mg and Al dissolution from these particles can result in the above-mentioned porous copper residue that is presumably highly cathodic due to its more positive open circuit potential (vs. the matrix). Copper from the intermetallic sites has been shown to migrate during the corrosion process. Secondary corrosion occurs at sites where it is deposited. Whether this migration results from dissolution into solvated ions or
Figure 2.1. Optical micrograph of AA2024-T3 polished to 0.05 μm Al₂O₃. Assignment of Al₂CuMg intermetallic is uncertain due to polishing in water (see Figure 1.8).
de-attachment of zero-valent particles due to dissolution of the surrounding constituents is not clear.

**Chromate as a corrosion inhibitor**

Chromate conversion coatings (CCC) have been used to control corrosion of AA2024-T3 and other metal alloys since the 1950's. In recent years, research has begun to develop alternative corrosion inhibitors due to the toxicity of chromate compounds. A major area of study in this regard is the elucidation of the inhibition mechanism of chromate species. Many aspects of CCC's have been examined. The mechanism of CCC formation during treatment with Alodine 1200™ has been examined, revealing the reduction of solution-phase Cr\textsuperscript{VI} to form a Cr\textsuperscript{III}(OH)\textsubscript{3} film.\textsuperscript{54, 56, 58, 60} Subsequently, Cr\textsuperscript{VI} is incorporated into the film as a Cr\textsuperscript{III}-Cr\textsuperscript{VI} mixed oxide. Furthermore, the release of the incorporated Cr\textsuperscript{VI} species into solution from the CCC has been demonstrated, as has migration to pits or defects. Cr\textsuperscript{VI} is released from the mixed oxide with decreasing solution concentration of Cr\textsuperscript{VI} and increasing pH. The pH and concentration dependent release of Cr\textsuperscript{VI} aids in explaining the active inhibitor (or self-healing) properties of CCC's. Protection of untreated AA2024-T3 was afforded by being in close proximity of a CCC coated AA2024-T3 sample. The activity of Cr\textsuperscript{VI} as a cathodic or anodic inhibitor - or both - has been the subject of many investigations in this regard.\textsuperscript{89, 96-103} Anodic inhibition mechanisms of chromate have been studied extensively. Initial ideas of CCC inhibition centered on the formation of a Cr\textsuperscript{III} film that sealed the alloy surface from the corrosive electrolyte.\textsuperscript{58, 104} In this model, cracks or holes formed in the film are plugged.
by Cr$_2$O$_3$ [or Cr(OH)$_3$] as a result of the reduction of Cr$^{VI}$ from the CCC. Accumulation of a Cr$^{VI}$-Al$^{III}$ mixed oxide has been observed in actively growing pits but reduction to Cr$^{III}$ was not reported. Others have presented research on pure aluminum indicating that CCC formation results in a positively charged surface that effectively repels aggressive chloride anions. However, solution-phase Cr$^{VI}$ was not observed to reduce aluminum dissolution according to one study. The possibility of cathodic inhibition by chromate compounds has not been studied thoroughly for aluminum alloys. However, thin films of Cr$^{III}$ formed on platinum and gold electrodes from reduction of Cr$^{VI}$ effectively inhibited several reduction reactions (including oxygen). Sehgal et al. showed that the attack of AA2024-T3 at open circuit was eliminated by the introduction of a small amount of dichromate into the chloride solution, whereas large amounts of dichromate were needed to have a small effect at an applied potential just above the open circuit value. This result implied strong cathodic inhibition by Cr$^{VI}$.

**Separation of reactions**

Difficulty in studying the corrosion of AA2024-T3 and its inhibition arises due to multiple reactions taking place in the same nominal surface area. Anodic reactions include oxidation of aluminum (followed by precipitation as the hydroxide or dissolution depending upon pH) and possibly other alloying elements present in the AA2024-T3. Cathodic reactions include reduction of dissolved oxygen, H$^-$, and water itself. Since all reactions occur on one electrode, interactions between areas of oxidation and reduction undoubtedly occur. Previous studies have utilized current density and potential mapping.
to study local phenomena on AA2024-T3 electrodes.\textsuperscript{94, 95, 110} The corrosion current that flows between anodic and cathodic sites on the surface of the corroding alloy is not easily measurable. A separation of the anodic and cathodic reactions might enable a better understanding of the inhibition mechanism by allowing measurement of this current. Furthermore, a galvanic coupling experiment in which a segregated anode and cathode are connected but allowed to float without an externally applied potential approximates the mixed potential relevant to field conditions. Instrumentation used in measuring the galvanic current is described in the next section. Major differences in chromate effects on AA2024-T3 corrosion have been reported when foil penetration experiments at open circuit were compared to potentiostatic experiments involving an imposed potential.\textsuperscript{102, 103} Previously, Liao and Wei used a segregated anode and cathode to establish relationships between the current density and cathode: anode area ratio for aluminum coupled to model alloys in order to understand intermetallic based pitting.\textsuperscript{111} In a similar study, Hihara and Latansion showed the usefulness of separation in studying aluminum with reinforcing constituents such as graphite and silicon carbide.\textsuperscript{112}

The approach followed here involves coupling two electrodes in either a single-cell or split-cell configuration. The schematic of the experimental cells are shown in Figure 2.2. The galvanic current is measured via a zero resistance ammeter as discussed in the next section. The split-cell contains a porous glass frit that allows ion migration (thus current flow) without bulk mixing of the solutions in the two compartments. One of the electrodes becomes the net cathode and the other the net anode. The "net" terminology is used because each electrode can support both oxidation \textit{and} reduction.
Figure 2.2. Schematic of single- and split-cell apparatus.
reactions. At the net cathode the rate of reduction reactions is much greater than the rate of oxidation reactions. The opposite is true at the net anode. In most cases, the rate of the reaction that dominates (oxidation or reduction) is many orders of magnitude greater than the rate of the opposing reaction such that the opposing reaction is no longer considered and the "net" terminology can be dropped. Five combinations of electrodes were examined. The couples were (1) Al/Cu, (2) AA2024-T3/Cu, (3) AA2024-T3/AA2024-T3, (4) Cu-Cu and (5) Al-glassy carbon. The first three couples were used to study reactions relevant to the corrosion of AA2024-T3. The fourth and fifth couples were used to investigate some of the properties of chromate itself and will be discussed more in the results section. Figure 2.3 shows the approach used in developing the first three couples. With the Al/Cu couple the individual corrosion reactions are for the most part segregated with cathodic reactions occurring on the Cu electrode and anodic reactions on the Al electrode. The galvanic current measured here should represent the majority of the corrosion current. The AA2024-T3/Cu couple presents a more complex model with cathodic reactions taking place on both the copper electrode and the AA2024-T3 electrode. Anodic reactions are confined to the AA2024-T3 electrode. In this case, not all of the galvanic current can be measured. Some is lost in local reactions taking place on the AA2024-T3 electrode. The AA2024-T3/AA2024-T3 couple can be turned into a galvanic couple by isolating the electrodes and deaerating (removing dissolved oxygen) one side of the couple with argon gas. Cathodic reactions now primarily occur on the aerated electrode while both electrodes support anodic reactions.
Figure 2.3. Simplified view of corrosion on AA2024-T3 showing galvanic couple between intermetallic particle and matrix and approach for studying galvanic current via separation of reactions.

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The same limitations on the current measurement as for the AA2024-T3/Cu couple are present here. Separation of the electrodes necessarily eliminates some of the interaction between reactions occurring on the surface of a single corroding electrode. Localized corrosion of Al or Al alloys in the form of pitting or grain boundary attack always involves some amount of local hydrogen evolution because of the low potential at the active site. The amount of hydrogen evolution has been measured to be about 15% of the anodic current.\textsuperscript{100, 113} However, the three separate conditions studied allow for monitoring of a galvanic current while controlling environmental conditions independently at the electrodes. The more complex couples allow some local interactions to take place while general galvanic corrosion current and observation of Cr\textsuperscript{VI} effects on individual processes is studied.

**Use of a zero-resistance ammeter (ZRA) to measure galvanic current**

The measurement of the galvanic current generated when two electrodes are connected and exposed to an electrolyte is achieved by the use of a zero-resistance ammeter. This differs from a conventional ammeter in the requirement of zero-resistance. Conventional ammeters introduce a meter resistance (\(R_m\)) that allows for the measurement of a potential drop and thus the calculation of current via Ohm's Law. The problem with this in electrochemical systems (vs. electronic systems) is that the potential drop caused by the meter resistance alters the cell potential and the potential difference between the two electrodes of the galvanic couple is no longer zero. This is illustrated in
Figure 2.4.3 p.181 Galvanostatic ZRA’s were first developed to measure galvanic current. They operate based upon an external voltmeter measuring the potential difference between the coupled electrodes. The galvanostat introduces a supplemental current that forces the potential of the electrodes to come to the same value. The current required to do this is the galvanic current. The problem with this type of system is that the galvanostat is manually adjusted and the measurements are not continuous. This also perturbs the system similarly to Figure 2.4 as the current is being adjusted.

Potentiostatic ZRA’s were first described by Jones\textsuperscript{114} and Devay, et al.\textsuperscript{115} They have since become a popular instrument for use in studying galvanic corrosion.\textsuperscript{116-126} They operate by connecting two electrodes to the leads of a three-electrode potentiostat. One electrode is connected to the working electrode lead and the other is connected to both the reference and the auxiliary electrode leads. By setting the difference between the reference electrode and the working electrode to zero volts, the potentiostat applies a current between the counter and working leads to affect this requirement. This applied current is the galvanic current. Since the reference lead is connected to one of the electrodes rather than an external reference electrode the potential of the system can drift as environmental conditions change during the course of an experiment. An external voltmeter can be used to monitor the system potential against a known reference.

Overview

The experiments described in this chapter have two goals. First, the use of galvanic coupling via separation of reactions to approximate the phenomena of AA2024-
Figure 2.4. Error introduced by measuring galvanic current with a traditional ammeter. The potential of the couple is not $E_{oc} \text{ couple}$ but $E_A$ at the anode and $E_C$ at the cathode. The measured current is less than the true current due to potential drop caused by meter resistance $R$. Adapted from Jones.\textsuperscript{3 p. 181}
T3 corrosion is examined. Secondly, the action of chromate compounds (as Alodine 1200™ produced CCC or solution chromate itself) is examined. It should be noted that the experiments described herein using the AA2024-T3/AA2024-T3 galvanic couple were performed outside of this study and described elsewhere. However, the use of electrochemical polarization studies to explain the results of the studies as a whole required the inclusion of the AA2024-T3/AA2024-T3 couple data.

EXPERIMENTAL

Barnstead NanoPure™ water with a resistivity of 18 MΩ-cm was used for rinsing and solution preparation in all cases. Reagent grade K₂Cr₂O₇ (Alfa Aesar) and Alodine™ 1200S powder (Henkel Corp.) were used to make Cr⁶⁺ solutions. Reagent grade HNO₃ (Fisher Scientific) was used for pH adjustment. Electrodes were made from commercial Al sheet (99.999%, 0.5 mm thick, Alfa Aesar), Cu sheet (99.99% 1.0 mm thick, Alfa Aesar), Cu rod (99.99%, 5 mm diameter, Goodfellow Metals), Cu wire (99.9%, 0.5 mm diameter, Aldrich), and Aluminum Alloy 2024-T3 sheet (0.025 in. thick, ALCOA). Electrode materials (sheet samples were cut to 1 cm² in all cases) were attached to copper wire with silver epoxy resin (SPI Supplies/Structure Probe Inc.), and embedded in epoxy (Buehler). They were then mechanically polished with successively finer SiC papers under running water (Buehler: 240, 400, 600, 800, 1200 grit), rinsed with water, and dried under a stream of hot air. Water was used as polishing solvent instead of an organic solvent to avoid adsorption of organic compounds as previously reported. Commercial glassy carbon electrodes (Bioanalytical Systems, GC20) were
used in some cases. They were polished in alumina slurries (1.0, 0.3, and 0.05 μm. Buehler) followed by approximately 5 minutes sonication in (1) water, (2) 3:1 v/v isopropanol (Mallinckrodt)/activated carbon (Charcoal Activated Powder Extra Pure, EM Industries), and (3) water before being dried with argon gas similar to the procedure described by Ranganathan, et al.128

Sample pretreatment with CrVI solutions was performed in some experiments as noted in the text. For Alodine™ 1200S pretreatment, the polished sample was immersed in Alodine™ 1200S solution (7.6314 g/L with HNO3 added to pH 1.25) for 5 minutes, rinsed with water, allowed to air-dry for 2 hours, and used immediately. For Cr2O72- pretreatment the polished sample was immersed in 0.4 M K2Cr2O7 for 2 hours, rinsed with water, allowed to air-dry for 2 hours, and used immediately.

Electrochemical measurements were performed using a Gamry Instruments PC3/300™ Potentiostat/Galvanostat/ZRA with Framework™ (Version 3.11) and DC105™ DC Corrosion Measurement software. Galvanic current experiments were performed in either single-cell or split-cell configuration as shown in Figure 2.1. Galvanic current between the two electrodes and potential of the system was measured using the Gamry hardware in zero-resistance-ammeter (ZRA) configuration.

Potentiodynamic polarization experiments were performed using a standard three-electrode electrochemical cell. Experiments utilized Ag/AgCl as the reference electrode (all potentials quoted are with respect to this reference), Pt wire as the counter electrode, and 0.1 M NaCl as the electrolyte. Compressed Ar (prepurified 99.998%, Praxair) gas was used for deaeration. Unless specifically stated otherwise “aeration” refers to systems

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that were open to the atmosphere and "deaeration" refers to systems that have been purged with argon for a minimum of 20 minutes. In a few cases (where stated) aeration was achieved by saturation with O₂ (extra-dry, Praxair). Solution additions of chromate were made using 0.05 M K₂Cr₂O₇ (0.1 M total Cr⁶⁺) in 0.1 M NaCl as noted in the text and figures. The pH of NaCl solutions preceding Cr⁶⁺ addition was uncontrolled, but was typically 5.5-6.0, and decreased by less than 1 unit upon addition of Cr⁶⁺. Injection experiments with controlled pH showed only minor differences in galvanic response for pH 4-6. Solution additions of H₂O₂ (30% AR grade, Mallinckrodt) were made using 0.9 M H₂O₂ in 0.1M NaCl.

Microscopy was performed using a microscope mounted on a Dilor X-Y Raman spectrometer. A 10x microscope objective was used. Samples to be observed were mounted and leveled by hand. Focusing for micrograph recording was performed by attempting to focus on unmarred areas of the surface. Movement of focus was made to determine the presence of pits (deeper focus) or precipitates (shallower focus) on the alloy surface.

RESULTS

The "single" cell (Figure 2.2) with pure Al and Cu electrodes was examined initially. This system should provide the greatest separation of anodic and cathodic reactions. The effects of convection, aeration, and inhibition by Cr⁶⁺ addition on the current for the Al/Cu couple are shown in Figure 2.5. A stable current of about -30 μA a
Figure 2.5. Current and potential vs. timeplots for single cell containing pure Al and pure Cu electrodes, saturated with Ar or O₂ as indicated. Electrolyte was 0.1 M NaCl. Stirring accomplished by injection of gas bubbles. K₂Cr₂O₇ was added at 2 h to give [Cr⁶⁺] = 50 mM. Both electrodes were 1 cm².
and mixed potential of about -650 mV was initially established under quiescent conditions in electrolyte solution exposed to the atmosphere. Negative current refers to electron flow from the net anode to the net cathode (in this case aluminum to copper). Solution stirring and oxygen saturation by bubbling caused an increase in the current by an order of magnitude while the potential shifted positive to about -550 mV. De-aeration of the solution with argon bubbling caused the current to decrease to a level similar to that of the quiescent solution even with solution stirring, while the potential shifted negative to about -750 mV. Re-introducing oxygen to the system returned the current and potential to previous levels. Addition of K₂Cr₂O₇ (to a total of 50 mM Cr⁶⁺) to the system resulted in an immediate reduction in the galvanic current. Even with oxygen saturation and stirring, the current was below that of the quiescent or deaerated solution prior to Cr⁶⁺ addition. Closer examination of the current reveals that the same trends occurred for aeration/de-aeration and stirring as observed for the uninhibited system but at greatly reduced current levels. The potential shifted negative after Cr⁶⁺ was added but gradually returned to -650 mV. After changing from Ar to O₂ saturation or back, the potential slowly returned to ~ -650 mV. In addition both the current and potential exhibited less noise after Cr⁶⁺ addition.

The effect of electrode pretreatment with Cr⁶⁺ from either exposure to Alodine™ 1200S or chromate solution was studied using a quiescent single-cell aluminum-copper couple. Pretreatment methods were explained in the Experimental section. Experiments were run in three configurations. These were (1) Cu electrode polished and pretreated – Al electrode polished only, (2) Cu electrode polished only – Al electrode polished and...
pretreated, and (3) the control experiment with both electrodes polished only. Results of pretreatment with Alodine™ 1200S are presented in Figure 2.6. Pretreatment of the copper electrode with Alodine™ 1200S resulted in an initial galvanic current significantly lower than the case for pretreatment of the aluminum electrode. Currents after Alodine pretreatment of the aluminum electrode were similar to the control, in which neither electrode was exposed to Cr⁶⁺. When K₂Cr₂O₇ was added to the solution to a final concentration of 50 mM Cr⁶⁺, the galvanic current decreased in all cases, but by varying amounts. Pretreatment in chromate (0.4 M K₂Cr₂O₇) instead of Alodine™ 1200S yielded very similar behavior as shown in Figure 2.7.

Split-cell experiments using an aluminum-copper couple were employed to better examine the individual anodic and cathodic reactions and current inhibition. The galvanic current and potential were monitored for aluminum-copper couples under varying conditions of mass transport and aeration. Employment of the split-cell allowed stirring and aeration/de-aeration to be studied in either the anodic or cathodic reaction chamber. The separation of anodic and cathodic reactions for the Al/Cu split cell is illustrated in Figure 2.8. Alternation of Ar and O₂ saturation in the copper side caused large variations in current, with a negative current again referring to electron flow from aluminum (net anode) to copper (net cathode). Introduction of oxygen stirring in the copper chamber caused the current to increase from its initial quiescent value of approximately -25 µA to about -125 µA. When argon stirring was employed, the current decreased to nearly the level of the aerated quiescent solution despite efficient mass transport. The same alternation of Ar and O₂ on the Al side had no observable effect,
Figure 2.6. Behavior of Al/Cu coupled in aerated, quiescent single-cell after pretreatment of either electrode in Alodine™ 1200S for 5 min. Electrolyte was 0.1 M NaCl. K$_2$Cr$_2$O$_7$ was added and the solution stirred momentarily at 1 h to give [Cr$^{VI}$] = 50 mM. Both electrodes were 1 cm$^2$. 

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Al/Cu Single Cell

Figure 2.7. Same as Fig. 2.5 but electrodes were pretreated by exposure to 0.4 M $K_2Cr_2O_7$ for 2 h. $K_2Cr_2O_7$ added at the times indicated.

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Figure 2.8. Current and potential behavior of Al/Cu couple in split-cell. Ar and O\textsubscript{2} were bubbled as indicated into either the (solid line) Cu or (dotted line) Al compartment with the other compartment quiescent and open to atmosphere. In the first (left) panel, both compartments were quiescent. Electrolyte was 0.1 M NaCl. Both electrodes were 1 cm\textsuperscript{2}.

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indicating that O₂ reduction was not active on aluminum, presumably due to the passive oxide film. The potential of the system shows corresponding shifts positive and negative with oxygen and argon stirring in the copper chamber that are absent when the aluminum chamber is stirred.

The effect of solution Cr⁶⁺ on the cathodic and anodic reactions of an aluminum-copper galvanic couple using the split-cell configuration are shown in Figure 2.9. The initial galvanic current established in this experiment is about -6 μA (as compared to larger values in earlier experiments) due to the use of a 0.20 cm² Cu rod as the cathode (vs. previously used 1 cm² Cu electrodes). After one hour of galvanic corrosion under quiescent conditions, K₂Cr₂O₇ was added (to ~5mM Cr⁶⁺) to either the aluminum or copper half-cell. The galvanic current was inhibited when Cr⁶⁺ was added to the copper cell with a decrease to approximately -2 μA. When Cr⁶⁺ was added to the aluminum cell the current remained essentially constant. The potential shifted slightly in both experiments but in opposite directions. When Cr⁶⁺ was added to the copper chamber the shift was negative. Interestingly, a positive potential shift was observed when Cr⁶⁺ was added to the aluminum chamber despite the lack of change in the galvanic current. The experiment was repeated with fresh electrodes and aerated solutions, with incremental addition of K₂Cr₂O₇ to the Cu compartment. After stabilization of the current to -58 μA, the addition of Cr₂O₇²⁻ to yield total Cr⁶⁺ concentrations of 1, 10, and 25 mM decreased the current to -18, -6, and -6 μA, respectively. For the same additions, the potential shifted negative from -575 mV to -650, -680, and -680 mV.
Figure 2.9. Effect of Cr$^{VI}$ addition to an Al/Cu couple in aerated, quiescent split-cell. K$_2$Cr$_2$O$_7$ was added to either Al or Cu compartment and the solution stirred momentarily at 1 h to give [Cr$^{VI}$] = 5 mM. Electrolyte was 0.1 M NaCl. Cu electrode was 0.20 cm$^2$ and the Al electrode was 1 cm$^2$. 

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Figure 2.10 compares current and potential profiles for a Cu cathode in aerated solution and either Al or AA2024-T3 in quiescent, aerated 0.1 M NaCl. After 30 minutes of galvanic corrosion, \( K_2Cr_2O_7 \) was added (to \( \sim 5 \text{mM } Cr^{VI} \)) to the anodic chamber (either aluminum or AA2024-T3) of the split-cell. Fifteen minutes later \( K_2Cr_2O_7 \) was added to the cathode (copper) chamber (to \( \sim 5 \text{mM } Cr^{VI} \)). The results were similar when the copper cathode was coupled to either aluminum or AA2024-T3. The galvanic current plots for either an Al or AA2024-T3 net anode track each other for the entire experiment. Little change in current was observed for either couple when \( Cr^{VI} \) was added to the anodic chamber. Predictably, from previous observations, the current dropped dramatically when \( Cr^{VI} \) was introduced to the copper-containing chamber. The potential of the copper/AA2024-T3 couple was initially more positive than the copper/aluminum couple, as expected, since the measured open circuit potential for AA2024-T3 is more positive than for pure aluminum thus causing a shift in the mixed potential profile of the system. A large current spike was observed immediately upon addition of the \( Cr^{VI} \) to the Cu chamber before the current decreased below initial values. This transient was not observed when \( Cr^{VI} \) was added to the AA2024-T3 or Al chamber. The spike was not observable in previous experiments (Figures 2.5-2.7, 2.9) because data acquisition was paused during \( Cr^{VI} \) addition.

With AA2024-T3 in both sides of the split cell, galvanic corrosion current may be generated by de-aerating one side with argon. As earlier stated data presented here for Figures 2.11-2.13 are adapted from Ramsey.\(^{87}\) pp. 211,220,223 The aerated side becomes a net cathode, and the deaerated side becomes a net anode. This approach is similar to

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Figure 2.10. Effect of Cr\textsuperscript{VI} addition to either Al/Cu or AA2024-T3 couples in aerated, quiescent split-cell. K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} was added to Al compartment 0.5 h and the Cu compartment at 0.75 h to give [Cr\textsuperscript{VI}] = 5 mM. Electrolyte was 0.1 M NaCl. Both electrodes were 1 cm\textsuperscript{2}. 

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differential aeration cells reported previously to study galvanic currents caused by concentration differences. Figure 2.11 demonstrates the ability to cycle the chambers between being net anodes and net cathodes by air or Ar saturation. Initially both chambers of the split cell were aerated and the resulting current fluctuated around zero under quiescent conditions. Presumably, this fluctuation was caused by local corrosion events on one electrode momentarily polarizing it either positive or negative of the other electrode. This is essentially identical to Electrochemical Noise techniques used to study corrosion. Argon saturation of side 2 of the split-cell resulted in positive current (e flow toward aerated side), and de-aeration of both sides returned the current to near zero. Since both sides were deaerated, local corrosion events were minimized and the resulting “zero” current was much smoother than with both sides aerated. The mixed potential decreased as would be expected with lower oxygen concentration. As air was reintroduced into side 2, the current became negative as electrons flowed toward the aerated electrode, and the potential returned to the range of -525 to -550 mV. The mixed potential was in this range when either or both sides were aerated, and only decreased when both sides were deaerated.

Figures 2.12 and 2.13 show the effect of CrVI addition on the deaerated and aerated chambers of the AA2024-T3/AA2024-T3 split cell couple. In both experiments a current is generated by deaeration of one side as shown in Figure 2.11. Addition of CrVI (to ~10 mM) to either the aerated (Figure 2.12) or deaerated (Figure 2.13) chambers caused a decrease in galvanic current, although a current spike was observed only for addition to the aerated chamber.
Figure 2.11. Behavior of AA2024-T3/AA2024-T3 couple in split cell under different aeration conditions as indicated. The solution was quiescent during measurement. Ar bubbling was used to deaerate chambers between segments as indicated. Electrolyte was 0.1 M NaCl. Both electrodes were 1 cm². Adapted from Ramsey. \(^{87}\) p. 211
Figure 2.12. Effect of chromate addition (to 10 mM Cr\textsuperscript{VI}) to the “cathode” (aerated compartment) of an AA2024-T3/AA2024-T3 couple in a quiescent split-cell. The “anode” was deaerated as described in the text. Electrolyte was 0.1 M NaCl. Both electrodes were 1 cm\textsuperscript{2}. Adapted from Ramsey.\textsuperscript{87} p. 223
Figure 2.13. Identical to Fig. 2.12 but with chromate addition to the "anode" (deaerated chamber). Adapted from Ramsey.87 p. 217
Microscopy was used to visually examine AA2024-T3 electrodes after corrosion experiments in the split-cell. Following six hours of exposure electrode samples were rinsed with water, dried with argon, and mounted on a Dilor X-Y microscope for observation. The results observed after experiments using AA2024-T3 in both chambers of the split-cell are shown in Figures 2.14 through 2.17. In each case five micrographs are shown. A freshly polished (to 1200 grit silicon carbide) sample of AA2024-T3 (micrograph (a) in all cases) is compared to micrographs of the deaerated (net anode - left) and aerated (net cathode – right) chambers after six hours of exposure to 0.1 M NaCl with other varied experimental conditions. It should be noted that the results are more easily interpreted with the naked eye than by using the two-dimensional black and white images recorded. Subtle variations in color cannot be observed on the printed page. Since a microscope does not have depth perception surface phenomena such as pitting or precipitation of hydroxides are not easily recorded. As a result, the described differences are more dramatic than can be apparent in the printed figures. The printed images presented in Figures 2.14 – 2.17 were taken by focusing on the general surface and not on pits (deeper focus) or precipitates (shallow focus). Evaluation of the surface as described below was performed with the aid of movement of focus. Figure 2.14(b,c) is the control experiment that shows the effects of exposure to 0.1M NaCl. Electrodes from both the aerated and deaerated chambers show the effects of corrosion albeit the appearance of each differs. The aerated electrode is marked by numerous large pits usually round in shape and noticeably deep. Also observed is the occurrence of precipitated hydroxide (probably aluminum based) corrosion product. The deaerated
Figure 2.14. Optical micrographs of AA2024-T3 after 6 h exposure to various conditions in an AA2024-T3/AA2024-T3 split-cell as in Fig. 2.11. Deaerated (net anode) is left column and aerated (net cathode) is right column. (a) is freshly polished to 1200 grit silicon carbide. Couple 1: (b) and (c) in 0.1M NaCl. Couple 2: (d) and (e) in 0.1M NaCl but not electrically connected.
Figure 2.15. Same as Fig. 2.14. except with the following. Couple 1: (b) 0.1M NaCl and (c) in 0.1M NaCl with 5 mM Cr\textsuperscript{VI}. Couple 2: (d) in 0.1M NaCl with 5 mM Cr\textsuperscript{VI} and (e) in 0.1M NaCl.
Figure 2.16. Same as Fig. 2.14. except with the following. Couple 1: (b) 0.1M NaCl and (c) in 0.1M NaCl with 5 mM Cr<sup>VI</sup> added at 30 m. Couple 2: (d) in 0.1M NaCl with 5 mM Cr<sup>VI</sup> added at 30 m and (e) in 0.1M NaCl.
Figure 2.17. Same as Fig. 2.14. except with the following. Couple 1: (b) 0.1M NaCl and (c) in 0.1M NaCl with 30 m Cr\textsuperscript{VI} pretreatment in 0.1 M Cr\textsuperscript{VI}. Couple 2: (d) in 0.1M NaCl with 30 m Cr\textsuperscript{VI} pretreatment in 0.1 M Cr\textsuperscript{VI} and (e) in 0.1M NaCl.
electrode also shows pitting but in a more general manner with the pits being smaller and more numerous. Little to no precipitate was observed on the deaerated electrode. Figure 2.14(d,e) shows a similar control experiment but with the two electrodes being electrically isolated (no connection). This “pseudo” split-cell experiment shows the effects of de-aeration on the corrosion of AA2024-T3. The aerated electrode again shows corrosion manifested as deep round pits however the extent of the damage is lessened compared to the aerated electrode in the connected galvanic cell shown in Figure 2.14(c). The deaerated electrode shows little effect save for slight roughening of the surface.

The effects of chromate addition (to ~5mM CrVI) to the aerated and deaerated chambers were studied with the results shown in Figures 2.15(b,c). When the aerated chamber contains chromate, dramatic changes in the appearance of the electrode occur. No visible pitting or hydroxide precipitate buildup occurs. The appearance of the deaerated electrode is very similar to the electrically isolated deaerated electrode in Figure 2.14(d) - slight surface roughening but little to no pitting. The presence of chromate in the deaerated chamber, shown in Figure 2.15(d,e) has some effect on the system. The appearance of the aerated electrode is similar to the electrically connected split-cell of Figure 2.14(c). The deaerated electrode appears slightly less corroded than the corresponding deaerated electrode of Figure 2.14(b).

Figures 2.16(b-e) are similar to 2.15(b,c) but chromate was added to either the deaerated or aerated chamber after the couple had been allowed to corrode in 0.1M NaCl for 30 minutes. The observed results are as expected based upon the previous
experiments with chromate present. The appearance of the deaerated and aerated electrodes after addition of chromate to the aerated chamber (Figure 2.16(b,c)) is somewhere between that of the freely corroding split-cell and the cell with chromate present in the aerated chamber from the beginning. The aerated electrode (Figure 2.16(c)) shows a limited presence of the large deep pits. The deaerated electrode (Figure 2.16(b)) has a similar decrease in the presence of surface pitting. Addition of chromate to the deaerated chamber (Figure 2.16(d,e)) showed results that nearly matched the results of having the chromate present in the deaerated chamber from the beginning of the experiment. Little difference could be observed from the electrically connected couple from Figure 2.14(b,c).

Finally, to examine pretreatment effects of chromate either the aerated or deaerated electrode were exposed to 0.1M Cr$^{VI}$ in 0.1M NaCl for 30 minutes. They were then connected and exposed to 0.1M NaCl as in Figure 2.14(b,c). The results show that pretreatment of the aerated electrode has a much greater inhibiting effect on corrosion than for pretreatment of the deaerated electrode. The couple with the pretreated aerated electrode (Figure 2.17(b,c)) shows only slight pitting on the aerated electrode and very little pitting on the deaerated electrode. The couple with pretreatment of the deaerated electrode (Figure 2.17(d,e)) shows extensive corrosion of both electrodes, possibly even exceeding corrosion for non-treated electrodes.

Figure 2.18 shows the results of a Cu-Cu couple. Two 1cm$^2$ copper electrodes were connected and exposed to aerated 0.1M NaCl. A galvanic current near zero was observed initially as the two electrodes are identical. After 30 minutes Cr$^{VI}$ (to 5mM)
Figure 2.18. Effect of chromate addition (to 5 mM Cr\textsuperscript{VI}) to both chambers of a Cu/Cu couple in a quiescent split-cell. Electrolyte was 0.1 M NaCl. Both electrodes were 1 cm\textsuperscript{2}.  

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was added to one chamber. This side corresponded to the side that the net anodes were connected (to the ZRA instrumentation) in other experiments. Upon addition a current spike was observed with positive sign (due to instrument connections) indicating a reduction reaction in this chamber. The galvanic current decreased but did not return to zero indicating a polarization of the electrodes (one becoming the net anode and the other the net cathode). After 15 minutes more Cr$^{VI}$ was added to the other chamber of the system. Another current spike was observed of similar size but opposite sign (again due to instrument connections) indicating another reduction process. The measured current then returned to approximately zero since the two electrodes were again in essentially identical environments.

Figures 2.19 through 2.24 show the effects of electrode area ratio on the current response of Al/Cu and AA2024-T3/Cu couples. In each case the Al or AA2024-T3 (net anode) surface area was approximately 1 cm$^2$ while the copper (net cathode) surface area was 1 cm$^2$ (Figures 2.19 and 2.22), 0.20 cm$^2$ (Figures 2.20 and 2.23), or 0.0020 cm$^2$ (Figures 2.21 and 2.23). The case of both electrode areas of 1 cm$^2$ (Figures 2.19 and 2.22) was identical to the results shown for Figure 2.6. Some general observations can be made from the results of the six sets of experimental conditions. The galvanic current established before the addition of Cr$^{VI}$ scales with the surface area of the copper electrode almost linearly. The initial current for the two smaller copper electrodes (in both Al/Cu and AA2024-T3/Cu couples) is about 40% and 0.8% of that for the largest. The surface area is about 20% and 0.2%. For all six experiments a current transient is observed with addition of Cr$^{VI}$ to the copper electrode. The height and area of the current transient
Figure 2.19: Effect of Cr$^{VI}$ addition to a 1 cm$^2$ Al / 1 cm$^2$ Cu couple in aerated, quiescent split-cell. K$_2$Cr$_2$O$_7$ was added to Al compartment 0.5 h and the Cu compartment at 0.75 h to give [Cr$^{VI}$] = 5 mM. Electrolyte was 0.1 M NaCl.
Figure 2.20: Same as Fig. 2.19 except electrodes were: Al 1 cm$^2$ and Cu 0.20 cm$^2$. 
Figure 2.21: Same as Fig. 2.19 except electrodes were: Al 1 cm$^2$ and Cu 0.0020 cm$^2$. 

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Figure 2.22: Effect of Cr\textsuperscript{VI} addition to a 1 cm\textsuperscript{2} AA2024-T3 / 1 cm\textsuperscript{2} Cu couple in aerated, quiescent split-cell. K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} was added to Al compartment 0.5 h and the Cu compartment at 0.75 h to give [Cr\textsuperscript{VI}] = 5 mM. Electrolyte was 0.1 M NaCl.
Figure 2.23: Same as Fig. 2.22 except electrodes were: AA2024-T3 1 cm² and Cu 0.20 cm².
Figure 2.24: Same as Fig. 2.22 except electrodes were: AA2024-T3 1 cm$^2$ and Cu 0.0020 cm$^2$. 

Cr$_2$O$_7^{2-}$ added 
[to 5mM Cr$^{3+}$] 
at indicated points

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scales approximately linearly with the surface area of the copper electrode. When $\text{Cr}^{\text{VI}}$ was added to either the Al or AA2024-T3 electrode a small current transient corresponding to a reduction reaction appeared as the copper surface area was decreased. In fact, a small transient was even observed on the AA2024-T3 electrode with the largest size copper electrode[Figure 2.22]. The size of the current transient (height and area) on the Al or AA2024-T3 remained relatively constant as the size of the copper electrode was changed. The current transient also appeared slightly more prevalent on the AA2024-T3 electrode (Figure 2.22) than for the aluminum electrode (Figure 2.19). The potential of each system followed the same trends to varying degrees. In general the initial potential of AA2024-T3/Cu couples was slightly positive of the Al/Cu couples. The initial potential for both couples also shifted negative as copper electrode surface area was decreased. The potential shifted positive slightly when $\text{Cr}^{\text{VI}}$ was added to the net anode (both the AA2024-T3 or aluminum). When $\text{Cr}^{\text{VI}}$ was added to the copper electrode the potential shifted negative but to greater degree on $1 \text{ cm}^2$ copper electrodes than on $0.0020 \text{ cm}^2$ copper electrodes where the shift was very slight.

Figure 2.25 shows polarization curves for Cu, AA2024-T3, and Al for conditions relevant to the split cell experiments. For all the polarization curves save one (aerated AA2024-T3) the electrode was allowed to remain at its open circuit potential for 10 minutes prior to scanning positive at 1 mV/s starting from a potential about 500 mV negative of open circuit. The AA2024-T3 aerated electrode polarization curve was constructed from two scans (one positive and one negative) starting at the open circuit potential after 10 minutes. Figure 2.25(a) shows the effects of $\text{Cr}^{\text{VI}}$ addition to aerated
Figure 2.25. Polarization curves for various electrodes and conditions as shown. Electrodes were held at open circuit potential for 10 m and were then scanned positive at 1 mV/s from a potential negative of open circuit. All electrodes were 1 cm². Electrolyte was 0.1 M NaCl. Solution quiescent. (a) copper, (b) aluminum, (c) aerated AA2024-T3, (d) deaerated AA2024-T3. Note: the aerated AA2024 scan was initiated at open circuit and scanned positive or negative to construct the polarization curve.
(Figure 2.25 continued)

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chloride solutions on the polarization curves for Cu. In the aerated Cr\textsuperscript{VI}-free chloride solution, the 1 cm\textsuperscript{2} Cu electrode exhibited a mass transport limited O\textsubscript{2} reduction current of 40 μA over a wide potential range between -300 and -650 mV vs. Ag/AgCl. In the Cr\textsuperscript{VI}-containing solution, the rate of the cathodic reaction on Cu was 1-2 orders of magnitude lower. Figure 2.25(b) shows polarization curves for aerated aluminum electrodes and the effects of Cr\textsuperscript{VI} addition. The curves with and without Cr\textsuperscript{VI} addition are essentially the same. The open circuit potential is well negative of copper as expected. The cathodic portion of the curve shows reduction processes on aluminum that have rates 2-4 orders of magnitude lower than corresponding rates on the copper electrode at the same potential. The effect of Cr\textsuperscript{VI} addition shifts the open circuit potential slightly positive.

The polarization curves for AA2024-T3 in aerated and deaerated chloride solution is shown in Figures 2.25(c) and 2.25(d). In aerated 0.1M NaCl (Figure 2.25(c)) the corrosion potential for AA2024-T3 was essentially pinned at the breakdown potential (E\textsubscript{pit}). It is characterized by a large increase in current over a relatively short potential range. The rate of the cathodic reaction on AA2024-T3 in the aerated Cr\textsuperscript{VI}-free solution was also lower than that for Cu probably due to less surface area for cathodic reactions on the AA2024-T3. In the Cr\textsuperscript{VI}-containing solution, the open circuit potential was more negative and the anodic breakdown potential was shifted positive. A better-defined passive region was also observed. The cathodic reaction rate on the aerated AA2024-T3 in Cr\textsuperscript{VI} was similarly decreased (as observed for the copper electrode). Deaeration resulted in a decrease in the cathodic current for AA2024-T3 electrodes [Figure 2.25(d)].
The open circuit potential shifted negative away from the breakdown potential but well-defined passive and breakdown regions were not observed. The current continually increased as the potential shifted positive (pseudo-passive) until a limiting current was reached (pseudo-breakdown). The current density in this pseudo-passive region was decreased and the pseudo-breakdown potential shifted slightly positive by the addition of Cr\textsuperscript{VI} to the deaerated electrode.

The split-cell apparatus was used in two further studies investigating properties of Cr\textsuperscript{VI} with regards to corrosion inhibition. In one investigation oxygen was replaced by hydrogen peroxide as an oxidizing agent and in the other the cathode substrate was changed from copper to glassy carbon. Figure 2.26 shows the galvanic current and potential changes when hydrogen peroxide is used as an oxidizing agent for an Al/Cu couple. As in previous experiments a galvanic current is generated and arrives at a steady-state of about -10 \( \mu \text{A} \) when the aluminum and copper electrodes are connected in an unstirred split-cell. After 15 minutes argon was bubbled into the cathode side to both de-aerate and stir the solution. It was bubbled throughout the remainder of the experiment. The current decreases similarly as observed in Figures 2.5 and 2.8. Hydrogen peroxide (to \( \sim 10 \text{ mM} \)) was added to the cathode chamber after 45 minutes. The current increased greater than an order of magnitude (to \( \sim 220 \mu \text{A} \)) and the potential shifted positive by approximately 300 mV. At one hour Cr\textsuperscript{VI} (to \( \sim 1.2 \text{ mM} \)) was added to the cathode chamber. The current immediately decreased to approximately -40 \( \mu \text{A} \) and upon further addition (to \( \sim 10 \text{ mM} \)) the current decreased to less than -10 \( \mu \text{A} \). Corresponding large negative shifts in the potential of the system occurred also.
Figure 2.26: Effect of Cr\textsuperscript{VI} addition on H\textsubscript{2}O\textsubscript{2} reduction at the cathode of a Al/Cu couple in a split-cell. Solution was stirred and deaerated by argon bubbling starting at 15 m. H\textsubscript{2}O\textsubscript{2} was added at 45 m and Cr\textsuperscript{VI} at 60 m and 90 m as indicated. Electrolyte was 0.1 M NaCl. Both electrodes were 1 cm\textsuperscript{2}. 

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Figure 2.27 shows the effect of Cr\textsuperscript{VI} on the galvanic current of an aluminum/glassy carbon couple studied in the split-cell apparatus. Figure 2.27(a) shows the establishment of galvanic current of approximately -8 \mu A with a 1 cm\textsuperscript{2} aluminum electrode and a 0.071 cm\textsuperscript{2} glassy carbon electrode in quiescent 0.1M NaCl. The negative current sign indicates that glassy carbon becomes the net cathode and aluminum the net anode. The current and potential remain relatively constant for the entire two-hour experiment. Figure 2.27(b) shows the effect of adding Cr\textsuperscript{VI} to the net cathode chamber (glassy carbon). The steady-state current was established and allowed to remain constant for one hour. Upon addition of Cr\textsuperscript{VI} (to \sim 1 mM) to the glassy carbon electrode the current immediately decreased to < 1 \mu A and the potential shifted approximately 300 mV negative. The appearance of a current transient upon the addition of Cr\textsuperscript{VI} occurs as for Figures 2.10, 2.12, and 2.19 - 2.24. The electrodes were removed from solution, rinsed with H\textsubscript{2}O, and replaced in fresh 0.1M NaCl and the galvanic current monitored further. The results are shown in Figure 2.27(c). The galvanic current remains less than 1 \mu A and the potential near -900 mV (as in Figure 2.23(b) after Cr\textsuperscript{VI} addition) even though no Cr\textsuperscript{VI} is present in solution.

DISCUSSION

The objectives of the experiments performed in this study were to validate the use of the concept of separation of reactions as a tool to study corrosion (and inhibition) of AA2024-T3 and to begin to use the methodology to investigate the actions of chromate as related to inhibition. Partial or complete separation of anodic (oxidation) and cathodic
Figure 2.27: Effect of Cr$_{VI}$ addition on a quiescent, aerated Al/glassy carbon couple in a split-cell. Electrolyte 0.1 M NaCl. (a) uninhibited galvanic couple. (b) chromate added (to 1 mM Cr$_{VI}$) at 1 h to glassy carbon chamber. (c) electrodes rinsed after (b) and placed in fresh 0.1 M NaCl.
(Figure 2.27 continued)
(reduction) corrosion reactions was achieved by the use of galvanically coupled electrodes of different materials in single or split-cell configurations. By using the split-cell and differential aeration, a galvanic couple was induced between two nominally identical electrodes. This separation allowed independent study of inhibitor effects and insights into the inhibition mechanism at cathodes and anodes. However, spatial separation of the net anode and net cathode decreases chemical interactions between surface sites, which might occur in real systems when anodic and cathodic regions are in close proximity. For example, a pH change occurring at a local cathode may influence the corrosion reactions at an adjacent anode. In order to localize inhibitor effects to the anode or cathode, these chemical interactions must be neglected. With these limitations acknowledged, several useful observations are available from the results.

**Evaluation of chromate inhibition properties related to AA2024-T3 via galvanic couples**

The separation of anodic and cathodic reaction for the case of pure Cu and pure Al electrodes is apparent for both the single cell (Figure 2.5) and split cell (Figure 2.8), and results in the observed galvanic current. For the Al/Cu couple, the observed current was observed to be dependent on the rate of mass transport of O₂ to the Cu electrode, i.e. faster stirring with oxygen increases galvanic current. Mass transport effects were not observed for reactions on the Al electrode. This is likely because the reaction products are precipitates rather than soluble species. The galvanic current was inhibited by the addition of Cr⁶⁺, but only if it could interact with the Cu electrode. The split cell shows
that Cr\textsuperscript{VI} addition to the Al side had no effect on the current, although it shifted the potential positive by about 20 mV (Figure 2.9). Pretreatment of Cu or Al electrodes with either Alodine or Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2} solution (Figures 2.6 and 2.7) had similar effects to addition of Cr\textsuperscript{VI} on the galvanic corrosion current. Copper electrodes pretreated with Cr\textsuperscript{VI} showed strongly decreased galvanic current as with Cr\textsuperscript{VI} addition. Aluminum electrodes pretreated with Cr\textsuperscript{VI} showed little difference in galvanic current from non-treated electrodes. Taken together, the Al/Cu experiments indicate that the predominant cathodic reaction is O\textsubscript{2} reduction under the present conditions. The galvanic current is limited by mass transport of O\textsubscript{2} and Cr\textsuperscript{VI} reduces the rate of O\textsubscript{2} reduction. For pure Al, Cr\textsuperscript{VI} had no effect on the anodic reaction rate. The observations on the Al/Cu system serve as important background information for the more realistic AA2024-T3/Cu and AA2024-T3/AA2024-T3 combinations.

The more complex systems utilizing AA2024-T3/Cu and AA2024-T3/AA2024-T3 couples allow local environmental conditions to develop that partially replicate corrosion conditions of AA2024-T3. Most likely local galvanic couples on each electrode compete with the overall galvanic current that flows between the separated electrodes, however the observed galvanic current between the electrodes should be significantly larger than the local current. Visual observations corroborate that local interactions are significant. The greater damage to the aerated electrode (net cathode) than the deaerated electrode (net anode) in the AA2024-T3/AA2024-T3 differential aeration arrangement under free corrosion in 0.1 M NaCl [Figure 2.14(b,c)] attests to the existence of local phenomena. The greater damage to the net cathode may be caused by
the generation of hydroxide ion near local cathodes as the result of oxygen reduction. The locally high pH could serve to dissolve the aluminum near the local cathodes. Despite this obvious local interaction, the Al/Cu and AA2024-T3/Cu couples behaved similarly when exposed to Cr$^{VI}$ (Figure 2.10). Cr$^{VI}$ addition to the Al or AA2024-T3 chamber had minor effects on galvanic current, while Cr$^{VI}$ inhibited the net cathodic reaction on Cu in both cases. This indicates that local galvanic couples and chemical interactions are not a controlling factor when the system is being driven by a strong external reduction reaction (in the copper chamber). The results for the AA2024-T3/AA2024-T3 split cell, shown in Figures 2.12 and 2.13, are consistent with those observed for Al/Cu and AA2024-T3/Cu with regards to cathodic inhibition by Cr$^{VI}$ but not for anodic inhibition. Cr$^{VI}$ inhibits the observed current when added to the aerated side (net cathode) of the AA2024-T3/AA2024-T3 split cell (Figure 2.12), similar to what was observed when it was added to the Cu side of the AA2024-T3/Cu and Al/Cu split cells. This again implies a cathodic inhibition mechanism for Cr$^{VI}$. However, Cr$^{VI}$ also reduces the current when added to the deaerated (net anode) side of the AA2024-T3/AA2024-T3 split cell (Figure 2.13). The apparent activity of Cr$^{VI}$ as an anodic inhibitor, which is implied by Figure 2.13, is not consistent with Figures 2.9 and 10 (and also 6 and 7), in which no effect was observed on the net anode (either Al or AA2024-T3) when the net cathode was Cu instead of AA2024-T3. It also seems to contradict other results indicating that Cr$^{VI}$ is not an effective inhibitor for pit growth.$^{102,103}$ Visual observation of AA2024-T3 samples that were exposed to various conditions as AA2024-T3/AA2024-T3 differential aeration couples were consistent with
the electrochemical measurements obtained by the separation of reactions. In Figure 2.14 the net anode (deaerated chamber) of the galvanically coupled cell was more corroded than the sample that was not coupled but placed in deaerated chloride solution. This indicates the oxidation was driven by the corresponding reduction reactions taking place on the net cathode (aerated chamber) as measured by the initial galvanic current in Figures 2.12 and 2.13. Figures 2.15 through 2.17 assess the effect of chromate. The presence of Cr\textsuperscript{VI} in the aerated chamber (net cathode) not only inhibited local reactions on the net cathode [Figure 2.15(c)] but the net anode damage [Figure 2.15(b)] was lessened as well. This corresponds to cathodic inhibition of the galvanic current observed in experiments with all three couple combinations. Cr\textsuperscript{VI} in the deaerated (net anode) chamber [Figure 2.15(d,e)] showed results consistent with the observed low galvanic current after Cr\textsuperscript{VI} was added to the net anode of the AA2024-T3/AA2024-T3 couple [Figure 2.13]. Local reactions continued on the net cathode as evidenced by damage [Figure 2.15(e)] but the net anode damage [Figure 2.15(d)] was lessened slightly as compared to the freely corroding couple. When Cr\textsuperscript{VI} was added after allowing the couple to begin freely corroding [Figure 2.16(b-e)] the damage was attenuated to a level somewhat between that for couples with no Cr\textsuperscript{VI} and couples with Cr\textsuperscript{VI} added at the beginning. This is in agreement with addition of Cr\textsuperscript{VI} inhibiting galvanic currents upon addition as shown in Figures 2.12 and 2.13. Finally, pretreatment of the aerated AA2024-T3 electrode (net cathode) with Cr\textsuperscript{VI} [Figure 2.17(b,c)] showed a resulting lessening of damage to both electrodes but pretreatment of the deaerated AA2024-T3 electrode (net anode) with Cr\textsuperscript{VI} [Figure 2.17(d,e)] showed no protection and possibly
more damage than was observed for the freely corroding couple [Figure 2.14(b,c)]. This follows closely with the galvanic current results for pretreatment by Cr\textsuperscript{VI} examined in the single-cell for Al/Cu couples in Figures 2.6 and 2.7.

**Validating galvanic couple observations with polarization curves**

The observations made for the electrode separation experiments can be examined by comparison with the results obtained from the polarization experiments run for the individual electrodes under various conditions. Mixed potential theory (discussed in Chapter 1) can be used to explain the results obtained by the separation of reactions approach thus validating the technique. Polarization curves for Al, AA2024-T3, and Cu (Figure 2.25) are combined and used to represent Al/Cu, AA2024-T3/Cu, and AA2024-T3/AA2024-T3 split-cell couples in Figures 2.28-2.30. Figure 2.28(a)-(c) are constructed by overlaying the polarization curves for copper (with and without Cr\textsuperscript{VI} addition) and aluminum (with and without Cr\textsuperscript{VI} addition). Together they represent the split-cell experiment conducted in Figure 2.10 for the Al/Cu couple. Figure 2.28(a) represents the Al/Cu couple in chloride solution without added Cr\textsuperscript{VI}. The cathodic portion of the copper curve (in the mass transport limited O\textsubscript{2} reduction region) crosses the anodic portion of the aluminum curve to define the mixed potential and galvanic (or corrosion) current. The predicted current and potential (indicated by the dashed arrows) compare well with that measured for the Al/Cu couple (Figure 2.10). Addition of Cr\textsuperscript{VI} to the aluminum chamber did not change the galvanic current appreciably and the polarization curve in Figure 2.28(b) predicts just this observation. The inclusion of the polarization curve for aluminum with added Cr\textsuperscript{VI} shows that the galvanic current remains controlled by the
Figure 2.28: Polarization curves corresponding to an aluminum/copper galvanic couple. Both electrodes 1 cm\(^2\). Conditions same as Fig. 2.25. (a) copper and aluminum. (b) copper and aluminum with 5 mM Cr\(^{VI}\). (c) copper with 5 mM Cr\(^{VI}\) and aluminum with 5 mM Cr\(^{VI}\). Intersections are noted with dashed lines.
Figure 2.29:  Polarization curves corresponding to an AA2024-T3/copper galvanic couple. Both electrodes 1 cm². Conditions same as Fig. 2.25. (a) copper and AA2024-T3. (b) copper and AA2024-T3 with 5 mM CrVI. (c) copper with 5 mM CrVI and AA2024-T3 with 5 mM CrVI. Intersections are noted with dashed lines.
Figure 2.30: Polarization curves corresponding to an AA2024-T3(aerated)/AA2024-T3(deaerated) galvanic couple. Both electrodes 1 cm². Conditions same as Fig. 2.25. (a) aerated AA2024-T3 and deaerated AA2024-T3. (b) aerated AA2024-T3 with 5 mM Cr VI and deaerated AA2024-T3 (c) aerated AA2024-T3 and deaerated AA2024-T3 with 5 mM Cr VI. Intersections are noted with dashed lines.
oxygen reduction reaction even though the mixed potential shifts positive. A slight positive shift in the potential of the split-cell couple in Figure 2.10 was observed. The observations with Cr\textsuperscript{VI} added to the copper chamber are predicted correctly in Figure 2.28(c). The slowing of cathodic reactions on the copper electrode cause the corrosion current to decrease about an order of magnitude and the mixed potential shifts negative. This matches observations for the same region in Figure 2.10.

Figure 2.29 represents the conditions encountered in Figure 2.10 for the AA2024-T3/Cu couple. The results of the split-cell measurement and polarization curve modeling are very similar to the Al/Cu couple with some notes worth mentioning. The observed corrosion current is once again determined by the mass transfer limited reduction of O\textsubscript{2} on Cu and the observed current and potential in the split cell (Figure 2.10) are approximately equal to those predicted from Figure 2.29(a) at the intersection marked by the dashed lines. Under this condition, the mixed potential occurred at a value that set the AA2024-T3 electrode (net anode) into a potential range well above the breakdown potential of AA2024-T3 where localized corrosion occurred at a relatively high rate. In the galvanic corrosion condition of the split cell (Figure 2.10), the rate of the localized attack was limited by cathodic reaction on the Cu electrode and local galvanic current on the AA2024-T3 electrode combined. The breakdown potential for AA2024-T3 is slightly more positive in the aerated Cr\textsuperscript{VI} - containing solution. However, when connected to the aerated Cu net cathode in the split cell the intersection [Figure 2.29(b)] was still positive of the breakdown potential for AA2024-T3, and the rate was still limited by the rate of oxygen reduction on Cu. There was little change in the current and
a small positive shift in potential when Cr\textsuperscript{VI} was added to the AA2024-T3 side, as observed in Figure 2.10. As observed for the Al/Cu couple, the rate of the cathodic reaction on Cu was considerably lower in the Cr\textsuperscript{VI}-containing solution, which limited the galvanic current when Cu was connected to AA2024-T3. Figure 2.29(c) represents the situation when Cr\textsuperscript{VI} was added to the Cu side in Figure 2.10.

The effect of Cr\textsuperscript{VI} in the AA2024-T3/AA2024-T3 split cell experiments of Figures 2.12 and 2.13 can be understood with the help of the polarization curves in Figure 2.30. Recall that the addition of \(~5\) mM Cr\textsuperscript{VI} shifted the breakdown potential of AA2024-T3 positive in deaerated 0.1 M NaCl by a small amount and decreased the passive current density. The positive shift in pitting potential was somewhat larger in the aerated solution. A defined passive region also appeared for the aerated solution. These observations are evidence of a form of anodic inhibition. The initial galvanic current and mixed potential before Cr\textsuperscript{VI} addition predicted by the intersection in Figure 2.30(a) reflect the measured values (Figures 2.12 and 2.13) quite well. It is important to note that the polarization curve for the deaerated AA2024-T3 electrode (net anode) does not show a distinct breakdown potential as for aerated AA2024-T3. Figure 2.30(b) represents the conditions for Figure 2.12 with Cr\textsuperscript{VI} added to the aerated (net cathode) chamber. The measured current decreased and the potential shifted negative. The polarization curves predict that the potential should decrease to the indicated intersection and that the current should decrease to the extent that the electrode polarity reverses. The AA2024-T3 sample in the aerated chamber with added Cr\textsuperscript{VI} solution should become the net anode. This did not occur for the couple probably due to local reactions occurring on each...
electrode that are not accounted for with the polarization curves. However, cathodic inhibition was still observed. When Cr$^{VI}$ is added to the deaerated chamber (net anode) of the AA2024-T3/AA2024-T3 couple the polarization curves in Figure 2.30(c) correctly predict (when compared to Figure 2.13) that the galvanic current should decrease and the potential shift positive as indicated by the intersection. This is a form of anodic inhibition but it is not inhibition of pitting corrosion characterized by a potential positive of the breakdown potential. It is simply a decrease in the passive current density on the deaerated AA2024-T3 electrode (net anode) caused by the addition of Cr$^{VI}$. The mixed potential was never positive enough to be in a pitting (breakdown) condition for this system. This observation does not contradict the prior reports that dichromate does not inhibit pit growth since sustained pit growth was not possible according to Figure 2.30(a) where AA2024-T3 in aerated and deaerated solutions were coupled.

The activity of Cr$^{VI}$ as both an anodic and cathodic inhibitor has been reported previously by several groups, and there is continuing controversy about which action, if any, is dominant in corrosion protection of AA2024-T3.$^{89,96-103}$ Ilbevare & Scully have reported that Cr$^{VI}$ inhibits dealloying of s-phase particles, thus reducing formation of Cu-rich cathodic sites.$^{89,96,97}$ In the current work, however, the AA2024-T3 was exposed to NaCl solution for approximately 1 hour before Cr$^{VI}$ injection (during which dealloying presumably occurred), and Cr$^{VI}$ still inhibited the galvanic current. Although Cr$^{VI}$ may inhibit dealloying in field applications, it also acts as a cathodic inhibitor on cathodic sites formed by dealloying or present initially. Furthermore, Cr$^{VI}$ inhibited O$_2$ reduction on pure Cu, which represents the upper limit of Cu dealloying and redistribution in terms
of cathodic activity. The results indicate that Cr\textsuperscript{VI} does act as an anodic inhibitor, in particular by inhibiting the initiation rather than growth of localized corrosion. However, they also establish that Cr\textsuperscript{VI} is a strong and irreversible cathodic inhibitor, which can play a dominant role in the prevention of localized attack.

Polarization curves may also be used to reasonably explain the split-cell results for variations in cathode area. The polarization profile is adjusted for surface area of the copper electrode as shown in Figure 2.31. The current data for the polarization curve was multiplied by 0.20 and 0.002 (to represent the fractional surface area of the smaller electrodes compared to the 1 cm\textsuperscript{2} electrode) and replotted. Curves are shown for copper electrodes with and without Cr\textsuperscript{VI} addition. The profiles are identical save for the total current which is decreased fractionally with smaller electrode size. Assuming identical profiles for smaller electrodes relies on the assumption that mass transport conditions will not change appreciably as the electrode size decreases. This should be valid considering the scan rate of 1 mV/s will allow natural convection to contribute to mass transport at the electrode. Also, the smallest electrode (0.5 mm diameter) is not considered small by microelectrode standards and radial diffusion should not dominate. These polarization curves can be combined with curves for Al and AA2024-T3 as shown in Figures 2.32 and 2.33 in the same way as for Figures 2.28-2.30. The observed current dependence on copper electrode area before Cr\textsuperscript{VI} addition for the Al/Cu and AA2024-T3/Cu couples [Figures 2.19 through 2.24] is reflected in Figures 2.32(a) and 2.33(a). The intersection of the cathodic and anodic reactions occurs at lower galvanic current values and the
Figure 2.31: Polarization curves for 1 cm$^2$ copper electrodes with replotting after adjustment for 0.20 cm$^2$ and 0.0020 cm$^2$ surface area. (a) in 0.1 M NaCl. (b) in 0.1 M NaCl with 5 mM Cr$^{VI}$. Solution quiescent. Scan rate 1 mV/s.
Figure 2.32: Polarization curves corresponding to an aluminum/copper galvanic couple with varying cathode size as for Fig 2.31. Conditions same as Fig. 2.25. (a) copper and aluminum. (b) copper and aluminum with 5 mM Cr$^{VI}$. (c) copper with 5 mM Cr$^{VI}$ and aluminum with 5 mM Cr$^{VI}$. 

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Figure 2.33: Polarization curves corresponding to an AA2024-T3/copper galvanic couple with varying cathode size as for Fig 2.31. Conditions same as Fig. 2.25. (a) copper and AA2024-T3. (b) copper and AA2024-T3 with 5 mM Cr\textsuperscript{VI}. (c) copper with 5 mM Cr\textsuperscript{VI} and AA2024-T3 with 5 mM Cr\textsuperscript{VI}. 

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mixed potential shifts negative as the Cu electrode area decreases. The positive shift was also noted for the galvanic couples in split-cell experiments. This shift in potential may account for slight deviation from linear scaling of initial current with copper electrode size. Shifts in potential may cause small changes in oxygen reduction current density on the copper electrode creating two variables (size and current density) contributing to the measured current. The corresponding curves for CrVI added to the net anode and net cathode chambers are shown in Figures 2.32(b,c) and 2.33(b,c). The expected trends are followed for the most part. The positive shift in potential predicted for addition of CrVI to the aluminum electrode (net anode) for the Al/Cu couple is observed along with constant galvanic current (i.e. no inhibition). The AA2024-T3/Cu couple is predicted to have a negative shift in potential and reduced current with CrVI addition to the AA2024-T3 electrode (net anode) for the smallest copper electrode size and this was not observed for the couple. However, the intersection occurs in the passive region of the AA2024-T3 electrode and small differences in the cathodic reaction rates on copper from assumptions (rather than actual polarization curves on the smaller electrodes) could have large effects on the predicted result. Addition of CrVI to the copper electrode for Al/Cu and AA2024-T3/Cu couples follows the predicted decreased current trends in all cases. Some differences in the magnitude of the potential shifts from predicted was observed most likely for similar reasons as mentioned above for CrVI additions to the net anode.
Current transients

The current spike observed upon addition of Cr$^{VI}$ to the net cathode chamber of the split-cell implies an electrochemical process is occurring. The direction of the current spike (negative) indicates the current is the result of a reduction reaction. For the copper-aluminum couple (Figure 2.10) the spike is observed only for addition to the net cathode (copper) chamber. This implies that an electrochemical reduction reaction occurs on copper that does not occur on aluminum or at least is kinetically unfavorable on Al at the experimental potentials. If this interaction did not depend upon substrate material, a current spike should be observed for additions of Cr$^{VI}$ to either net cathode or net anode chambers as they are held at the same potential. The only difference would be the direction (sign) of the spike. A reduction process at the net anode chamber would result in a spike of opposite sign (i.e. positive spike would be a reduction process) based on the instrumental setup used. This was demonstrated by using a split-cell with copper serving as both electrodes. Figure 2.18 showed current spikes of approximately equal magnitude but opposite sign when Cr$^{VI}$ was added to either chamber. The transient reduction process is evidently kinetically favorable on copper substrates as the potential of the system was quite positive of the mixed potentials of the split-cell couples examined using Al or AA2024-T3 for at least one electrode yet the transient still occurred.

If current transients can be observed on both the net cathode and net anode given the proper substrate then a spike should be observed for addition of Cr$^{VI}$ to the anode of the AA2024-T3-copper galvanic couple. The net anode (AA2024-T3) has intermetallic
particles that are high in copper content. In addition, a current transient is observed for 
CrVI addition to AA2024-T3 when it was used as a net cathode in AA2024-T3/AA2024-
T3 couples (Figure 2.12). Reducing net cathode surface area allowed for the observation 
of these current transients on the net anode (Figures 2.22 - 2.24). The fact that the small 
reduction transient on the net anode is less visible as the net cathode size is increased is 
probably simply due to the increase in background current overshadowing the transient. 
The size (height and area) of the current transients are proportional to the size of the 
electrode as evidenced by the scaling of the size with net cathode area. The net anode 
remained the same size for all the experiments so the transient size remained relatively 
constant also. The appearance of transients on the pure Al surface (no copper sites) 
indicates there are active sites on the surface. These active sites are probably defects in 
the passive oxide layer or crystal defects (grain boundaries, etc.).

The current spike observed upon CrVI addition to the net cathode chamber in all 
split-cell experiments implies a transient reduction reaction is occurring. No current 
spike was observed for the control experiment (not shown) upon the addition of a NaCl 
solution containing no CrVI, indicating that the spike in fact resulted from the reduction 
of CrVI. The most probable reduction product is CrIII possibly precipitated as a 
hydroxide. A discussion of the processes occurring during the current transient is given 
in Chapter 3.
Other systems

The examinations of other systems with the separation methodology serve to probe the specific actions of chromate as an inhibitor. In Figure 2.26 the observation of inhibition of H$_2$O$_2$ (peroxide) reduction by chromate indicates that more than one reduction process may be inhibited by chromate. Peroxide is an intermediate in many reduction mechanism schemes for oxygen. The reduction of peroxide (to H$_2$O or OH\(^-\)) is much more thermodynamically favorable than the initial reduction step of oxygen to form the peroxide [1.776 V for H$_2$O$_2$ reduction to H$_2$O vs. 0.682 V for O$_2$ reduction to H$_2$O$_2$ (vs. NHE)]. Kinetically, the rate-limiting step in the entire process (O$_2$ to peroxide to H$_2$O) is usually the initial interaction of O$_2$ with a surface, meaning that the peroxide reduction is kinetically faster. The inhibition of this reaction indicates that Cr$^{VI}$ may also inhibit kinetically favorable reactions.

The use of an alternate substrate for the net cathode (in this case glassy carbon) as illustrated in Figure 2.27 demonstrates the versatility of the separation of reactions approach and provides further insights into Cr$^{VI}$ inhibition properties. Carbon (graphite fiber) has been used previously in galvanic corrosion studies of aluminum composites. The results from Figure 2.27(a) show that indeed a galvanic couple forms between aluminum and glassy carbon and that the current is sustainable for an extended period. Based upon the previous report oxygen reduction is most likely the dominant cathodic reaction in this case. The addition of Cr$^{VI}$ in Figure 2.27(b) to the glassy carbon chamber results in the same type of current inhibition that is observed for copper.

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cathodes. The continuing inhibition after exposure and rinsing [Figure 2.27(c)] is reminiscent of pretreatment experiments for Al/Cu couples [Figures 2.6 and 2.7]. This indicates that the effectiveness of Cr\textsuperscript{VI} inhibition of cathodic processes may extend to a number of systems besides aluminum alloys.

CONCLUSIONS

To better understand corrosion and its inhibition for aluminum alloy 2024-T3 and the actions of chromate inhibitors in general, an approach was taken utilizing separation (partially or fully) of anodic and cathodic reactions to establish and study various galvanic couples. The use of a split-cell configuration allows segregation of anodic and cathodic reactions and consideration of the effect of chromate on each reaction independently.

Specific conclusions are:

- Partial or complete segregation of anodic and cathodic reactions was achieved either by choice of electrode material or by differential aeration. Corroboration of results was performed visually and via the use of polarization curves.
- Dilute chromate solution greatly decreased the $O_2$ reduction rate on both Cu and AA2024-T3.
- Decreased $O_2$ reduction rates after pretreatment with Cr\textsuperscript{VI} solution and subsequent rinsing imply an irreversible inhibition process occurs.
- Cathodic inhibition on Cu surfaces by Cr\textsuperscript{VI} solution was accompanied by a transient reduction current. This is presumed to be the reduction of Cr\textsuperscript{VI} to Cr\textsuperscript{III} oxy-hydroxide.

- Anodic inhibition by Cr\textsuperscript{VI} was observed for the AA2024-T3/AA2024-T3 galvanic couple, but not for AA2024-T3/Cu or Al/Cu couples. The apparent difference was shown to be inhibition of passive current not localized (pitting) corrosion current as explained with polarization curves.

- Cathodic inhibition by Cr\textsuperscript{VI} is not limited to AA2024-T3 but was shown to be effective on a non-metal (glassy carbon) and for a different redox system (H\textsubscript{2}O\textsubscript{2}).
CHAPTER 3

THE FORMATION OF MONOLAYER FILMS OF TRIVALENT CHROMIUM (Cr\textsuperscript{III}) ON ELECTRODE SURFACES AND SUBSEQUENT EFFECTS ON CORROSION-RELATED REDUCTION PROCESSES

INTRODUCTION

Corrosion inhibitors can work either by slowing oxidation (anodic) or reduction (cathodic) processes. The results presented in chapter 2 imply that hexavalent chromium (Cr\textsuperscript{VI}) – either in solution or via pretreatment – significantly inhibits reduction reactions related to corrosion. With regards to aluminum alloy corrosion protection, investigations of chromium oxyanions (CrO\textsubscript{4}\textsuperscript{2-}, HCrO\textsubscript{4}\textsuperscript{-}, Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-}, etc.) have been dominated by studies of the inhibition of the dissolution half-reaction (oxidation or anodic inhibition) of the corrosion process. The role of chromate in cathodic inhibition pertaining to aluminum alloy corrosion (i.e. the inhibition of the reduction of oxygen) has only recently started to be investigated in this context.\textsuperscript{96, 97, 103, 130-132} The results thus far have included claims for \textit{and} against chromate as a cathodic inhibitor. The kinetics of the oxygen reduction reaction (ORR) on AA2024-T3 and copper-bearing intermetallic compounds present have been examined in the presence of a chromate conversion coating (CCC) and solution-phase chromate.\textsuperscript{96, 97} The ORR rate was reduced although uncertainty existed...
whether the role of the CCC or chromate was true cathodic inhibition or slowing of anodic processes that subsequently resulted in less reduction occurring. Inhibition of cathodic reactions on Cu-containing aluminides was attributed to hexavalent chromium adsorption in another recent study.\(^{130}\) Furthermore, as outlined in chapter 2 and published by the author, separation of the corrosion process by the use of a split-cell with various combinations of aluminum, copper, and aluminum alloy (AA2024-T3) electrodes allowed individual study of cathodic and anodic reactions.\(^{131}\) Solutions of chromate strongly inhibited the ORR on copper, AA2024-T3, and glassy carbon surfaces, and inhibition persisted after Cr\(^{VI}\) was removed from solution. Studies of pit growth by foil penetration suggested that chromate acts primarily as a cathodic inhibitor.\(^{103}\) Bazzi, et al. studied chromate effects on another aluminum alloy (AA6063) and indicated cathodic inhibition as an effect.\(^{132}\)

The inhibition of cathodic corrosion reactions by chromate has been noted in other systems besides aluminum alloys. Chyzewski and Evans found potassium chromate and potassium dichromate to inhibit galvanic current when added to iron cathodes coupled to zinc anodes.\(^{133}\) Zinc potassium chromate was shown to inhibit corrosion of mild steels in another study.\(^{134}\) The mechanism was deemed cathodic protection due to electron probe microanalysis findings of zinc chromate on cathodic surface areas. Zin, et al. used electrochemical impedance spectroscopy (EIS) to demonstrate cathodic inhibition as the primary mode of protection by strontium chromate for galvanized steel in artificial acid rain solution.\(^{135}\) Strontium chromate primers were also examined in their role of inhibition of delamination of an organic coating (polyvinyl
butyral) from galvanized steel. The protection was deemed to have come as a result of "replacement of underfilm O₂ reduction by a self-limiting CrO₄²⁻ reduction process".

**Properties and formation of chromate conversion coatings (CCC)**

Investigations of chromate conversion coatings have revealed much about their composition and formation mechanisms. The reduction of hexavalent chromium (Cr VI as CrO₄²⁻, HCrO₄⁻, Cr₂O₇²⁻, etc.) to trivalent chromium (Cr III as Cr(OH)³⁺, Cr₂(OH)₄(OH₂)⁸⁺, Cr₃(OH)₄(OH₂)⁹⁺, etc.) has been shown to be an integral part of the formation process of CCC's. Previous studies have revealed the mechanism for CCC formation and its composition, as well as its distribution on the various surface phases of AA2024-T3. In particular the CCC on AA2024-T3 has been shown to contain approximately a 3:1 ratio of Cr III:Cr VI with the Cr III serving as the polymeric backbone to which Cr VI adsorbs to form a Cr III-O-Cr VI mixed oxide. CCC formation on intermetallic phases has been shown to be less or significantly different than on the bulk matrix. Studies have also been conducted on high purity aluminum showing thinner CCC's with less Cr VI incorporation. The storage and release of Cr VI in CCC films have been invoked to explain the self healing properties of chromate coatings, whereby active inhibitor is released by the CCC in response to a scratch or defect. Demonstration of adsorption and desorption of Cr VI from Cr III has been shown and is dependent upon pH and [Cr VI]. Cr VI migration to exposed alloy provides remote protection of newly formed coating defects, possibly years after initial coating.
application. While these studies have shown the importance of Cr$^{VI}$ in the CCC protection system, they did not directly investigate the corrosion inhibition mechanism.

While the copper containing intermetallic phases of aluminum alloy 2024-T3 have been implicated in both cathodic and anodic corrosion reactions,\textsuperscript{53} this chapter addresses inhibition of cathodic reactions related to corrosion and inhibition of several simple redox systems. In particular, how does exposure to Cr$^{VI}$ inhibit the oxygen reduction reaction (ORR) on Cu, Cu-containing intermetallic phases, and redistributed Cu particles on AA2024-T3? In chapter 2 it was shown that ORR inhibition in a split cell was preceded by a cathodic current spike tentatively attributed to the reduction of Cr$^{VI}$ to Cr$^{III}$\textsuperscript{131} Is this cathodic current spike involved in ORR inhibition? How does chromate affect inhibition of electron transfer for outer-sphere aqueous and organic systems?

**Chromate reduction electrochemistry**

Chromate reduction has been studied in the context of electroplating and industrial chlorate production, and the reactions are quite complex.\textsuperscript{109} Although the overall stoichiometry is well known (Equation 3.1), the multiple H$^+$ and e$^-$ transfers require a very complex sequence of elementary reactions.

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- = 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E^0 = 1.33 \text{ V (vs. NHE)}
\]  \quad (3.1)
An obvious consequence of Equation 3.1 is the strong pH dependence of the reduction potential. Previous studies of the Cr\textsuperscript{VI} reduction mechanism were conducted under conditions similar to industrial processes (acidic or strongly basic), rather than the near neutral or acidic chloride solutions relevant to corrosion. However, several observations relevant to the present study are available. Kolthoff, et al. first reported the formation of a "unimolecular film of Cr\textsuperscript{III} on the [rotating platinum] electrode".\textsuperscript{109} This film inhibited numerous redox systems (under varying solution conditions) and was self-inhibiting under mildly acidic conditions (0.001 M HCl). Under strongly acidic conditions (1 M HCl), slight or negligible self-inhibition occurred. Inhibition persisted after rinsing with chromate-free solution. Several studies of Cr\textsuperscript{VI} reduction to Cr\textsuperscript{III} in acidic electrolytes have focused on the role of other anions such as SO\textsubscript{4}\textsuperscript{2-} and Cl\textsuperscript{-} in the mechanism.\textsuperscript{144-151}

The chlorate process is dependent upon the addition of chromate to prevent the reduction of intermediate hypochlorite ions that are formed. Similar studies on Cr\textsuperscript{VI} reduction have taken place under the highly basic conditions encountered in chlorate production.\textsuperscript{108,152-155} In 1 M NaOH on platinum and gold electrodes, self-inhibition is incomplete, attributed to Cr(OH)\textsubscript{4}\textsuperscript{-} formation and dissolution, but monolayer films were formed based upon oxidation current measurements. Inhibition of several redox systems was observed (Fe[CN]\textsubscript{6}\textsuperscript{3-}, O\textsubscript{2}, and hypochlorite) in 1 M NaOH.\textsuperscript{108}

Reduction of Cr\textsuperscript{VI} in relation to the mechanisms by which chromium oxyanions and conversion coatings provide protection from corrosion has been investigated.\textsuperscript{156} Cr\textsuperscript{VI} reduction was examined on platinum electrodes in acidic media (0.18 M H\textsubscript{2}SO\textsubscript{4} and 0.022 M H\textsubscript{3}PO\textsubscript{4}). An insoluble Cr\textsuperscript{III}-phosphate product was formed which inhibited Cr\textsuperscript{VI}
reduction after several cycles. It also inhibited the oxidation of ferrocene (in organic solvent), a system that does not require adsorption to the electrode for electron transfer to occur.

**Oxygen reduction**

The reduction of oxygen, like chromate, is a very complex process and has been studied extensively. The reduction can occur via two or four electrons and has a strong pH dependence.

\[
\begin{align*}
O_2 + 4H^+ + 4e^- & \equiv 2H_2O & E^0 = 1.229 \text{ V (vs. NHE)} \quad (3.2) \\
O_2 + 2H^+ + 2e^- & \equiv H_2O_2 & E^0 = 0.67 \text{ V (vs. NHE)} \quad (3.3)
\end{align*}
\]

The outer-sphere reduction mechanism (not involving an adsorption step) is kinetically slow, thus catalysis via adsorption to the electrode surface is usually involved. Studies on glassy carbon (GC) electrodes have illustrated one example of how adsorption sites can be blocked and the outer-sphere process observed. For aluminum alloys, oxygen reduction is the primary cathodic reaction occurring. H\(^+\) reduction can also be an important reaction, but occurs mainly in actively corroding pits. An important question to answer regarding the inhibition of oxygen reduction is whether the mechanism involves blockage of adsorption sites or if the electron-transfer process itself is inhibited.
Overview

The investigation presented in this chapter sought to determine the relationship between the reactions of Cr$^{VI}$ and the cathodic inhibition of the ORR under common field conditions encountered by AA2024-T3. The effects of Cr$^{VI}$ on the ORR were examined, initially using Cu electrodes as models of Cu-containing intermetallic compounds and redistributed Cu found on AA2024-T3. Cr$^{VI}$ reduction was examined on Pt and glassy carbon electrodes to permit a wider potential range than possible with Cu. Additionally, other electrochemical systems (both aqueous and organic) were examined to learn about specific mechanistic details of the inhibition process of chromate.

EXPERIMENTAL

Barnstead NanoPure™ water with a resistivity of 18 MΩ-cm was used for rinsing and solution preparation in all cases. NaCl (Fisher Scientific), K$_2$Cr$_2$O$_7$ (Alfa Aesar), Ru(NH$_3$)$_6$Cl$_3$ (Ruthenium hexaamine, Aldrich), C$_{10}$H$_{10}$Fe (Ferrocene, Sigma), C$_{12}$H$_4$N$_4$ (7,7,8,8-tetracyanoquinodimethane or TCNQ, Acros Organics), K$_3$Fe(CN)$_6$ (Potassium Ferricyanide, J. T. Baker), K$_2$HPO$_4$ (Mallinckrodt), Na$_3$BO$_3$ (Fisher Scientific), NaOH (Mallinckrodt), HCl (Fisher Scientific), CH$_3$CN (Acetonitrile, Mallinckrodt), and [CH$_3$(CH$_2$)$_3$]$_4$BF$_4$ (tetrabutylammonium tetrafluoroborate, Aldrich) were reagent grade and used as received. Electrodes were commercial Pt or Glassy carbon (Bioanalytical Systems, Inc.) or were made from 0.5 mm diameter copper wire (99.9% Cu, Aldrich). Copper wire electrodes were attached to standard copper electrical wire with silver epoxy resin (SPI Supplies/Structure Probe Inc.), and embedded in epoxy (Buehler). They were
mechanically polished with successively finer Si:C papers (Buehler: 240, 400, 600, 800, 1200 grit), rinsed with water, and dried under a stream of hot air. Prior to each experiment all electrodes were polished using Al₂O₃ slurries (Buehler, 1.0, 0.3, and 0.05 μm) and rinsed with water. Glassy carbon electrodes were further cleaned via sonication in water, 3:1 v/v isopropanol: activated carbon, water as prescribed by Ranganathan, et al.¹²⁸

Hydrodynamic and potentiostatic electrochemical measurements were performed using a Gamry Instruments PC3/300™ Potentiostat/Galvanostat/ZRA with Framework™ (Version 3.11) and DC105™ DC Corrosion Measurement software. Cyclic voltammetry was performed using a Bioanalytical Systems BAS100B Electrochemical Analyzer using BAS100W software (version 2.3). Evaluation of current transient area was performed using Grams/32 Spectral Notebase Version 4.02 (Galactic Industries Corporation). Calculation of heterogeneous rate constants was performed using Digisim Version 3.03 (Bioanalytical Systems, Inc.) cyclic voltammetry simulator. Experiments were performed using a standard three-electrode electrochemical cell. Experiments in water utilized Ag/AgCl as the reference electrode (potential = 0.197 V vs. NHE) and all potentials quoted are with respect to this reference. Experiments in acetonitrile used Ag/Ag⁺ (filling solution: 0.01 M Ag(NO₃)₃ and 0.1M [CH₃(CH₂)₃]₄NBF₄ in CH₃CN) as the reference electrode. Pt wire was used as the counter electrode. Unless otherwise noted, 0.1 M NaCl served as the background electrolyte for aqueous solutions and 0.1M [CH₃(CH₂)₃]₄BF₄ for acetonitrile. "Aerated" refers to solutions open to air and "deaerated" refers to solutions purged with argon (prepurified, Praxair) for >15 minutes.
Where noted, solutions were also saturated with oxygen (extra dry, Praxair). Solution additions were made using 0.05 M K₂Cr₂O₇ (0.1 M total Cr⁶⁺) in 0.1 M NaCl, and 10 mM Ru(NH₃)₆Cl₃ as noted in the text and figures. Unless stated otherwise, Cr⁶⁺ concentrations are stated as total [Cr⁶⁺] in the form of HCrO₄⁻, CrO₄²⁻, Cr₂O₇²⁻, etc. Unbuffered solutions, except by the presence of Cr⁶⁺ itself resulted in a pH of ~6.

Electrochemical experiments were performed as follows:

**Constant potential with Cr⁶⁺ injection.** The solution was stirred with a magnetic stir bar and aerated or deaerated as noted. The electrode was held at -1.500 V for 60 seconds to reduce surface oxides before setting to the desired experimental potential. At a specified time an aliquot of analyte was injected into the solution. If the solution was deaerated, the injection aliquot was deaerated also. The current response was monitored as a function of time.

**Hydrodynamic voltammetry.** The solution was stirred and aerated or deaerated as noted. A magnetic stirrer was used rather than a rotating disc electrode because the variety of electrode materials required a flexible cell and electrode mount. The stir rate of the magnetic stirrer was held as constant as possible from experiment to experiment. The electrode was held at -1.000 V for 60 seconds to reduce surface oxides. Potential control was then removed and the electrode allowed to come to its open circuit value for 600 seconds. Analyte species were added during this step if desired. The potential was then scanned negatively from the open circuit value to -1.300 V at 1 mV/s. Current response was monitored as a function of potential. In some cases, the open circuit potential period was omitted and the potential was scanned from +0.500 V to -1.300 V.
Analyte species were added with the potential at positive values if desired to prevent reduction prior to the commencement of the experiment.

**Potential step.** The solution was stirred and aerated or deaerated as noted. The electrode was held at -1.000 V for 60 seconds to reduce surface oxides. The potential was then held at +0.750 V for a specified time period. Analyte species were added during this step if desired. The potential was then stepped to a specified value and held for a fixed time. The current response was monitored as a function of time. If the electrode was to be used in a subsequent experiment without additional polishing, it was removed from the solution under potential control (electrochemical cell “on” or controlled by the potentiostat) while being rinsed with water. This removed any remaining analyte as quickly as possible when the electrode was emmersed (and returned to open circuit potential) from the solution.

**Cyclic Voltammetry.** Experiments were performed in both aqueous and organic (acetonitrile) media. The solutions were quiescent and oxygenated or deaerated as noted. The potential was cycled between potential limits at scan rates as indicated in the text and figures. In some cases the electrode was pretreated with Cr^VI as described in the "Results" section.

**RESULTS**

Figures 3.1 and 3.2 show results of constant-potential hydrodynamic experiments using a copper electrode. The electrode was held at a constant potential of −550 mV while stirring vigorously. This potential was chosen due to its proximity to the open
Figure 3.1: Current response of a copper electrode vs. time at constant potential (-0.550 V vs Ag/AgCl) in 0.1 M NaCl. The solution was stirred and aerated or deaerated as indicated. K₂Cr₂O₇ was injected (to ~10 mM Cr⁶⁺) at 600 s. Inset shows response in time frame near injection point.
Figure 3.2: Effect of Cr\textsuperscript{VI} concentration on current response of a copper electrode at constant potential (-0.550 V \textit{vs.} Ag/AgCl) in stirred, deaerated 0.1 M NaCl. At the indicated time $K_2Cr_2O_7$ was injected to (a) $5 \times 10^{-3}$ M, (b) $5 \times 10^{-4}$ M, (c) $5 \times 10^{-5}$ M, and (d) $5 \times 10^{-6}$ M.
circuit potential for AA2024-T3 reported in chapter 2. In figure 3.1, both aerated and deaerated solutions of 0.1 M NaCl are shown. The higher current density before chromate injection for the aerated solution is attributed to the reduction of dissolved oxygen. At 600 seconds, potassium dichromate was injected to yield a total Cr\textsuperscript{VI} concentration of 10 mM. The current immediately increased and then rapidly decreased for both solutions. The current density of each solution after chromate addition decreased to less than 3% of its value prior to injection. The inset in Figure 3.1 shows the current spike more clearly and indicates that it occurs for both aerated and deaerated solutions, with approximately equal peak area. Table 3.1 lists the area of the current spike for Cr\textsuperscript{VI} injections at -600 mV which yielded several final concentrations of Cr\textsuperscript{VI} ranging from $5 \times 10^{-3}$ M to $5 \times 10^{-8}$ M. The spike area decreased by about one-half over the first three orders of magnitude of decreased [Cr\textsuperscript{VI}]. The mean spike area for $5 \times 10^{-3}$ M to $5 \times 10^{-6}$ M [Cr\textsuperscript{VI}] was 1.6 mC/cm\textsuperscript{2} on the copper electrode. Figure 3.2 shows the experiments with final [Cr\textsuperscript{VI}] from $5 \times 10^{-3}$ M to $5 \times 10^{-6}$ M graphically. Higher concentrations of Cr\textsuperscript{VI} resulted in increased spike height but narrowed width. In fact, the peaks for the lowest Cr\textsuperscript{VI} additions, $5 \times 10^{-7}$ M and $5 \times 10^{-8}$ M (not shown), were drawn out to the extent that the smaller peak areas listed in Table 3.1 for these concentrations may be caused by measurement difficulty rather than a trend.

The decreased current following the spike upon Cr\textsuperscript{VI} injection has two important ramifications. First, cathodic processes (namely oxygen reduction) occurring on the Cu electrode before Cr\textsuperscript{VI} addition are greatly inhibited by Cr\textsuperscript{VI} or its reduction products. Second, the continuing reduction of Cr\textsuperscript{VI} is inhibited after the current spike. For a normal
redox process under hydrodynamic conditions, injection of an analyte at a potential sufficient for reduction (or oxidation) would result in an increase in current to a steady-state value. The rate of mass transport to the surface determines the current unless it is limited by charge-transfer kinetics. The result would look something like a step function, rather than the spike shown. The known redox chemistry of Cr\textsuperscript{VI} and previous reports on electrochemical Cr\textsuperscript{VI} reduction\textsuperscript{108,109,152-156}, lead to the assignment of the cathodic spike to reduction of solution Cr\textsuperscript{VI} to Cr\textsuperscript{III} most probably as an adsorbed film of Cr\textsuperscript{III} hydroxide.

<table>
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<th>Potential (V)</th>
<th>-0.6</th>
<th>-0.6</th>
<th>-0.6</th>
<th>-0.6</th>
<th>-0.6</th>
<th>-0.6</th>
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<tr>
<td>[Cr\textsuperscript{VI}] (M)\textsuperscript{a}</td>
<td>5 x 10\textsuperscript{-3}</td>
<td>5 x 10\textsuperscript{-4}</td>
<td>5 x 10\textsuperscript{-5}</td>
<td>5 x 10\textsuperscript{-6}</td>
<td>5 x 10\textsuperscript{-7}</td>
<td>5 x 10\textsuperscript{-8}</td>
</tr>
<tr>
<td>Transient area (mC/cm\textsuperscript{2})</td>
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<td>1.6</td>
<td>1.1</td>
<td>0.5</td>
<td>0.6</td>
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<td>5.5</td>
<td>3.6</td>
<td>1.8</td>
<td>2.0</td>
</tr>
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<td>1.6</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>std. dev.\textsuperscript{b}</td>
<td>5.4</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Concentration dependence of Cr\textsuperscript{VI} reduction transient on copper electrode at constant potential in deaerated 0.1 M NaCl.  
\textsuperscript{a} Final concentration of total Cr\textsuperscript{VI} after injection.  
\textsuperscript{b} Mean and standard deviation for the first four columns.

Results shown in Figure 3.3 further establish the existence of an irreversibly adsorbed species on the copper electrode. The injection experiment is identical to that in Figure 3.1. Run 1 shows the current spike and rapid inhibition upon addition of Cr\textsuperscript{VI} to deaerated 0.1 M NaCl at -550 mV as previously observed. The electrode was then rinsed with water and replaced in fresh deaerated electrolyte for a second injection experiment to yield Run 2 in Figure 3.3. The initial current was greatly decreased compared to Run 1.
Figure 3.3: Effect of previous Cr$^{VI}$ exposure on the current response of a copper electrode at constant potential (-0.550 V vs. Ag/AgCl) in stirred, deaerated 0.1 M NaCl. Cr$^{VI}$ was injected (to ~10 mM) at 600 s. Run 1 is a freshly polished electrode. Run 2 is the same electrode but rinsed only and replaced in fresh electrolyte.
1 (<0.01 mA/cm² vs. ~0.17 mA/cm²) despite the absence of Cr⁶⁺ in solution. Upon injection of Cr⁶⁺ a very small current spike was observed (spike height <0.02 mA/cm²) as compared to the freshly polished electrode from Run 1 (spike height ~2.5 mA/cm²). The results indicate that an adsorbed layer is formed upon the initial injection of Cr⁶⁺ that remains after rinsing the electrode. Since the current spike observed upon Cr⁶⁺ injection occurred immediately prior to the inhibition of reduction currents, the events taking place during the spike must be critical to the inhibition mechanism.

A series of constant potential experiments were conducted to examine the spike area dependence upon several variables for a copper electrode. The results are presented in Tables 3.2 and 3.3 (with data from Table 3.1 included). The data compiled in the table come from several sets of conditions as listed in Table 3.2. Variables included Cr⁶⁺ concentration, stirring, aeration, and choice of electrolyte. Also included are several experiments that were conducted with a galvanically coupled split-cell (either Al/Cu or AA2024-T3/Cu) as discussed in chapter 2. The potential in these cases was not truly controlled but held relatively constant at a mixed potential dictated by the reactions at the anode and cathode. The values listed for the split-cell couples are the open circuit potentials just prior to Cr⁶⁺ injection. Table 3.3 shows several subsets of the full table after sorting for various conditions. The spike area remained relatively constant over a wide range of conditions.

Table 3.4 lists a specific subset of the results in Table 3.2(a) for unbuffered 0.1 M NaCl and [Cr⁶⁺] = 5 mM. Various potential ranges have been specified and the mean
<table>
<thead>
<tr>
<th>[Cr(VI)] (M)</th>
<th>Potential (mV)</th>
<th>Stirred?</th>
<th>aerated/ deaerated</th>
<th>Electrolyte</th>
<th>pstat or ZRA</th>
<th>Spike area mC/cm²</th>
<th>Cr reduced mmol Cr/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00E-03</td>
<td>-780</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-Al)</td>
<td>0.33</td>
<td>1.15</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-705</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-Al)</td>
<td>0.48</td>
<td>1.65</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-705</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-Al)</td>
<td>0.54</td>
<td>1.88</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-695</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-Al)</td>
<td>0.73</td>
<td>2.51</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-685</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-Al)</td>
<td>0.45</td>
<td>1.57</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-675</td>
<td>n</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-Al)</td>
<td>1.21</td>
<td>4.18</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-640</td>
<td>n</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-Al)</td>
<td>2.60</td>
<td>8.97</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-570</td>
<td>n</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-Al)</td>
<td>1.16</td>
<td>4.01</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-530</td>
<td>n</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-AA2024)</td>
<td>0.84</td>
<td>2.90</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-505</td>
<td>n</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-AA2024)</td>
<td>1.35</td>
<td>4.65</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-490</td>
<td>n</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>ZRA (Cu-AA2024)</td>
<td>1.12</td>
<td>3.86</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-1000</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.74</td>
<td>6.00</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-800</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.70</td>
<td>5.87</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-800</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>0.99</td>
<td>3.43</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>2.73</td>
<td>9.44</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>0.77</td>
<td>2.65</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>0.77</td>
<td>2.67</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>d</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>0.66</td>
<td>2.29</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>d</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>2.17</td>
<td>7.50</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-550</td>
<td>y</td>
<td>d</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.32</td>
<td>4.55</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-550</td>
<td>y</td>
<td>d</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.12</td>
<td>3.87</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-400</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>0.82</td>
<td>2.82</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-400</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.26</td>
<td>4.35</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-400</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.30</td>
<td>4.49</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-200</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.07</td>
<td>3.69</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-200</td>
<td>y</td>
<td>a</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.26</td>
<td>4.36</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>d</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.42</td>
<td>4.90</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>d</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.59</td>
<td>5.49</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>d</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>1.05</td>
<td>3.64</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>d</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>0.51</td>
<td>1.76</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>d</td>
<td>0.1M NaCl</td>
<td>pstat</td>
<td>0.57</td>
<td>1.98</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-1000</td>
<td>y</td>
<td>a</td>
<td>pH 7 buffer</td>
<td>pstat</td>
<td>2.68</td>
<td>9.26</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-800</td>
<td>y</td>
<td>a</td>
<td>pH 7 buffer</td>
<td>pstat</td>
<td>2.12</td>
<td>7.33</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-600</td>
<td>y</td>
<td>a</td>
<td>pH 7 buffer</td>
<td>pstat</td>
<td>1.79</td>
<td>6.17</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-100</td>
<td>y</td>
<td>a</td>
<td>pH 7 buffer</td>
<td>pstat</td>
<td>1.10</td>
<td>3.79</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-203</td>
<td>y</td>
<td>a</td>
<td>pH 7 buffer</td>
<td>pstat</td>
<td>1.79</td>
<td>6.18</td>
</tr>
<tr>
<td>5.00E-03</td>
<td>-200</td>
<td>y</td>
<td>a</td>
<td>pH 7 buffer</td>
<td>pstat</td>
<td>1.37</td>
<td>4.72</td>
</tr>
</tbody>
</table>

Table 3.2: Results of constant potential experiments using copper electrodes with CrVI injection.

a pH 7 buffer is 0.1M PO₄³⁻ / 0.1 M NaCl adjusted with NaOH and HCl.
b Controlled via potentiostat or zero-resistance ammeter (open circuit) in split-cell configuration. Galvanic couple is listed where applicable.
<table>
<thead>
<tr>
<th>Condition</th>
<th>N</th>
<th>Mean Spike Area</th>
<th>Cr Reduced</th>
<th>Cr Reduced +/-</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Data</td>
<td>37</td>
<td>1.2 mC/cm²</td>
<td>4.3 nmol/cm</td>
<td>±2.2 nmol/cm</td>
</tr>
<tr>
<td>All cases with [Cr(VI)] = 0.005 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All Stirred Cases</td>
<td>32</td>
<td>1.3 mC/cm²</td>
<td>4.5 nmol/cm</td>
<td>±2.2 nmol/cm</td>
</tr>
<tr>
<td>All Quiescent Cases</td>
<td>31</td>
<td>1.2 mC/cm²</td>
<td>4.3 nmol/cm</td>
<td>±2.2 nmol/cm</td>
</tr>
<tr>
<td>All Aerated Cases</td>
<td>29</td>
<td>1.3 mC/cm²</td>
<td>4.4 nmol/cm</td>
<td>±2.3 nmol/cm</td>
</tr>
<tr>
<td>All Deaerated Cases</td>
<td>8</td>
<td>1.2 mC/cm²</td>
<td>4.2 nmol/cm</td>
<td>±1.9 nmol/cm</td>
</tr>
<tr>
<td>All Cases under potential control via potentiostat</td>
<td>26</td>
<td>1.4 mC/cm²</td>
<td>4.7 nmol/cm</td>
<td>±2.1 nmol/cm</td>
</tr>
<tr>
<td>All Cases with ZRA (split-cell)</td>
<td>11</td>
<td>1.0 mC/cm²</td>
<td>3.4 nmol/cm</td>
<td>±2.2 nmol/cm</td>
</tr>
<tr>
<td>All Cases with 0.1 M NaCl</td>
<td>31</td>
<td>1.2 mC/cm²</td>
<td>4.0 nmol/cm</td>
<td>±2.0 nmol/cm</td>
</tr>
<tr>
<td>All Cases with pH 7 buffer</td>
<td>6</td>
<td>1.8 mC/cm²</td>
<td>6.2 nmol/cm</td>
<td>±1.9 nmol/cm</td>
</tr>
</tbody>
</table>

Table 3.3: Various sorting schemes for data from Table 3.2.
Table 3.4: Potential dependence of Cr\textsuperscript{VI} reduction on Cu electrode.

\textsuperscript{a} A range of potentials indicates that the spike area is the mean of \( n \) runs with Cr\textsuperscript{VI} injection at a potential in that range.

<table>
<thead>
<tr>
<th>Potential\textsuperscript{a}</th>
<th>-0.2 to -0.3</th>
<th>-0.3 to -0.5</th>
<th>-0.5 to -0.7</th>
<th>-0.7 to -0.9</th>
<th>-0.9 to -1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cr}^{\text{VI}}]) (M)</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Transient area (mC/cm\textsuperscript{2})</td>
<td>1.2</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.1</td>
<td>0.2</td>
<td>0.6</td>
<td>0.9</td>
<td>n/a</td>
</tr>
<tr>
<td>Cr reduced (nmol/cm\textsuperscript{2})</td>
<td>4.0</td>
<td>3.9</td>
<td>4.0</td>
<td>3.9</td>
<td>6.0</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.5</td>
<td>0.8</td>
<td>2.1</td>
<td>3.2</td>
<td>n/a</td>
</tr>
<tr>
<td>N</td>
<td>2</td>
<td>4</td>
<td>13</td>
<td>6</td>
<td>1</td>
</tr>
</tbody>
</table>

Mean 1.2 s.d. 0.6
Mean 4.1 s.d. 2.1

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spike area for each range is listed. The applied potential has little effect on the spike area over the range studied for Cu electrodes. The average spike area from 26 injection experiments for the potential range of -200 mV to -1000 mV and final [Cr\textsuperscript{VI}] = 5 mM was 1.2 ± 0.6 mC/cm\textsuperscript{2}.

The pH dependence of current response to Cr\textsuperscript{VI} injection is shown in Figure 3.4. Injection experiments were run at various constant potentials between -0.200 V and -1.000 V in stirred, aerated solutions that were unbuffered (0.1 M NaCl), pH 1 (0.1 M HCl), pH 7 (0.1 M PO\textsubscript{4}\textsuperscript{3-} + 0.1 M NaCl, adjusted with HCl), and pH 13 (0.1 M NaOH + 0.1 M NaCl). Figure 3.4(a) shows the response in the unbuffered 0.1 M NaCl solution. The initial current before Cr\textsuperscript{VI} injection increased with more negative applied potentials. A particularly large increase was noted between -0.600 V and -0.800 V that did not increase further at -1.000 V but plateaued at ~3 mA/cm\textsuperscript{2}. At all potentials, injection of Cr\textsuperscript{VI} resulted in a current spike and subsequent decrease in current. The current for -1.000 V did not return to near zero as the others but leveled out at about 1.0 mA/cm\textsuperscript{2}.

Figure 3.4(b) shows the current response in pH 1 HCl solution. In these experiments, the initial current level behaved similarly, with an increase as potentials were made more negative. However, the initial current did not level out as it did for the unbuffered solution [Figure 3.4(a)] and the current values reached much greater levels (~40 mA/cm\textsuperscript{2} at -1.000 V). Injection of Cr\textsuperscript{VI} did not result in a current spike but rather an increase to a new steady-state plateau about 30 mA/cm\textsuperscript{2} greater than the initial current value at all applied potentials. Figure 3.4(c) shows results for pH 7 buffered phosphate + chloride solution and the results are quite similar to the unbuffered results (~pH 6) in Figure.
Figure 3.4: Effect of Cr$^{VI}$ injection (to ~5 mM) at various constant potentials and pH values on the current response of a copper electrode in stirred, aerated electrolyte of (a) 0.1 M NaCl, (b) 0.1 M HCl, (c) 0.1 M NaCl + 0.1 M PO$_4^{3-}$ adjusted to pH 7 with HCl, (d) 0.1 M NaCl and 0.1 M NaOH. Potentials were held at indicated potentials (vs Ag/AgCl). Cr$^{VI}$ was added at 120 s.

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(Figure 3.4 continued)

![Graphs showing current density over time after adding different concentrations of Cr VI to a solution at various potentials:]

- Top: Cr VI added (to ~5 mM) \(E_{\text{aq}} = -0.200\) V
- Second: Cr VI added (to ~5 mM) \(E_{\text{aq}} = -0.400\) V
- Third: Cr VI added (to ~5 mM) \(E_{\text{aq}} = -0.600\) V
- Bottom: Cr VI added (to ~5 mM) \(E_{\text{aq}} = -0.800\) V

Time (s) vs. Current Density (mA/cm²)
Cr\textsuperscript{VI} added (to ~5 mM) \quad E_{\text{ox}} = -0.200V

Cr\textsuperscript{VI} added (to ~5 mM) \quad E_{\text{ox}} = -0.400V

Cr\textsuperscript{VI} added (to ~5 mM) \quad E_{\text{ox}} = -0.500V

Cr\textsuperscript{VI} added (to ~5 mM) \quad E_{\text{ox}} = -0.800V

Cr\textsuperscript{VI} added (to ~5 mM) \quad E_{\text{ox}} = -1.000V

Time (s)

Current Density (mA/cm\textsuperscript{2})
(Figure 3.4 continued)
3.4(a). The peaks upon injection of Cr\textsuperscript{VI} appear to be sharper and smoother than for unbuffered solution. Injection of Cr\textsuperscript{VI} into the NaOH + NaCl solution of pH 13 are shown in Figure 3.4(d). Experiments were conducted at constant applied potentials of -0.400 V to -1.000 V. Initial currents before Cr\textsuperscript{VI} injection followed similar increasing trends with more negative potentials as for the other pH values. The current density, however, was lower with the maximum value being ~2 mA/cm\textsuperscript{2} at -1.000 V. The current generally decreased upon injection of Cr\textsuperscript{VI} but the decrease was gradual rather than abrupt for pH 13. The final current values also did not fall as low as for the unbuffered and pH 7 solutions. A current spike appeared upon injection only for the experiments at -0.800 V and -1.000 V at pH 13 and its appearance was more noisy and less defined than for the unbuffered and pH 7 solutions.

The potential dependence of O\textsubscript{2} reduction and inhibition was examined with hydrodynamic voltammetry, shown in Figure 3.5 for copper, platinum, and Glassy carbon (GC) electrodes. Platinum and Glassy carbon electrodes were used as they allow wider potential ranges than Cu, particularly for potentials positive of Cu oxidation at \textasciitilde 0 V vs. Ag/AgCl. Although the current densities for O\textsubscript{2} reduction differ for the three electrodes, the potentials observed for O\textsubscript{2} and Cr\textsuperscript{VI} reduction follow similar trends as expected from thermodynamic considerations. In aerated Cr\textsuperscript{VI}-free solutions, the O\textsubscript{2} reduction current begins to increase between -0.200 V and -0.400 V on Cu (Figure 3.5(a)). With constant stirring the current increases as the potential is scanned negative, then levels off to a mass transport limited value. The same experiment in deaerated electrolyte yields little current until very negative potentials (negative of -1.2 V) possibly
Figure 3.5: Current response vs. potential for electrodes in stirred 0.1 M NaCl under various conditions. The potential was scanned negative at 0.001 V/s beginning at the open circuit potential. (a) Copper electrode in aerated and deaerated electrolyte only. (b) Copper electrode as for (a) with added chromate (aerated and deaerated) and pretreated conditions. The trace listed as pretreated with Cr was an electrode from a previous scan in CrVI-containing solution that was removed, rinsed with water, and replaced in fresh 0.1 M NaCl. (c) as for (b) with platinum electrode. (d) as for (b) with glassy carbon electrode.
Pt electrode in stirred 0.1M NaCl under indicated conditions.
Figure 3.5 continued

Glassy C electrode in stirred 0.1M NaCl under indicated conditions

(d)

<table>
<thead>
<tr>
<th>Current Density (mA/cm²)</th>
<th>Potential (V) vs. Ag/AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.1</td>
</tr>
<tr>
<td>0.02</td>
<td>-0.3</td>
</tr>
<tr>
<td>0.04</td>
<td>-0.5</td>
</tr>
<tr>
<td>0.06</td>
<td>-0.7</td>
</tr>
<tr>
<td>0.08</td>
<td>-0.9</td>
</tr>
<tr>
<td>0.10</td>
<td>-1.1</td>
</tr>
<tr>
<td>0.12</td>
<td>-1.3</td>
</tr>
</tbody>
</table>

- aerated
- aerated in 5mM Cr
- aerated pretreated w/Cr
- de-aerated in 5mM Cr
- de-aerated

scan 1mV/s

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due to the reduction of water. The experiments were repeated (both aerated and deaerated) in the presence of 5 mM CrVI with the results shown in Figure 3.5(a). The current density remains well below the current density for the aerated CrVI-free solution until the potential reaches values about -1 V. Since the current increases at -1 V for both aerated and deaerated CrVI-containing solutions this current is attributed to reduction of CrVI to CrIII. For the Pt electrode [Figure 3.5(b)], the mass-transport limited current for CrVI reduction is observed at about -0.9 V. The mass-limited current for CrVI reduction is about 3-4 times that for O2 reduction on both the Cu and Pt electrodes. Finally, each electrode was removed, rinsed, and replaced in fresh CrVI-free aerated solution after a negative scan in CrVI solution. The current after this pretreatment was similar to that in the CrVI-containing solutions, showing little current attributable to oxygen reduction and none for CrVI. Since the catalytic properties of Cu, Pt, and GC for O2 reduction differ substantially, the products, potentials, and limiting current densities also differ. However, CrVI exposure has the same overall effects on all three electrodes. A reduction spike such as that shown in Figure 3.1 was observed when CrVI was injected at a constant potential (not shown), the current for the ORR was greatly decreased, and a persistent film was formed that resists removal by rinsing.

Figure 3.6(a) shows a hydrodynamic voltammogram of a deaerated CrVI solution on a GC electrode, starting at +500 mV vs. Ag/AgCl and scanning negative. This takes advantage of the more positive potential limit of GC compared to Cu. This is essentially the same experiment as that shown in Figure 3.5(c) but started at a more positive potential. Also, CrVI was added to the solution while the electrode was at about +500 mV.
Figure 3.6: Current response vs. potential for electrodes in stirred, deaerated 0.1 M NaCl with and without 5 mM Cr\textsuperscript{VI}. The potential was scanned negative at 0.001 V/s beginning at 0.500 V (vs Ag/AgCl). Cr\textsuperscript{VI} was added to the indicated trace while the potential was at 0.500 V. (a) glassy carbon electrode. (b) platinum electrode.
Figure 3.6 continued

Pt electrode in stirred, deaerated 0.1M NaCl under indicated conditions

-10
-8
-6
-4
-2
0
2
Current Density (μA/cm²)

0.5 0.3 0.1 -0.1 -0.3 -0.5
Potential (V) vs. Ag/AgCl

with 5mM Cr₆⁺
blank
scan 1mV/s

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instead of at the beginning of the experiment. Since the solution is stirred, a typical mass transport limited reduction should yield a steady state current plateau as the potential reaches values negative of the reduction potential of Cr\textsuperscript{VI}. However, the negative scan revealed a peak, rather than a plateau, at about +0.32 V and quite positive of the potentials yielding a steady state Cr\textsuperscript{VI} reduction observed on previous hydrodynamic scans [Figure 3.5(a)]. A quite similar reduction peak was observed on a Pt electrode in the same solution [Figure 3.6(b)]. These reduction peaks are attributed to Cr\textsuperscript{VI} reduction as the same scans in blank electrolyte solution (0.1 M NaCl) revealed no peaks. The areas under these peaks in the potential range of +0.4 to +0.2 V are approximately 2.8 mC/cm\textsuperscript{2} for GC and 6.5 mC/cm\textsuperscript{2} for Pt.

The reduction peak in Figure 3.6(a) was examined more closely using potential step experiments on glassy carbon electrodes. Potential steps were performed from +0.750 V to various potentials in 5 mM Cr\textsuperscript{VI}, with the Cr\textsuperscript{VI} being added while the potential was held at +0.750 V to prevent reduction before the potential step. The results of several of the potential step experiments are shown in Figure 3.7 overlaid onto the hydrodynamic voltammogram of Figure 3.6(a) for comparison. The insets show current transients when the potential is stepped, and the arrows indicate the potential to which the step was made. If the potential was stepped to a value more positive than the Cr\textsuperscript{VI} reduction peak of the voltammogram, no current spike was observed. When the potential was stepped to values negative of the hydrodynamic peak the current spike appeared, with a shape that depended on the final potential. More negative steps resulted in the spike becoming narrower and higher. The results of numerous step experiments are
Figure 3.7: Potential-step experiments using glassy carbon electrodes in stirred, deaerated 0.1 M NaCl with 5 mM Cr\textsuperscript{VI}. The potential was held at 0.750 V and stepped to different potentials as indicated by the arrows. The insets show the current response vs. time at the moment of the potential step. This is overlayed onto Figure 3.6(a). The vertical bar represents 0.6 mA/cm\textsuperscript{2} for all of the insets. Each inset covers a 60 s time window. Cr\textsuperscript{VI} was added while the potential was held at 0.750 V.
tabulated in Table 3.5. The areas of the spikes shown in Figure 3.7 are plotted in Figure 3.8 (open squares). Despite significant variation in peak height, the area is fairly constant with potential in the range +200 to -400 mV. This limiting value corresponds to 2.4 mC/cm$^2$ of reduction for seven potential steps in the range of +0.250 to -0.400 V.

The glassy carbon electrodes used in the potential step experiments of Figure 3.7 were removed under potential control, rinsed, and replaced in fresh aerated 0.1 M NaCl. The electrodes were removed while being held at the final potential after the step with rinsing while emersion occurred to retain the final state of the electrode as best possible. Electrodes were then held at -1.000 V for 60 seconds in 0.1 M NaCl to reduce any adsorbed Cr$^{VI}$. Following this pretreatment, the potential was scanned from the open circuit potential to -1.300 V at 5 mV/s with aeration and stirring as in Figure 3.5. Figure 3.8 (solid circles) shows a plot of the current density at -0.600 V (from the hydrodynamic voltammetry) vs. the final potential after the negative step used to construct Figure 3.7.

Based on Figure 3.5(c), the current at -0.60 V in aerated, Cr-free electrolyte corresponds to $O_2$ reduction. Figure 3.8 shows a strong inverse correlation between the observed current spike area in Cr$^{VI}$ solution and the $O_2$ reduction current following Cr$^{VI}$ exposure. Stated differently, the Cr$^{VI}$ reduction spike area (Figure 3.8) and Cr$^{VI}$ reduction peak [Figure 3.5(a)] correspond directly to the onset of inhibition of $O_2$ reduction. The results also indicate that Cr$^{VI}$ does not adsorb strongly enough at potentials positive of the reduction peak (+0.32 V vs. Ag/AgCl) to remain on the electrode after rinsing. If it did, the constant-potential pretreatment before hydrodynamic voltammetry should reduce the adsorbed Cr$^{VI}$ layer to Cr$^{III}$ and some inhibition should have been observed.
<table>
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<th>0.250</th>
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<tr>
<td>[Cr(^{VI})] (M)</td>
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<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
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<tr>
<td>Spike area(^{(b)}) (mC/cm(^2))</td>
<td>0.0054</td>
<td>&lt;0.0001</td>
<td>0.095</td>
<td>1.3</td>
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<tr>
<td>Cr reduced (nmol/cm(^2))</td>
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<td>&lt; 0.01</td>
<td>0.3</td>
<td>4.6</td>
<td>7.4</td>
</tr>
<tr>
<td>N</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
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</table>

<table>
<thead>
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<th>0</th>
<th>-0.200</th>
<th>-0.400</th>
<th>-0.600</th>
<th>Mean(^{(c)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(^{VI})] (M)</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>Mean(^{(c)})</td>
</tr>
<tr>
<td>Spike area(^{(b)}) (mC/cm(^2))</td>
<td>2.2</td>
<td>2.6</td>
<td>2.6</td>
<td>2.5</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Cr reduced (nmol/cm(^2))</td>
<td>7.7</td>
<td>9.1</td>
<td>9.1</td>
<td>8.6</td>
<td>6.9</td>
<td>7.7</td>
</tr>
<tr>
<td>N</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>6</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 3.5 Potential dependence of Cr\(^{VI}\) reduction on glassy carbon electrode
\(^{(a)}\) potential stepped to from 750 mV
\(^{(b)}\) background charge in the absence of Cr\(^{VI}\) was subtracted
\(^{(c)}\) for 7 runs in the potential range +0.250 V to -0.600 V
Figure 3.8: Correlation between the onset of Cr$^{VI}$ reduction transient (spike) and inhibition of oxygen reduction on glassy carbon electrodes. The Cr$^{VI}$ reduction transient area (open squares) is from potential step experiments from 0.750 V to the indicated potential in stirred, deaerated 5 mM Cr$^{VI}$/0.1 M NaCl (as described in Figure 3.7). The current density value (solid circles) is taken at -0.600 V from a hydrodynamic voltammogram (as described in Figure 3.5(c)) in stirred, aerated 0.1 M NaCl following the potential step experiment (to the indicated value).
Cyclic voltammetry was used to examine the reversibility and repeatability of the adsorption process and its effect on oxygen reduction current. The results are shown in Figure 3.9. Scans were performed in an O₂-saturated solution buffered by borate (BO₃²⁻) at pH 11 in 0.9 M NaCl. The conditions were chosen to be similar to conditions used to study oxygen reduction on glassy carbon electrodes by Yang and McCreery. The potential was cycled from 0.000 V to either +1.000 V or −1.000 V at 200 mV/s while observing current response. Scans A (bottom) and B (top) show the current response of a GC electrode in an oxygenated pH 11 buffer solution when scanned in both positive and negative directions. A wave corresponding to the reduction of oxygen is observed on the negative scan (scan B) at about -0.600 V. The electrode was then treated with Cr⁶⁺ by scanning between 1.000 V and -0.750 V (ending at the negative potential) in chromate ([Cr⁶⁺] = 5mM). Scan C (top) shows that after the GC electrode was removed, rinsed, and replaced in Cr-free electrolyte, negligible O₂ reduction current was observed. An oxidative stripping peak was observed at ~ +0.600 V vs. Ag/AgCl on a subsequent positive scan as shown in scan D (bottom), with an approximate area of 3.8 mC/cm². After stripping, the O₂ reduction wave returned as shown in scan E (top) with nearly identical current-potential response to the original background scan (scan B).

The observation of Cr⁶⁺ reduction onto the surface of a glassy carbon electrode after positive scans is shown in Figure 3.10. A 5 mM solution of Cr⁶⁺ in 0.1 M NaCl was scanned positive at 200 mV/s from a starting potential of -0.500 V. The scans were reversed starting at 0 V and then 0.1 V more positive on each subsequent scan. As the
Figure 3.9: Cyclic voltammetry of a glassy carbon electrode in oxygenated pH 11 buffer (0.1 M BO₄⁻³/0.9M NaCl). The scan rate was 0.200 V/s. The top graph shows negative scans beginning at 0 V before and after exposure to Cr⁶⁺ (scan from 1.000 to -0.750 V in 5 mM Cr⁶⁺ followed by rinsing with water) and again after Cr⁶⁺ stripping from electrode. Bottom graph shows positive scans beginning at 0 V before and after exposure to Cr⁶⁺. The scans follow A-E chronologically with Cr⁶⁺ exposure between scans B and C.
Figure 3.10: Cyclic voltammetry of a glassy carbon electrode in deaerated 0.1 M NaCl with 5 mM Cr\textsuperscript{VI}. The scan rate was 0.200 V/s. Positive scans were started at -0.500 V and reversed at increasingly positive potentials. Each scan travels 0.100 V more positive than the previous.
reversal potential passed about 0.5 V the return scan exhibited a reduction wave starting at about +0.2 V. Scans further positive began to show an oxidative current and the reduction wave on the reverse scan increased in size. O₂ reduction is known to be catalyzed by chemisorption₂⁴. It is likely that part of the mechanism of the ORR inhibition by chromate is blockage of O₂ adsorption sites by a Cr³⁺ layer. A Cr³⁺ layer may also be an effective barrier to electron transfer, even if chemisorption by the analyte is not involved in the redox mechanism. To investigate this possibility, several systems were studied that are known not to require adsorption for electron transfer. These are known as outer-sphere redox systems.¹⁵⁷⁻¹⁵⁹ Copper electrodes were used to study the reduction of Ru(NH₃)₆³⁺. Ru(NH₃)₆³⁺ was also studied on glassy carbon electrodes along with Fe(CN)₆³⁻ reduction. The oxidation of ferrocene and reduction of tetracyanoquinodimethane (TCNQ) in acetonitrile were examined on glassy carbon.

Figure 3.11 shows minimal steady state current for a GC electrode in a stirred, deaerated solution of 1 mM Ru(NH₃)₆³⁺ (in 0.1M NaCl) at an initial potential of +750 mV. When the potential was stepped to -600 mV at 200 seconds, the mass transport limited reduction of Ru(NH₃)₆³⁺ produced a steady-state current density of ~0.7 mA/cm² in a step-like function expected for hydrodynamic reduction. At t = 500 seconds, Cr⁶⁺ was injected to a level of 5 mM, producing a current spike similar to those shown in Figure 3.1. After this spike, the Ru(NH₃)₆³⁺ reduction current decreased to 0.54% of its mass transport limited value. Ru(NH₃)₆³⁺ reduction was inhibited on a copper electrode in a similar fashion as shown in Figure 3.12. Hydrodynamic voltammetry was used - similarly to Figure 3.5 - to examine Ru(NH₃)₆³⁺ properties. The potential was scanned...
Figure 3.11: Current response of a glassy carbon electrode vs. time for a stirred, deaerated 0.1 M NaCl with 1 mM Ru(NH\(_3\))\(_6^{3+}\). At 200 s the potential was stepped from 0.750 V to -0.600 V (vs. Ag/AgCl). At 500 s Cr\(_{VI}\) was injected (to ~5 mM).
Figure 3.12: Current response vs. potential of a copper electrode in a stirred, deaerated 0.1 M NaCl solution containing 10 mM Ru(NH$_3$)$_6^{3+}$. The potential was scanned positive from -1.500 V (vs. Ag/AgCl) at 0.001 V/s. The pretreated electrode was exposed to 5 mM Cr$^{VI}$ in 0.1 M NaCl for 600 s at -0.600 V before rinsing with water.
positive from a potential well negative of the reduction potential of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. In deaerated 0.1M NaCl the reduction current for a deaerated, stirred solution containing 0.5 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> in the absence of Cr<sup>VI</sup> reached an almost steady-state plateau between -0.6 V and -0.9 V of ~0.8 mA/cm<sup>2</sup>. After pretreatment with 5 mM Cr<sup>VI</sup> at a constant potential of -0.600V, the electrode was removed, rinsed, and replaced in fresh 0.5 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> in the absence of Cr<sup>VI</sup> and another hydrodynamic scan was performed. The Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> reduction current at -0.600 V decreased to ~3% of its value before Cr<sup>VI</sup> treatment.

Figure 3.13 shows a cyclic voltammetry of 1 mM TCNQ and 0.5 mM ferrocene on a glassy carbon electrode in acetonitrile (with 0.1 M tetrabutylammonium tetrafluoroborate background electrolyte), and for the same electrode after pretreatment with Cr<sup>VI</sup>. For the TCNQ experiment the pretreatment entailed 10 cyclic voltammograms at 100 mV/s in aqueous 1 mM Cr<sup>VI</sup> between +0.4 V and -0.7 V (vs. Ag/AgCl). In the case of ferrocene the electrode was held at a constant potential of -0.600V (vs. Ag/AgCl) in aqueous 5 mM Cr<sup>VI</sup>. The results of TCNQ reduction scan before and after Cr<sup>VI</sup> treatment are shown in Figure 3.13(a) and ferrocene oxidation in Figure 3.13(b). The oxidation and reduction waves of TCNQ and ferrocene are clearly apparent for the untreated electrodes but current on the treated electrode is nearly absent after Cr<sup>VI</sup> treatment in both cases. Similar results are observed for the aqueous systems of Fe(CN)<sub>6</sub><sup>3-</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. 1 mM solutions in 0.1 M NaCl yielded well-defined voltammograms as shown in Figure 3.14. Cr<sup>VI</sup> treatment (via 10 scans as noted above)
Figure 3.13: Cyclic voltammograms of a glassy carbon electrode in deaerated acetonitrile containing 1 mM tetracyanoquinodimethane (TCNQ) (top) and 0.5 mM ferrocene (Fc) (bottom). 0.1 M tetrabutylammonium tetrafluoroborate was the supporting electrolyte. Reference electrode was Ag/Ag⁺. Where indicated the electrode had been pretreated with Cr⁶⁺ as described in the text. Scan rate was 0.200 V/s for TCNQ and 1.000 V/s for Fc. Scans in background electrolyte were performed and subtracted to give the graphs shown.

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Figure 3.14: Cyclic voltammograms of a glassy carbon electrode in deaerated 0.1 M NaCl containing 1 mM Fe(CN)$_6^{3-}$ (top) and 1 mM Ru(NH$_3$)$_6^{3+}$ (bottom). Reference electrode was Ag/AgCl. Where indicated the electrode had been pretreated with Cr$^{VI}$ as described in the text. Scan rate was 1.000 V/s in both cases. Scans in background electrolyte were performed and subtracted to give the graphs shown.
resulted in a very small current response on the electrodes. However, observable currents with peak shaped voltammetry waves were observed in each case for the aqueous systems after Cr\textsuperscript{VI} treatment.

Examination of the response of post-Cr\textsuperscript{VI} treatment glassy carbon electrodes to aqueous outer-sphere systems [Fe(CN)\textsubscript{6}\textsuperscript{3-} and Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+}] is shown in Figure 3.15. The dashed line in each voltammogram is a scan in 1 mM solution of the analyte within 1-5 minutes after treatment of the electrode with Cr\textsuperscript{VI}. The solid lines are voltammograms in background solution (0.1M NaCl) after Cr\textsuperscript{VI} treatment and subsequent exposure to the analyte solution for 30 minutes. The electrodes were rinsed with water after the exposure to Fe(CN)\textsubscript{6}\textsuperscript{3-} and Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+}. As shown, the current response is greater after 30 minutes exposure to the analytic solutions implying that adsorption to the Cr\textsuperscript{VI} treated electrode is occurring.

DISCUSSION

The known chemistry of Cr\textsuperscript{VI} supports the conclusion that the product of Cr\textsuperscript{VI} reduction at the electrode surface is Cr\textsuperscript{III}. The species Cr\textsuperscript{V} and Cr\textsuperscript{IV} might be plausible but they are considered transient species in water with lifetimes in the submillisecond timescale as reported in pulse radiolysis experiments.\textsuperscript{160} They rapidly disproportionate to form Cr\textsuperscript{VI} and Cr\textsuperscript{III}. Recently, Raman spectroscopy was used to corroborate this conclusion by identifying Cr\textsuperscript{III} species on the surface of copper and silver electrodes.\textsuperscript{161}. Once Cr\textsuperscript{III} has been formed, presumably as a hydrated Cr\textsuperscript{+3} ion, it polymerizes to...
Figure 3.15: Cyclic voltammograms of a Cr$^{VI}$ modified (see text) glassy carbon electrode in deaerated 0.1 M NaCl containing 1 mM Fe(CN)$_6^{3-}$ (top) and 1 mM Ru(NH$_3$)$_6^{3+}$ (bottom) compared to background scans (in 0.1 M NaCl only) after adsorption of the analyte. For adsorption the electrode was exposed to 1 mM solutions of the analyte [Fe(CN)$_6^{3-}$ or Ru(NH$_3$)$_6^{3+}$] in 0.1 M NaCl for 30 m. Scan rate was 1.000 V/s. Reference electrode was Ag/AgCl.
yield an insoluble Cr$^{III}$ oxy-hydroxide.$^{5a,162}$ The rate of the Cr$^{III}$ polymerization is strongly dependent on both Cr$^{III}$ concentration and pH, and it is not clear from the present experiments how fast the oxy-hydroxide film forms after Cr$^{VI}$ reduction. Despite uncertainties about the kinetics of polymer formation, the present results indicate that the resulting film is irreversibly adsorbed on the electrode surface, and is removed only at potentials positive of 0.5 V vs. Ag/AgCl.

Quantification of Cr$^{III}$ film

With the assumption that the process occurring during the current spike in Figures 1-3 is the reduction of Cr$^{VI}$ to Cr$^{III}$, the area of the spike can be used to calculate the quantity of Cr$^{VI}$ reduced to Cr$^{III}$ via Faraday's law:

$$\text{Cr reduced} = \frac{\text{[Spike Area]}}{nFA} \tag{3.4}$$

Where spike area has units of A-s (or C), F is Faraday's constant (96485 C/mol e$^-$), n is moles electrons per mole of Cr$^{VI}$ reduced, and A is electrode area (cm$^2$). The mean spike area on glassy carbon of 2.4 mC/cm$^2$ for 5 mM [Cr$^{VI}$] (Table 3.5) corresponds to 8.4 nanomoles/cm$^2$ of Cr$^{III}$. Calculated Cr$^{III}$ coverages for each spike area are shown in tables 3.1 through 3.5. Classical experiments of Cr$^{VI}$ reduction on Pt reported deposition of 1.9 and 2.2 - 3.0 nanomoles Cr/cm$^2$. Using the octahedral geometry of Cr$^{III}$ (with bond length of 0.1964 nm for Cr$^{III}$-O bonds) and unit cell structure of Cr$_2$O$_3$, a close-packed Cr$^{III}$ monolayer is predicted to contain 2-6 nanomoles of Cr/cm$^2$ depending...
upon orientation of the Cr\textsuperscript{III} octahedron.\textsuperscript{163, 164} An examination of hydroxylated Cr\textsubscript{2}O\textsubscript{3} thin films in high vacuum using XPS, TDS, LEED, and STM reported a Cr\textsuperscript{III} surface density of 1.9x10\textsuperscript{15} atoms Cr/cm\textsuperscript{2}, or 3.2 nanomoles Cr/cm\textsuperscript{2}.\textsuperscript{165} Figure 3.16 shows possible orientations for a Cr\textsuperscript{III} octahedron on a surface with coverage (nmol/cm\textsuperscript{2}) shown. The projected areas for monolayer coverage were used to calculate the Cr coverages for measured Cr\textsuperscript{VI} reduction spike areas. Calculations of surface coverage for various orientations are listed in Table 3.6. Surface roughness as a result of polishing would increase the microscopic surface area and apparent coverage by a factor of about 1.5 to 2.0 compared to a geometrically flat surface. Within the uncertainty caused by surface roughness and film geometry, the present results as well as those reported by Kolthoff for Pt electrodes indicate formation of a monolayer of Cr\textsuperscript{III} on Cu electrodes.\textsuperscript{109} The mean Cr\textsuperscript{III} coverage observed on glassy carbon was slightly higher than that on Cu, but still corresponds to 1-2 monolayers. This coverage varied little over wide ranges of conditions as shown in Tables 3.1 through 3.6.

\textbf{Cr\textsuperscript{III} film formation dynamics and properties}

The formation process of the Cr\textsuperscript{III} monolayer has some important implications for its usefulness as an inhibitor for AA2024-T3. First, it forms at potentials of approximately +0.30 V vs. Ag/AgCl (+0.50 V vs. NHE) or more negative on Cu, Pt, and GC surfaces (Figures 3.6 – 3.8). Examination of the Pourbaix diagram (Figure 3.17) for chromium shows that for solutions of pH 6-7 the Cr\textsuperscript{VI} - Cr\textsuperscript{III} reduction potential is near 0.5 V (vs. NHE) depending on the hydration state of the ions.\textsuperscript{23} Consequently, the open
Figure 3.16: Possible orientations of Cr$^{III}$ octahedron on a surface with calculations of coverage for a monolayer film. A bond length of 1.964 Å for Cr$^{III}$-O bonds was used. Simple close-packing schemes were used to calculate coverage. Bonding/valency considerations were not taken into account.
### Table 3.6: Fractional coverage of Cr$^{III}$ film on copper (Cu) and glassy carbon (GC) surfaces based on geometric calculations and measured values for a monolayer of Cr$^{III}$.

Geometric configurations are as follows: a, b, and c are calculated from Figure 3.16. d is from Maurice, et al.\textsuperscript{165} e is from Galasso.\textsuperscript{164, pp. 235-237} $f_{\text{mono}}$ is the fraction of a monolayer coverage calculated from measured Cr$^{VI}$ reduction current spike area. $f_{\text{mono,corr}}$ is corrected assuming a 1.5 roughness factor for a polished surface. Mean refers to the average current transient observed. High and low refer to the limits of largest and smallest current transients observed.

<table>
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<tr>
<th>Geometric configuration</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>average</th>
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<td>Cr$^{III}$ coverage per monolayer (nmol/cm$^2$)</td>
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<td>4.485</td>
<td>3.2</td>
<td>2.962</td>
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<td>3.2</td>
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<tr>
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<td>1.3</td>
<td>1.5</td>
<td>1.4</td>
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<tr>
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<td>0.3</td>
<td>0.4</td>
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<tr>
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<td>2.4</td>
<td>2.6</td>
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<tr>
<td>$f_{\text{mono}}$(GC,low)</td>
<td>2.1</td>
<td>1.5</td>
<td>1.0</td>
<td>1.4</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>$f_{\text{mono,corr}}$(GC,high)</td>
<td>2.8</td>
<td>2.0</td>
<td>1.4</td>
<td>1.9</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$f_{\text{mono,corr}}$(GC,mean)</td>
<td>2.4</td>
<td>1.7</td>
<td>1.1</td>
<td>1.6</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>$f_{\text{mono,corr}}$(GC,low)</td>
<td>1.4</td>
<td>1.0</td>
<td>0.7</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 3.17: Pourbaix potential-pH diagram for chromium. Adapted from Pourbaix.23

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circuit potentials of Cu (~ -0.1 V vs. Ag/AgCl) or AA2024-T3 (~ -0.6 V vs. Ag/AgCl) are sufficiently negative to rapidly form a Cr$^{III}$ monolayer. Under conditions generally expected to occur for AA2024-T3 in field applications, the potential will be sufficiently negative to reduce Cr$^{VI}$ to Cr$^{III}$, and to form the Cr$^{III}$ monolayer, even if the solution Cr$^{VI}$ concentration is at the sub-micromolar level, as shown in Figure 3.2 and Table 3.1.

Second, the Cr$^{VI}$ reduction is self-inhibiting (Figures 3.1-3.4, 3.6-3.7), in the sense that further reduction of Cr$^{VI}$ is extremely kinetically hindered by the Cr$^{III}$ monolayer. Based on Figure 3.5, bulk Cr$^{VI}$ reduction does not occur on electrodes covered by the Cr$^{III}$ monolayer until the potential is negative of -0.8 V vs. Ag/AgCl. The Cr$^{III}$ layer causes more than 1.0 V of kinetic overpotential, shifting the Cr$^{VI}$ reduction from +0.3 V to -0.8 V vs. Ag/AgCl. This large shift presumably accounts for limitation of Cr$^{III}$ formation at one monolayer unless the electrode potential is very negative. It is fortunate that the open circuit potential of AA2024-T3 is sufficiently negative to form a monolayer, but not so negative that reduction continues past a monolayer, or else Cr$^{VI}$ reduction would act as an oxidizer and cause severe corrosion! This property permits Cr$^{III}$ monolayer formation, but prevents bulk reduction of Cr$^{VI}$ in the CCC or primer layers. Third, the reduction of Cr$^{VI}$ observed at about 0.325 V aids in explaining contradictions in the effectiveness of chromate as a cathodic inhibitor. Ilevbare and Scully claimed no inhibition of oxygen reduction kinetics on a gold electrode after exposure to a chromate solution.97 The open circuit potential for gold is expected to be positive of the reduction potential observed here for Cr$^{VI}$ to Cr$^{III}$. As a result there is no strong driving force for the reduction and subsequent formation of a Cr$^{III}$ film. As shown in Figure 3.8, Cr$^{VI}$ does not adsorb
strongly enough to remain on a glassy carbon electrode after rinsing if the potential is held above 0.325 V.

pH studies shown in Figure 3.4 corroborate results observed by several reports related to cathodic inhibition by Cr\textsuperscript{VI}. Again, the Pourbaix diagram (Figure 3.17) for chromium is informative\textsuperscript{23}. Low pH values do not show self-inhibition of Cr\textsuperscript{VI} reduction [Figure 3.4(b)] and the Pourbaix diagram shows that Cr\textsuperscript{III} is soluble at about pH 3 or lower. Many Cr\textsuperscript{VI} reduction and inhibition reports noted lack of self-inhibition at low pH\textsuperscript{109,133-135,167}. Results of high pH solutions [Figure 3.4(d)] indicate that the formation of the inhibiting film is slow and fast reduction of Cr\textsuperscript{VI} requires more negative potential values. These results are consistent with the incomplete film formation shown at higher pH by several studies\textsuperscript{108,152-155}. The film formed may be less well-defined due to rapid polymerization of Cr\textsuperscript{III} hydroxides expected at this higher pH\textsuperscript{54,55}. The Pourbaix diagram (Figure 3.17) also indicates that at high pH values soluble Cr(OH)\textsubscript{4}\textsuperscript{2-} can form. In addition, the reduction potential of Cr\textsuperscript{VI} is strongly dependent upon pH. pH values above 9 may move the reduction potential sufficiently negative that current spikes were not observed until potentials as negative as \(-0.800\) V. The observation of more well-defined spikes for the pH 7 buffered solution compared to the unbuffered solution (ph \(~6\)) is probably the result of the buffer maintaining the local pH constant. In unbuffered solutions (even with stirring) momentary pH changes may occur that perturb the system.

The self-inhibition of Cr\textsuperscript{VI} reduction by a Cr\textsuperscript{III} film is apparently inconsistent with the formation of a thick (several \(\Phi\)m) Cr\textsuperscript{III}-Cr\textsuperscript{VI} mixed oxide film during CCC formation. For example, the Alodine\textsuperscript{TM} 1200 process subjects AA2024-T3 to a solution containing
\(~40 \text{ mM Cr}^{\text{VI}}, \) plus \(F^-\) ion and ferricyanide, and chromate film formation proceeds far beyond a monolayer to a thickness of 1-5 \(\Phi_m\). The conditions for CCC formation are very different from those examined here or anticipated in the field. The high \(\text{Cr}^{\text{VI}}\) concentration and \(\text{Fe(CN)}_6^-\) "accelerator" generate a high \(\text{Cr}^{\text{III}}\) concentration at the alloy surface, which polymerizes to a \(\text{Cr}^{\text{III}}\) oxy-hydroxide. \(^{54,55}\) \(F^-\) etching will continue to expose fresh \(\text{Al}\) and provide reducing sites for further \(\text{Cr}^{\text{VI}}\) reduction, and the low pH in Alodine 1200 will slow \(\text{Cr}^{\text{III}}\) polymerization. The work presented in this chapter dealt with \(\text{Cu}\) surfaces as models of \(\text{Cu}-\text{rich}\) phases in AA2024-T3. Raman and IR microscopy have revealed that the CCC is significantly thinner over \(\text{Cu}-\text{rich}\) phases, compared to the \(\text{Al}\) matrix. \(^{137}\) Inhibition of \(\text{Fe(CN)}_6^-\) redox mediation or of \(\text{Cr}^{\text{VI}}\) reduction by a \(\text{Cr}^{\text{III}}\) film on \(\text{Cu}-\text{rich}\) phases would account for slow CCC formation on \(\text{Cu}\), and is shown in Figure 3.14.

**Inhibition of oxygen reduction by \(\text{Cr}^{\text{III}}\) blockage of catalytic sites**

Figure 3.8 indicates a strong correlation between \(\text{Cr}^{\text{III}}\) film formation and \(\text{O}_2\) reduction inhibition. It is tempting to conclude that the \(\text{Cr}^{\text{III}}\) film is acting as a "barrier" to the electrolyte, thus preventing \(\text{O}_2\) reduction or alloy dissolution. However, a hydrated \(\text{Cr}^{\text{III}}\) monolayer would be an imperfect barrier, and would permit electron tunneling and probably permeation by \(\text{O}_2\). The present results permit identification of some more definite properties of the "barrier" film that are important to inhibition of the ORR. First, the \(\text{Cr}^{\text{III}}\) film should block sites for \(\text{O}_2\) chemisorption, thus greatly reducing the electrocatalytic activity of the surface. Without chemisorption, slow kinetics decreases
the effective O₂ reduction potential from approximately +0.8 (vs. NHE) volts down to the outer sphere reduction potential of about -0.5 V (vs. NHE)¹²⁹. At the outer sphere reduction potential, O₂ is reduced to superoxide, which disproportionates in solution to eventually form HO₂⁻ or H₂O₂. With chemisorption blocked, the catalytically inactive surface significantly decreases the driving force for O₂ reduction, resulting in partial or complete ORR inhibition.

Since CrVI is itself an oxidizing agent, it may react with the same surface sites as O₂. As shown in Figure 3.5, CrVI reduction is slow in the absence of adsorption. It is likely that both O₂ and CrVI adsorb to similar sites on a Cu surface, presumably bare copper atoms. The difference is that O₂ is reduced and eventually desorbed, while CrVI reduction leads to permanent occupation of the site. CrIII is substitutionally inert due to its existence in a d³ atomic configuration. In fact, CrIII has one of the lowest ligand exchange rate constants among common inorganic species.¹⁶⁸, pp. 486-489 Once bonds to the electrode surface form, they are very difficult to break, and the CrIII layer should block O₂ adsorption indefinitely.

**Effects of CrIII layer on electron transfer**

In addition to occupation of catalytic sites, a CrIII monolayer can also inhibit electron transfer. Numerous reports have shown that electrons can tunnel through nonconducting monolayers, with an exponential dependence of tunneling rate on monolayer thickness. Electron transfer through an aliphatic hydrocarbon monolayer
yields a linear plot of the natural log of the electron transfer rate vs. layer thickness, with a slope of $-1 \text{ Å}^{-1}$. In general,

$$k_{\text{apparent}} = k_{\text{true}} e^{-\beta d} \quad (3.5)$$

where $k$ is the electron rate transfer constant, $\beta$ (Å$^{-1}$) is a tunneling constant that depends upon barrier height of the layer and $d$ is the thickness (Å) of the monolayer. In other words, each Å of monolayer thickness causes a $e^{-1}$ decrease in electron tunneling rate for aliphatic monolayers. A Cr$^{III}$ oxy-hydroxide monolayer made under UHV conditions was measured to be ~4 Å thick. By itself, such a monolayer would decrease the electron tunneling rate by $e^{-4}$ if $\beta = 1 \text{ Å}^{-1}$, or to ~2% of the rate without the monolayer. However, the Cr$^{III}$ film may adsorb a layer of Cr$^{VI}$ to form a Cr$^{III}$-Cr$^{VI}$ mixed oxide. Such a bilayer would decrease the tunneling rate by at least another factor of $e^{-4}$. The strong inhibition of electron transfer to Ru(NH$_3$)$_6^{3+}$, Fe(CN)$_6^{3-}$, TCNQ, and from ferrocene apparent in Figures 3.13 and 3.14 is consistent with decreased tunneling rates to outer sphere redox systems (presumably including O$_2$/O$_2^-$), but the results permit only a semi-quantitative estimate of the magnitude of the effect.

The observation of adsorbed species on the electrode surface as evidenced by current response in background solution of electrodes previously exposed to Ru(NH$_3$)$_6^{3+}$ or Fe(CN)$_6^{3-}$ brings up questions regarding the validity of the monolayer/bilayer ideas put forth. Adsorption of Ru(NH$_3$)$_6^{3+}$ and Fe(CN)$_6^{3-}$ to the Cr$^{III}$ layer does not necessarily imply that Cr$^{III}$-OH$_2$ bonds are labile. The ligands CN$^{-}$ and NH$_3$ are likely to replace H$_2$O
and OH\(^-\) ligands due to their ligand-field splitting strength in octahedral complexes.\(^{168}\) As such, it may be likely for interactions between the analytes and the Cr\(^{III}\) layer leading to bound species on the surface of that layer. CN\(^-\) and NH\(_3\) are not likely to be encountered in field conditions, thus their adsorption to the Cr\(^{III}\) layer does not imply that Cr\(^{III}\) is not a stable species on the surface. That said, it is interesting to note the kinetic differences between electron transfer to the Ru(NH\(_3\))\(_6\)\(^{3+}\) bound to the Cr\(^{III}\) layer and free solution Ru(NH\(_3\))\(_6\)\(^{3+}\) on a bare glassy carbon electrode. Table 3.7 lists kinetic parameters calculated for using Digisim 3.03a. The rate constants for Ru(NH\(_3\))\(_6\)\(^{3+}\) on the bare electrode were calculated using a semi-infinite linear diffusion model with diffusion coefficients of 5.1 \(\times\) 10\(^{-6}\) cm\(^2\)/s for both the oxidized and reduced species. For the bound species, the rate constants were calculated using a finite diffusion model with thickness of 10 Å and diffusion coefficients of 5.1 \(\times\) 10\(^{-6}\) cm\(^2\)/s to approximate a bound species. The average rate constant value calculated for a bare electrode (5.1 \(\times\) 10\(^{-2}\) cm/s) is almost six orders of magnitude greater than the average calculated for the Ru(NH\(_3\))\(_6\)\(^{3+}\) bound to the Cr\(^{III}\) layer (7.3 \(\times\) 10\(^{-8}\) cm/s). Recent research has indicated that a chromium(III) oxide layer has a barrier height of about 0.740 eV.\(^{169}\) This corresponds to a \(\beta \sim 0.9\) Å\(^{-1}\) based on calculations according to Mujica and Ratner.\(^{170}\) This value along with a tunneling distance of 4 Å would give about two orders of magnitude change in the rate constant according to Equation 3.5. To achieve the decrease in rate constant observed here the layer would need to be approximately 15 Å thick, or about 3 Cr\(^{III}\) layers.
Table 3.7: Comparison of rate constants calculated for Ru(NH$_3$)$_6^{3+}$ reduction on bare glassy carbon electrodes and adsorbed on Cr$^{III}$ modified glassy carbon electrodes.

<table>
<thead>
<tr>
<th>scan rate (mV/s)</th>
<th>$\Delta E_{\text{peak}}$ (mV)</th>
<th>$k$ (cm/s)</th>
<th>$\Delta E_{\text{peak}}$ (mV)</th>
<th>$k$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>63</td>
<td>0.038</td>
<td>100</td>
<td>9.8 x 10$^{-4}$</td>
</tr>
<tr>
<td>250</td>
<td>67</td>
<td>0.034</td>
<td>131</td>
<td>1.6 x 10$^{-7}$</td>
</tr>
<tr>
<td>500</td>
<td>71</td>
<td>0.034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>66</td>
<td>0.075</td>
<td>252</td>
<td>1.7 x 10$^{-7}$</td>
</tr>
<tr>
<td>5000</td>
<td>83</td>
<td>0.055</td>
<td>335</td>
<td>3.8 x 10$^{-7}$</td>
</tr>
<tr>
<td>10000</td>
<td>83</td>
<td>0.078</td>
<td>545</td>
<td>1.0 x 10$^{-7}$</td>
</tr>
<tr>
<td>50000</td>
<td>144</td>
<td>0.044</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>5.1E-02</td>
<td>mean</td>
<td>1.8 x 10$^{-7}$</td>
<td></td>
</tr>
</tbody>
</table>

*a* calculated based on semi-infinite linear diffusion, $D_{\text{Ru(NH}_3)_6} = 5.1 \times 10^{-6}$ cm$^2$/s

*b* calculated based on finite diffusion, layer thickness = 10 Å, $D_{\text{Ru(NH}_3)_6} = 5.1 \times 10^{-6}$ cm$^2$/s to approximate a surface-bound species.
Overview

The results presented in this chapter refine the present understanding of the performance of chromate-based anticorrosion coatings, specifically with regards to the mechanistic details by which chromate acts to inhibit cathodic reduction reactions related to corrosion. Past reports identified the storage and release of Cr VI in conversion coatings and chromated primers as essential prerequisites for the "self healing" observed in chromate coatings. The release and migration of active Cr VI species from a chromate coating to a newly formed defect appears to be essential for the long effective lifetimes of chromate coatings. The present results address the fate of Cr VI once it migrates to a corroding defect. It is clear that reduction of Cr VI leads to a stable, insoluble Cr III film, which apparently does not grow beyond one or two layers in dilute, neutral aqueous solutions. The Cr VI is a "site-directed" inhibitor in that it is adsorbed to an active site, then is reduced to permanently block the site. The reduction of oxygen is a principal target of inhibition for the aluminum alloys for which chromate conversion coatings are used, but certainly not exclusively so. The properties of the Cr III layer as a electron transfer barrier most probably kinetically hinder other less prominent reduction reactions (H2O, H+, etc.) in the corrosion process. The irreversible reduction of Cr VI to form a Cr III monolayer could also afford protection to anodic sites, such as Mg rich s-phase intermetallic particles. The unusual combination of storage, release, reduction, and inhibition by Cr VI inhibitors make them outstanding agents for corrosion protection.

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CONCLUSIONS

- $\text{Cr}^{\text{VI}}$ inhibits reduction of oxygen under conditions relevant to corrosion.

- The mechanism of inhibition involves a reduction and irreversible adsorption of $\text{Cr}^{\text{III}}$ to the surface of the electrode to block sites of adsorption. Once adsorption sites are blocked, $\text{O}_2$ chemisorption is prevented and $\text{O}_2$ becomes a much weaker oxidizing agent.

- The $\text{Cr}^{\text{III}}$ film is formed in near-monolayer quantities.

- The $\text{Cr}^{\text{III}}$ film acts as an electron-transfer barrier and inhibits outer-sphere redox processes.

- The $\text{Cr}^{\text{III}}$ film formed inhibits further $\text{Cr}^{\text{VI}}$ reduction until very negative potentials can drive outer sphere electron transfer. This allows storage of $\text{Cr}^{\text{VI}}$ in the $\text{Cr}^{\text{III}}$ backbone of CCC's without reduction.

- The reduction of $\text{Cr}^{\text{VI}}$ and inhibition of $\text{O}_2$ reduction occur over the entire potential range relevant to corrosion of AA2024-T3 alloys.
CHAPTER 4

REPLACING CHROMATES AS CORROSION INHIBITORS: TWO ALTERNATIVE APPROACHES INVESTIGATED AND EVALUATED WITH RAMAN SPECTROSCOPY AND ELECTROCHEMICAL TECHNIQUES

INTRODUCTION

The mechanism of chromate's superior inhibitive properties towards corrosion – particularly of aluminum alloys (specifically AA 2024-T3) – was the subject of Chapters 2 and 3. It was shown that a primary action of chromate is as a cathodic inhibitor. Oxygen reduction, the primary cathodic reaction on AA 2024-T3, is effectively inhibited in two manners. Adsorption sites that serve to catalyze the reduction of oxygen are blocked permanently by the reduction of Cr^VI and binding to the metal surface as a near-monolayer of Cr^III. In addition, the Cr^III layer was shown to be an effective barrier to electron transfer, thus slowing non-adsorptive (outer-sphere) reduction mechanisms as well. With the ultimate goal of replacement of chromate-containing compounds as corrosion inhibitors, alternative compounds must perform nearly as well or better than the currently used hexavalent chromium processes. A logical approach to take is to investigate or design inhibitors that work in a similar manner mechanistically as chromate.
In this chapter, two alternative approaches are discussed that ultimately do not provide corrosion protection at the level of current chromate schemes. However, valuable information is gained that may lead to modifications improving the usefulness of the discussed approaches. Each system is based upon binding organic compounds to sites of cathodic activity. The first system discussed is based upon sulfur-containing compounds (dithiocarbamates) and is similar to the ideas of binding of self-assembled monolayers (SAM) to noble metal surfaces. The second system is based on the reduction of diazonium salts to form strong bonds to the surface of the metal. Some background information for each system will be discussed in turn.

**Dithiocarbamates**

As demonstrated in the late 1980’s, sulfur-containing organic compounds, specifically alkanethiols, bind to the surface of noble metals. They bind as a so-called self-assembled monolayer or SAM through the interaction of the sulfur atom with the metal surface. Gold is the most common substrate studied, as the Au-S bond that forms is strong compared to other metal bonds (besides oxygen), albeit nowhere near the strength of a purely covalent carbon-carbon bond. Interactions of thiols with other noble metals such as silver and copper have been studied, although the formation of the layer is not as easily achieved, possibly due to oxide films on the surfaces that are not present on gold. Generally, the preparation of SAM surfaces is done in an organic solvent such as ethanol. SAMs have been studied in the context of corrosion - mainly copper corrosion - but their effectiveness has been limited in part due to the aforementioned oxide films,
limited substrates, and complex preparation procedures.\textsuperscript{172-178} Many preparations of SAMs for corrosion protection involve secondary modification after the surface layer is formed to provide more effective corrosion inhibition.\textsuperscript{179-185} Application of SAMs as sodium salts of thiols in aqueous solutions have been reported but the results were less successful.\textsuperscript{186} The far larger applications of SAMs are in the areas of molecular electronics, where ultra-pure and clean substrates are routinely achieved; biochemistry; and electroanalytical chemistry.\textsuperscript{187-189}

Another sulfur-containing group of compounds that is more aggressive in binding are the dithiocarbamates. The species studied in this chapter is diethylidithiocarbamate (DETC). DETC has a -1 charge and exists as a resonance structure as shown in Figure 4.1. Dithiocarbamates are strong chelating agents and have been used in various ways including colorimetric identification, fungicides, pesticides, chromatography, and biochemistry.\textsuperscript{190-195} They are manufactured by the reaction of carbon disulfide (CS\textsubscript{2}) and the corresponding amine [e.g. (CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}NH]. The sodium salt Na(DETC) is water soluble but decomposes in acidic media. Transition metal complexes are easily formed with DETC and are water-insoluble. Dithiocarbamates have also been investigated as corrosion inhibitors for copper, brass, aluminum, steel, and tinplate.\textsuperscript{196-200} In most cases investigations were performed with the inhibitor present in the corrosive solution but in one case pretreatment was performed with the inhibitor prior to immersing the sample in the corrosion solution.\textsuperscript{201} The general observations indicated that dithiocarbamates have increased effectiveness as their concentration in the corrosive solution is increased. Their
Figure 4.1: Structure of diethyldithiocarbamate (DETC) ligand. Resonance structures shown.
mechanism was attributed to the formation of complexes at the surface of the metal that serve as a barrier to attack by solution species.

**Diazonium salts**

Diazonium salts are compounds that are prepared by the reaction of amines with nitrous acid.\(^{202}\) pp. 852-862 The general reaction is given as

\[
R\text{-NH}_2 + \text{NaN}_{2}\xrightarrow{\text{H}^+}\text{R-N=N}^+\text{X}^- \tag{4.1}
\]

The salts are highly unstable compounds that decompose spontaneously if the R group is aliphatic. If the R group is aromatic, the diazonium salt is stable if kept at low temperatures. Because of the unstable nature of these compounds, they are often used as intermediates in synthesis of other aromatic compounds, with the diazonium (N=N) group being replaced by other groups.

Electrochemical reduction of diazonium salts results in the formation of N\(_2\) and an aryl radical. The aryl radical has been shown to react with the surface of carbon electrodes to form modified surface electrodes via covalent bonds.\(^{203,204}\) The general scheme for the reduction reaction is shown in Figure 4.2. As long as the conjugated ring (phenyl ring) is present, many different substituents can be used as the -R group shown in Figure 4.2 to give a wide variety of choices for electrode modification. The modification of carbon electrodes in this manner has been extensively studied to investigate the mechanisms of the modification and the structure of layers formed.\(^{204-209}\) The reduction
Figure 4.2: The diazonium salt modification reaction and structures of the diazonium salts investigated in the present study.
reaction is a self-limiting process much like chromium (III) oxide deposition from chromium (VI) reduction as described in Chapter 3. Generally, the films formed are one to many layers thick - approximately 10 to 100 Å. However, they are not bulk films in the sense of being micron-scale in thickness. Many investigations have also taken place on the effects of various modified surfaces on heterogeneous electron transfer processes and potential uses for modified electrodes.¹²⁹, ¹⁵⁷, ²¹⁰-²¹⁸

The reduction of diazonium salts has also recently been shown to result in attachment of the aryl radical to the surface of metal electrodes.²¹⁹, ²²⁰ This attachment was proposed in an earlier study by Ahlberg, et al.²²¹ The attachment to iron electrodes was reported to be via a Fe-C bond and preliminary reports indicated similar reactions take place with other metals such as zinc, copper, nickel, cobalt, gold, and platinum. This observation introduces the idea of using diazonium modification as a method of corrosion inhibition, as has been initially investigated by Chausse, et al. on iron electrodes.²²⁰ Several different species were investigated for the functional group (-R from Figure 4.2) including variable length alkanes, substituted alkanes, and fluorinated phenyl. The corrosion inhibition was reported in terms of polarization resistance (R_p) and corrosion current (i_corr) (defined in Chapter 1) and in all cases a modified electrode showed greater resistance to corrosion than the bare metal. No comparison was made, however, to traditional corrosion inhibitors.
Raman spectroscopy

As discussed in Chapter 1, Raman spectroscopy is a powerful tool for the identification of chemical compounds, especially organic compounds. The investigations in this chapter make use of Raman spectroscopy (and microscopy) of surfaces to identify species qualitatively and to determine spatial location. It is not the intention of the investigation to probe the intricacies of vibrational assignment or exact quantification of the surface species. That information can certainly be obtained from techniques presented here and may become important in the future. As such, most of the spectra presented will not include intensity scales. They will be compared to known spectra to deduce the nature of the species observed.

Overview

As stated previously, the investigations put forth in this chapter do not conclude with discovery of inhibitors that, in present form, offer the hope of replacing chromate. The new information is intended to provide guidance during the design of chromate replacements. The powerful action of chromate as a cathodic inhibitor through its specific near-monolayer deposition at sites of oxygen reduction indicates that similar acting compounds are required to interact at the same sites. The choices of the compounds investigated were based on properties observed in other environments. For instance, a strong chelating effect for transition metals indicates that dithiocarbamates may interact at intermetallic phases (sites of oxygen reduction - see Chapter 2) on AA
2024-T3, which are higher in transition metal content than the overall composition of the alloy. The use of Raman spectroscopy for identification of surface species and previously discussed electrochemical tests (separation of reactions in Chapter 2 and hydrodynamic polarization in Chapter 3) to evaluate the compounds demonstrate the use these techniques in evaluation of potential chromate replacements.

**EXPERIMENTAL**

Barnstead NanoPure™ water with a resistivity of 18 MΩ-cm was used for rinsing and aqueous solution preparation. CH₃CN (Mallinckrodt) was used as the solvent for organic solutions. NaCl (Fisher Scientific), [CH₃(CH₂)₃]₄NBF₄ (Aldrich), sodium diethylidithiocarbamate (Acros), CuSO₄ (JT Baker), Fe(NO₃)₃ (JT Baker), Cd(NO₃)₂ (JT Baker), Pb(NO₃)₂ (Mallinckrodt), MgCl₂ (Mallinckrodt), MnCl₂ (Aldrich), and Al(NO₃)₃ (Alfa Aesar) were reagent grade and used as received. Diazonium salts were synthesized in the McCreery research lab by others in the manner described by Yang. The species used in this study are listed in Figure 4.2. Electrodes for surface Raman spectroscopy and electrochemical testing were made from commercial Al sheet (99.999%, 0.5 mm thick, Alfa Aesar), Cu sheet (99.99% 1.0 mm thick, Alfa Aesar), Cu wire (99.9%, 0.5mm diameter, Aldrich), and Aluminum Alloy 2024-T3 sheet (0.025 in. thick, ALCOA). Electrode materials (sheet samples were cut to 1 cm² in all cases) were attached to copper wire with silver epoxy resin (SPI Supplies/Structure Probe Inc.), and embedded in epoxy (Buehler). They were then mechanically polished with successively finer Si:C papers with running water (Buehler: 240, 400, 600, 800, 1200 grit), rinsed...
with water, and dried under a stream of hot air. Water was used as polishing solvent instead of an organic solvent to avoid adsorption of organic compounds as previously reported.\textsuperscript{127} In cases where Raman microscopy of AA 2024-T3 was performed, the samples were polished in aqueous alumina slurries (1.0, 0.3, and 0.05 μm. Buehler), rinsed with water, and dried with a stream of argon (Praxair) for better surface resolution.

Samples were exposed to the alternate inhibitors before spectroscopic or electrochemical measurements were performed. DETC exposure was accomplished by submersion of the sample electrode in an aqueous solution of 0.1 M or 0.001 M Na(DETC) for various times up to 24 h. After treatment, the samples were rinsed with water and dried with argon before testing. Specific test parameters will be listed in the text and figures as discussed.

The formation of surface layers by diazonium modification was performed either with potential control or at open circuit. A Bioanalytical Systems BAS100B Electrochemical Analyzer using BAS100W software was used to prepare diazonium-modified surfaces. Samples were modified via potential control in two manners. Some were placed in a 0.001 M solution of the appropriate diazonium salt (with 0.1 M \([\text{CH}_3(\text{CH}_2)_3]_4\text{NBF}_4\) background electrolyte) in acetonitrile while the potential of the system was held at a value positive enough to prevent reduction of the diazonium salt. The potential was then scanned (cyclic voltammetry) at 0.100 to 0.250 V/s to a value negative of the observed reduction wave. Figure 4.3 shows a typical modification via cyclic voltammetry using a glassy carbon electrode and nitroazobenzene (NAB) diazonium salt. One to ten scans were generally performed to form a surface layer. Care
Figure 4.3: Typical voltammogram for a diazonium salt electrode modification reaction. In this case the salt is 0.001 M nitroazobenzene (NAB) diazonium salt in acetonitrile on a glassy carbon electrode. Scan rate was 0.250 V/s. Background electrolyte was (CH₃(CH₂)₃)₄NBF₄.
was taken not to scan too far negative as multiple layers that are less ordered can result.\textsuperscript{209} Other samples were modified by holding a constant potential negative of the reduction wave of the diazonium salt in background solution (as above without the diazonium salt) and injecting a 0.010 M solution of the diazonium salt to give a final concentration of 0.001 M. The potential was held constant for 60 seconds. Diazonium modification without potential control was accomplished by simply immersing the electrode in 0.001 M diazonium salt solution (in acetonitrile) for 1-5 minutes. After modification, the samples were rinsed with acetonitrile and dried with a stream of argon. Some samples were sonicated for various times in activated carbon/isopropanol slurries and water as described in the text to assess the binding strength of the layer.

Raman spectroscopy was performed with either of two spectrometers. Macroscopic Raman spectra were collected with a Kaiser spectrometer system utilizing an 85 mm focal length HoloSpec\textit{f/} 1.8i spectrograph (Kaiser Optical Systems), a Canon 50 mm\textit{f/} 1.4 collection lens, a holographic super notch plus band rejection filter (Kaiser Optical Systems), a holographic transmission grating with linear dispersion of 3.0 nm/mm (Kaiser Optical Systems), and a charge coupled device (CCD) detector (CH260 - Photometrics). Microscopic Raman spectra were collected using a Dilor X-Y spectrometer utilizing a 600 mm focal length Dilor\textit{f/} 6 single spectrograph, 1800 lines/mm grating, holographic notch filter, and Olympus BX40 microscope with 40X immersion objective. The figures are noted "Kaiser" or "Dilor" to indicate which spectrometer was used. Laser excitation with 514.5 nm wavelength was used in all Raman experiments. Surface (and solid sample) spectroscopy was performed in general
as follows. For macroscopic spectral collection, the sample was placed on the focusing stage, focused first with a video camera, and then by collection of successive spectra while moving the stage. Before collecting the desired experimental spectra the sample was moved laterally with the focusing stage just enough to expose fresh sample to the focused laser beam. This procedure resulted in no appreciable change in spectral intensity (due to changes in focus) within the limitations of the investigations conducted here. The laser intensity was kept at a minimum (less than 10 mW at the sample - generally around 1 mW) to prevent damage to the sample during Raman collection. In general, the laser intensity was decreased until a short integration still showed indications of spectral peaks then multiple exposures were taken and averaged. A timed shutter was placed before the sample to block the laser beam between integrations. In cases where intensity comparisons are noted the spectra were collected and normalized by dividing spectral intensity ($e'$) by the product of laser power (mW) and integration time ($s$).

Electrode samples are often very reflective. For all electrode surface samples, the electrode was placed at an angle to direct reflected light away from the collection optics. Reflected laser light is theoretically rejected by the band-reject filter of the spectrometer. However, the laser intensity is so much greater than the scattered Raman shifted light that even a small amount passing the filter can overload the detector and distort the collected spectrum. Raman microscopy was performed by using a 40X submersion objective that allowed spectra to be collected under water. The electrode sample to be investigated was mounted on the microscope stage with an O-ring to hold a reservoir of water on the surface. This allowed the laser to be operated at relatively high intensity without sample
damage. The water allowed for the dissipation of heat. This is necessary as the microscope imparts extremely high power density to the sample due to the small spot size of the focused beam.\textsuperscript{69} Damage to the sample can easily occur.

Electrochemical experiments were performed to assess the inhibition characteristics of dithiocarbamates and diazonium salts. Dithiocarbamate treatment was tested using a split-cell apparatus as described in Chapter 2. Diazonium modified surfaces were examined with hydrodynamic voltammetry as outlined in Chapter 3. A Gamry Instruments PC3/300\textsuperscript{TM} Potentiostat/Galvanostat/ZRA with Framework\textsuperscript{TM} (Version 3.11) and DC105\textsuperscript{TM} DC Corrosion Measurement software was used for split-cell and hydrodynamic polarization measurements. Pertinent details will be described in the results section below.

RESULTS

Dithiocarbamate treatment

The first alternative to chromate examined was exposure to sodium diethyldithiocarbamate [Na(DETC)] solution. Figure 4.4 shows a Raman spectrum of solid Na(DETC) taken on the Kaiser spectrometer with the Raman shift of many peaks noted. A 0.1 M Na(DETC) solution was prepared and a sample of AA2024-T3 was immersed in the solution overnight (~18 h). Upon visual inspection the sample surface became discolored with a brick-red appearance that could be partially removed with a Kimwipe. Evidence of the interaction prompted the experiments shown in Figure 4.5.
Figure 4.4: Raman spectrum of sodium diethylthiocarbamate solid. 514.5 nm excitation.
Kaiser spectrometer.
Figure 4.5: Raman spectra of copper surface after exposure to 0.1 M Na(DETC) with AA 2024-T3 surface for various times. All spectra are absolute intensity. (a) bare alloy, (b) 45 min, (c) 3 h, (d) 18 h. 514.5 nm excitation. Kaiser spectrometer.
AA 2024-T3 samples were exposed to the Na(DETC) solution for 0.75, 3, and 18 hours and spectra were taken after each time period. The appearance of bands not present on the bare sample and their subsequent increase in intensity with time indicate deposition of a material on the surface. A spectrum of the AA 2024-T3 surface species after 18 hours in 0.1 M Na(DETC) is shown in Figure 4.6, with many peaks noted. Comparison of the surface spectrum to solid Na(DETC) (Figure 4.4) indicates that the species are different.

Figure 4.7 shows the spectrum resulting from the interaction of 0.1 M Na(DETC) with a copper electrode for 18 hours, compared to the spectrum of a bare copper electrode. Once again, the exposed sample shows the development of surface Raman peaks in comparison to the bare copper sample (save for a peak due to O$_2$ from air around 1552 cm$^{-1}$). In Figure 4.8, a comparison is made between AA 2024-T3, copper, and aluminum electrodes exposed to 0.1 M Na(DETC) for 18 hours. The AA 2024-T3 and copper samples have spectra that are very similar to each other while the aluminum sample shows no sign of peaks.

To better determine the identity of the surface species, various DETC complexes were prepared and a Raman spectrum was taken of each. Aqueous solutions of CuSO$_4$, Fe(NO$_3$)$_3$, Cd(NO$_3$)$_2$, Pb(NO$_3$)$_2$, MgCl$_2$, MnCl$_2$, and Al(NO$_3$)$_3$ were mixed with a solution containing excess Na(DETC). Cu, Fe, Mg, Mn, and Al salts were chosen because they all are constituents in AA 2024-T3 and are concentrated in the intermetallic phases as described in Chapters 1 and 2. All solutions formed a DETC complex that precipitated, except for Mg and Al. The precipitates were subjected to suction filtration.
Figure 4.6: Raman spectrum of AA 2024-T3 surface after exposure to 0.1 M Na(DETC) for 18 h. 514.5 nm excitation. Kaiser spectrometer.
Figure 4.7: Raman spectra of pure copper sample before and after interaction with 0.1 M Na(DETC) for 18 h. 514.5 nm excitation. Kaiser spectrometer.
Figure 4.8: Raman spectra of copper, AA 2024-T3, and aluminum surfaces after exposure to 0.1 M Na(DETC) for 18 h. 514.5 nm excitation. Kaiser spectrometer.
and several rinses with water. The samples were not dried but suction filtration was left on for at least 30 minutes for each sample precipitate. Raman spectra of the precipitates were collected using the Kaiser spectrometer and the results are presented along with a spectrum of solid Na(DETC) in Figure 4.9. Each spectrum shown is quite distinct from the others.

Raman microscopy was performed on polished surfaces of AA 2024-T3 to determine if the observed species initially covered the entire surface or if interaction is specific to particular sites on the surface. Samples of AA 2024-T3 were polished with 0.05 μm aqueous alumina slurry and exposed to a 0.001 M solution of Na(DETC) for 24 hours. After rinsing and drying, the sample was affixed on the microscope stage of the Dilor X-Y spectrometer. As explained in the experimental section, a rubber O-ring was placed on the surface of the sample to allow water to cover the surface. Figure 4.10 shows a micrograph of the surface and spectra taken through a 40X objective that could be immersed in the water covering the surface. The micrograph of the surface clearly shows both Al₆Cu(Fe,Mn) and “possible Al₂CuMg” intermetallic phases as defined in Chapters 1 and 2. The laser spot size for the 40x objective is approximately 10 μm diameter so collection of spectra for individual intermetallic particles was possible. Arrows indicate the spot sampled for each of the three spectra shown. The spectrum of the “possible Al₂CuMg” phase clearly shows peaks and has a larger background than that of the matrix or Al₆Cu(Fe,Mn) phase which both have featureless Raman spectra.
Figure 4.9: Raman spectra of various diethyldithiocarbamate (DETC) salts. Made by combining solutions of MnCl₂, Fe(NO₃)₃, CuSO₄, Cd(NO₃)₂, and Pb(NO₃)₂ with Na(DETC) and collecting the precipitate formed. (a) Cu-, Fe-, and Mn-DETC salts. (b) Cd- and Pb-DETC salts and Na(DETC) solid. 514.5 nm excitation. Kaiser spectrometer.
Figure 4.9 continued:

Cd(DETC) salt

Pb(DETC) salt

Na(DETC) salt

Raman shift (cm$^{-1}$)
Figure 4.10: Raman microscopy of a AA 2024-T3 surface after exposure to 0.001 M Na(DETC) for 24 h. Micrograph (top) shows points where spectra were acquired. Spectra acquired under water using 40X immersion objective. 514.5 nm excitation. Dilor spectrometer. See Chapter 1 (Figure 1.8) for discussion of uncertain assignment of $\text{Al}_2\text{CuMg}$ phase.
Figure 4.11 shows the results of a Raman spectral scan of a 48 μm x 80 μm area of AA 2024-T3 prepared as for Figure 4.10 using the Dilor X-Y spectrometer. Micrographs of the surface with the sampling area are shown. Two hundred forty (12 x 20) separate 15-second spectra were taken and used to construct the Raman image shown at the top. The magnified image of the sampling area clearly shows both Al₆Cu(Fe,Mn) and “possible Al₂CuMg” intermetallic phases as defined in Chapter 1 (Figure 1.8). The image represents the intensity of the 425 cm⁻¹ band of the spectrum. Areas of greatest intensity correspond to locations of “possible Al₂CuMg”. The Al₆Cu(Fe,Mn) intermetallic phase shows a low intensity for the 425 cm⁻¹ band while the matrix shows none.

Electrochemical experiments were performed using the split-cell approach discussed in Chapter 2 to evaluate the effectiveness of DETC treatment as an inhibitor for cathodic processes. Galvanic current of an aluminum/copper couple was measured using a zero-resistance ammeter and a separated cell as described previously. Results are shown in Figure 4.12. Negative current values indicate that electrons are flowing from the aluminum to the copper. Corrosion was initially allowed to take place in 0.1 M NaCl unimpeded as shown in Figure 4.12(a). The initial current was approximately -50 μA. After 15 minutes DETC was added [as Na(DETC)] to the copper electrode chamber to give a DETC concentration of approximately 0.005 M. After 10 minutes more, the concentration of DETC was increased to approximately 0.025 M. After each of the DETC additions, the galvanic current decreased, eventually leveling off at about -5 μA. The experiment was continued for another hour as shown in Figure 4.12(b).
Figure 4.11: Raman spectral image of AA 2024-T3 surface after exposure to 0.001 M Na(DETC) for 24 h. Micrographs show surface area where scan was obtained. Raman image (top) was constructed from the intensities of the 425 cm\(^{-1}\) band of the spectra. Scan consists of 12 X 20 (240) spectra. Spectra acquired under water using 40X immersion objective. 514.5 nm excitation. Dilor spectrometer. See Chapter 1 (Figure 1.8) for discussion of uncertain assignment of Al\(_2\)CuMg phase.
Figure 4.12: Effect of DETC addition to a Al/Cu couple in an aerated, quiescent split-cell. DETC added to the copper chamber in (a) at the times indicated. Experiment was continued in (b). (c) is continuation of experiment with copper chamber flushed and replaced with fresh electrolyte. Electrolyte was 0.1 M NaCl. Both electrodes were 1 cm².
(Figure 4.12 continued)
galvanic current remained low (< -10 μA) but had a slight increasing slope for this
segment of the experiment. The electrodes were removed, rinsed with water, and
replaced in fresh 0.1 M NaCl containing no DETC for the third portion of the
experiment. As shown in Figure 4.12(c) the current in 0.1 M NaCl starts at about -20 μA
and quickly levels to about -15 μA. Over the hour-long experiment, the current steadily
increased returning to about -20 μA at the end.

Finally, visual observation of a sample of AA 2024-T3 was used as a measure of
the inhibition imparted by DETC. The micrographs presented in Figure 4.13 give a
comparison of the action of DETC vs. chromate. The image in Figure 4.13(a) is a bare
AA 2024-T3 electrode polished with 1200 grit silicon carbide paper. Figures 4.13(b)
through 4.13(d) show electrodes after 48 hours in 0.1 M NaCl under various conditions.
The sample in Figure 4.13(b) shows corrosion to the bare untreated alloy. Large amounts
of hydroxide precipitate and numerous deep pits were observed. Figure 4.13(c) shows an
electrode that had been treated with Alodine™ 1200 to form a chromate conversion
coating. After 48 hours in chloride solution, the sample looks virtually identical to the
bare electrode [Figure 4.13(b)]. Figure 4.13(d) shows a bare electrode that was exposed
to 0.1M NaCl with 0.001 M Na(DETC). The electrode shows pitting and some
hydroxide precipitate but not as severely as the freely corroding sample in Figure 4.13(b).

**Diazonium modification**

As discussed in the introduction to this chapter, diazonium salts have recently
been shown to bond to metal surfaces via electrochemical reduction.219,220 To investigate
Figure 4.13: Corrosion of AA 2024-T3 with various surface treatments. (a) is bare electrode polished to 1200 grit with SiC paper. (b) - (d) have been exposed to 0.1 M NaCl for 48 h. (b) has no treatment. (c) was treated with Alodine™ 1200S to form a chromium conversion coating. (d) had 0.001 M Na(DETC) in the electrolyte solution.

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the possibility of enhanced corrosion protection as applied to AA 2024-T3, diazonium salts were used to modify copper electrodes. The first step after surface modification was identification of the surface species with Raman spectroscopy. Figure 4.14 shows Raman spectra of copper electrode surfaces after modification with nitroazobenzene (NAB) diazonium salt. The structure of NAB diazonium salt is shown in Figure 4.2. Two spectra are shown in Figure 4.14. The top trace (with greater intensity) is the result of potentiostatic control of the modification process. The copper electrode was held at -0.700 V in background solution (0.1 M [CH₃(CH₂)₃]₄NBF₄ in acetonitrile) and NAB diazonium salt solution was injected (to 0.001 M) and the potential held for 60 seconds. Distinct peaks are shown in the spectrum after this procedure. The bottom trace is the result of immersion of the copper electrode in the NAB solution for 5 minutes without potential control. The two spectra appear identical except for differences in intensity. After each of the modification procedures, the electrodes were subjected to rinsing with acetonitrile. To test the durability of the NAB bonding to the copper surface, sonication was used. Figure 4.15 shows Raman spectra of the copper surface after exposure to 0.001 M NAB diazonium salt solution for 5 minutes followed by varying amounts of sonication. Sonication was performed in a 1:3 v/v activated carbon/isopropanol (AC/IPA) mixture and in water, the dried with argon prior to spectroscopy. The intensity of the surface spectral bands decreases to about 20% of the intensity for the unsonicated samples after the first sonication cycle. However, the intensity decreases more slowly for successive sonication cycles.

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Figure 4.14: Raman spectra of copper surface after exposure to nitroazobenzene (NAB) diazonium salt. Bottom trace is after 1 min in 0.001 M NAB diazonium salt. Top trace is after modification with NAB diazonium salt under potential control as described in the text. Solvent was acetonitrile. Background electrolyte was 0.1 M \((\text{CH}_3\text{CH}_2)_3\text{NBF}_4\). 514.5 nm excitation. Kaiser spectrometer.
Figure 4.15: Effects of sonication on copper surface modified with nitroazobenzene (NAB) diazonium salt. Raman spectra of copper surface after 1 m exposure to 0.001 M NAB diazonium salt in acetonitrile [with 0.1 M (CH₃(CH₂)₃)₄NBF₄] with sonication times as follows. (a) no sonication. (b) 5 m in activated carbon/isopropanol (AC/IPA) mixture, 5 m in water. (c) 30 m in AC/IPA, 10 m in water. (d) 60 m in AC/IPA, 10 m in water. Note: the same electrode was used continuously (i.e. bottom trace exposed to treatment of top and middle traces) so the times are additive. 514.5 nm excitation. Kaiser spectrometer.
Nitrophenyl (NP) diazonium salt was also used to modify the surface of copper electrodes. Figure 4.16 shows Raman spectra of two copper electrode surfaces after potential scans between -0.600 V and -1.200 V in acetonitrile (with 0.1 M \([\text{CH}_3(\text{CH}_2)_3]_4\text{NBF}_4\) electrolyte). One solution contained 0.001 M NP diazonium salt and the other was a control containing only the solvent and electrolyte. After rinsing with acetonitrile and drying with argon spectra were collected. The sample exposed to NP diazonium salt shows distinct spectral bands that are not present on the control sample.

Since aluminum alloy corrosion is the focus of the investigations presented herein experiments were performed to determine if AA 2024-T3 could be modified with diazonium salts. Figure 4.17 shows Raman spectra collected for AA 2024-T3 electrodes that were scanned between -0.200 V and -1.000 V in either 0.001 M NAB or NP diazonium salt solutions (with 0.1 M \([\text{CH}_3(\text{CH}_2)_3]_4\text{NBF}_4\) in acetonitrile). Distinct spectral bands were acquired in each case that are qualitatively similar to those acquired on copper samples.

Raman microscopy using the Dilor X-Y spectrometer was used to probe the surface of AA 2024-T3 electrode that had been modified with NAB diazonium salt. The sample was prepared in the same fashion as that for Figure 4.17. The 40X immersion objective (as described earlier) was used to record optical micrographs and acquire Raman spectra under water. Results are shown in Figure 4.18. The micrograph and magnified section show two spots where the laser was focused to collect spectra. One was on a “possible Al\textsubscript{2}CuMg” intermetallic phase as defined in Chapter 1 (Figure 1.8).
Figure 4.16: Raman spectra of copper surfaces after exposure to nitrophenyl (NP) diazonium salt and blank solution. Both samples were subjected to two cyclic voltammetry scans between -0.600 V and -1.200 V (vs. Ag/Ag⁺) at 0.100 V/s in acetonitrile. Top trace was in 0.001 M NP diazonium salt. Bottom trace was in blank solution. Background electrolyte was 0.1 M \((\text{CH}_3\text{(CH}_2)_3\text{)}_4\text{NBF}_4\). 514.5 nm excitation. Kaiser spectrometer.
Figure 4.17: Raman spectra of AA 2024-T3 surface after modification with nitroazobenzene (NAB) (top) and nitrophenyl (NP) (bottom) diazonium salts. Samples were scanned between -0.200 V and -1.000 V (vs. Ag/Ag⁺) at 0.100 V/s in 0.001 M diazonium salt solution. Background electrolyte was 0.1 M (CH₃(CH₂)₃)₄NBF₄. 514.5 nm excitation. Kaiser spectrometer.
Figure 4.18: Raman microscopy of a AA 2024-T3 surface after modification with 0.001 M nitroazobenzene (NAB) diazonium salt. Modification procedure described in the text. Micrograph (top) shows points where spectra were acquired. Spectra acquired under water using 40X immersion objective. 514.5 nm excitation. Dilor spectrometer.
and the other on the matrix. The spectra show distinct bands for the "possible Al₂CuMg" phase that are barely observed on the matrix.

Electrochemical experiments were performed on copper electrodes modified with diazonium salts. Hydrodynamic voltammetry was performed similarly to experiments presented in Chapter 3 to assess the effects of the modified surfaces on oxygen reduction in aqueous solutions. Three different modified surfaces were tested. These were modified using nitroazobenzene (NAB), ter-phenyl (TP), and n-butyl phenyl (C4) diazonium salts. The structure of each salt is shown in Figure 4.2. Modification was performed by five potential scans at 0.100 V/s between -0.200 V and -1.000 V (vs. Ag/Ag+) in acetonitrile (with 0.1 M [CH₃(CH₂)₃]₄NBF₄). Each sample was rinsed with acetonitrile and dried with argon. Figure 4.19 shows the results of hydrodynamic voltammetry in aerated 0.1 M NaCl scanning from open circuit to -1.000 V at 0.001 V/s of the three modified surfaces compared with a bare electrode and an electrode pretreated with chromate as described for Figure 3.5(a) in Chapter 3. The electrode with no pretreatment shows an increase in current density as the potential is scanned negative from -0.300 V which levels to a mass transport limited value of about 2.0 mA/cm² at -0.800 V. The TP and NAB modified surfaces showed similar results to one another. Each shows an abrupt increase in current density at about -0.250 V to about 0.2 mA/cm². This current density is about three times greater than that on the bare electrode. The current density steadily increased as the potential was scanned negative. At approximately -0.5 V the current density for the bare electrode matched that for the TP and NAB modified electrodes. As the potential was scanned more negative the TP
Figure 4.19: Current response vs. potential for diazonium salt modified copper electrodes in stirred 0.1 M NaCl. The electrodes were modified with the diazonium salt listed using procedures described in the text. The potential was scanned negative at 0.001 V/s beginning at the open circuit potential. The trace listed as “chromate” was an electrode from a previous scan in Cr\(^{VI}\)-containing solution that was removed, rinsed with water, and replaced in fresh 0.1 M NaCl [see Figure 3.5(a)].
modified layer mirrored the bare electrode leveling off at about 2.0 mA/cm². The NAB modified electrode current density leveled off at about 1.5 mA/cm². The scan for the C4 modified electrode was similar to that of the TP and NAB modified electrode but there were some notable differences. There was no abrupt increase in current density at the beginning of the scan. The current density initially was higher than for the bare electrode but only about one-third of the value for the TP and NAB modified electrodes. As the potential is scanned negative the current increases but more gradually than for the TP and NAB surfaces with the bare electrode current density value surpassing that of the C4 modified surface by -0.4 V. The final mass limited current density was lower, leveling off at approximately 1.0 mA/cm². Finally, all of the surfaces show much greater current density than for the chromate treated surface, which had a maximum current density of about 0.1 mA/cm² at the negative limit of the experiment.

DISCUSSION

The investigation of the inhibition mechanism of chromate for aluminum alloys gives valuable information to guide the choice (or design) of possible compounds for its replacement. The results presented have demonstrated two approaches towards this end. Each will be discussed in turn.

Diethylidithiocarbamate modified surfaces

The deduction of surface species present upon interaction of sodium diethylidithiocarbamate [Na(DETC)] with the surface of AA 2024-T3 was undertaken via
several steps using spectral comparison. As presented in Figure 4.5 it is obvious that exposure to Na(DETC) with time shows the buildup of a species on the surface. The observation of increasing intensity is not necessarily a good sign for corrosion protection as will be discussed shortly. Based upon interactions of sulfur-containing species with noble metals (discussed in the chapter introduction) a logical first choice for the species on the surface was a copper-DETC complex as it is the most noble constituent of AA 2024-T3. The exposure of pure copper and aluminum samples were to Na(DETC) as shown in Figures 4.7 and 4.8 support this initial idea. The results indicated no interaction with aluminum. The spectra of copper surfaces after interaction appear nearly identical to that of the AA 2024-T3 surface.

The comparison of spectra of synthetic DETC salts allowed for the definitive assignment of the surface species. Of the seven salts that were attempted to be produced, five were based on the major constituents of AA 2024-T3 (Al, Cu, Mg, Mn, Fe). The failure of Al and Mg salts to precipitate in the simple mixtures implies that the surface species present is not a complex of one of these elements. The three remaining constituents fortuitously have quite different spectral fingerprints as shown in Figure 4.9. The appearance of the copper-DETC complex looks similar to bands observed on AA 2024-T3 and Cu samples. The three spectra are compared in Figure 4.20 and are in fact virtually identical at the spectral resolution employed.

As mentioned in the introduction to this chapter, the goal of the investigation was not to perform intricate spectral analysis, but a few notes deserve mention. The spectra of sodium diethyldithiocarbamate presented in Figure 4.4 and the AA 2024-T3 surface

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Figure 4.20: Raman spectra of DETC species on AA 2024-T3 and copper surfaces compared to a Cu-DETC salt. From Figures 4.6, 4.7, and 4.9(a). Vertical lines are for comparison. 514.5 nm excitation. Kaiser spectrometer.
species [Cu-(DETC) complex] presented in Figure 4.6 have Raman shift peak values assigned for the prominent peaks. Vibrational analysis of various dithiocarbamate species (including diethyldithiocarbamtes) have been presented in the literature for complexes with several metals. Some variations in assignments exist but there are some general observations. The peaks below about 800 cm\(^{-1}\) are dominated by complex mixing of vibrations involving carbon, sulfur, nitrogen, and the metal center. Trendfilova, et. al indicated that no CS characteristic frequency could be determined as no frequency involved more than 50\% of the CS stretching mode. The metal-sulfur stretching frequencies are also combined with other modes but are mainly below 400 cm\(^{-1}\). A specific band that will be used as a marker in microscopy is the most intense band centered at 425 cm\(^{-1}\). Similar bands have been reported to be a mixture of C-S and S-C-S stretching vibrations for Na, Ag, Zn, Cd, and Pb complexes.

It is interesting that the various DETC salts have such distinct spectral fingerprints (Figure 4.9). One might expect that there would be changes in the Raman shift due to changes in atomic weight of the metal. Generally, however, one would expect similar band intensity ratios for different metals. However, it has been shown that different metal species can cause differences in the molecular structure of the metal-DETC complex resulting in significant spectral changes from one complex to another. DETC may bond as a unidentate, bidentate, or bridging ligand. Differences in structure may occur even when the metals compared are all +2 cations (Cu, Mn, Zn, Cd, Pb) with bidentate bonding through the S-C-S moiety of DETC to form M(DETC)\(_2\) complexes (see Figure 4.1). The bidentate bonding of the S-C-S moiety of the DETC
to the metal may be symmetric (both C-S bonds equal length and both M-S bonds equal length) or asymmetric (C-S bonds of different lengths and M-S bonds of different lengths) resulting in symmetry changes for the complex. For example, Pb complexes with DETC have $C_{2v}$ symmetry while Zn and Cd have $D_{2d}$ symmetry. In addition, solid complexes may be monomeric (Pb-DETC complexes), dimeric (Zn- and Cd-DETC complexes), or polymeric (Hg-DETC complexes).

Once the surface species observed on AA 2024-T3 was identified as a Cu-DETC complex, the question arises of which specific interactions occur with different parts of the AA 2024-T3 surface. Raman microscopy was able to show that the interaction occurred primarily with the "possible Al$_2$CuMg" phase on the AA 2024-T3 surface (Figures 4.10 and 4.11). This phase has a high concentration of copper compared to the overall alloy composition (~4% Cu) so the appearance of the Cu-DETC complex here is logical. A comparison of the spectrum obtained with microscopy on a "possible Al$_2$CuMg" phase (Figure 4.10) is compared with the surface spectrum from Figure 4.6 as shown in Figure 4.21. Once again the bands match nearly identically indicating a Cu-DETC complex as the species present. By using the most intense spectral band located at 425 cm$^{-1}$, a spectral map was constructed showing that the occurrence of the Cu-DETC complex is centered on the "possible Al$_2$CuMg" phase (Figure 4.11). It is clear from the Raman microscopy experiments that the Cu-DETC complex forms on the "possible Al$_2$CuMg" phase but is minimal or nonexistent on the Al$_6$Cu(Fe,Mn) phase or the matrix.

The lack of bands on the Al$_6$Cu(Fe,Mn) phase is troublesome. It also contains a high copper concentration in comparison to the overall alloy composition so a similar
Figure 4.21: Comparison of macroscopic (bottom) and microscopic (top) Raman spectra of AA 2024-T3 after DETC exposure. From Figures 4.6 and 4.10. Microscopic spectrum taken on an Al$_2$CuMg intermetallic phase particle. The top sample was exposed to 0.001 M Na(DETC) for 24 h. The bottom sample was exposed to 0.1 M Na(DETC) for 18 h. 514.5 nm excitation. Kaiser and Dilor spectrometers.
observation of spectral bands would be expected. This is especially important in corrosion of AA 2024-T3 as this phase is proposed to be a site of oxygen reduction.\textsuperscript{227} Effective coverage of this phase is necessary if oxygen reduction is to be inhibited using an approach similar to the mechanism of chromate inhibition.

The electrochemical experiment results presented indicate that DETC treatment is not an effective corrosion inhibitor. This is true for either oxygen reduction on copper (Figure 4.12) or general observations on AA 2024-T3 (Figure 4.13). A possible mechanism for DETC interaction with the alloy surface may explain both the lack of corrosion inhibition and the observation of Cu-DETC complex on "possible Al\textsubscript{2}CuMg" phases but not on Al\textsubscript{6}Cu(Fe,Mn) phases. The DETC precipitate that was formed was made by combining Cu\textsuperscript{2+} with DETC to form the neutral complex. This same complex was observed on the various surfaces examined. A requirement for interaction may be the presence of the oxidized form of copper. During the corrosion process of AA 2024-T3 it has been reported that the Al\textsubscript{2}CuMg phase is initially more active (more likely to oxidize).\textsuperscript{228} It dissolves and redistributes copper around the perimeter of the dissolved phase. If DETC is present with copper in its oxidized state, a precipitate of the Cu-DETC complex will form. This would explain why little or no complex is observed around the Al\textsubscript{6}Cu(Fe,Mn) phase particles. This phase has been shown to be a noble phase on the surface of AA 2024-T3 (i.e. more likely to support oxygen reduction). As such this phase is less likely to contain copper in its oxidized form, or at least only a few layers of the oxide would be present, as copper nearly always has an oxide covering.\textsuperscript{229}
observations of the electrochemical experiments corroborate this as a possible mechanism of interaction. For the Al/Cu couple in the split-cell experiment (Figure 4.12), the copper electrode probably only has minimal coverage of an oxide layer due to its action as the cathode supporting oxygen reduction. The open circuit potential of such a system was shown to be around -0.600 V (vs. Ag/AgCl) in Chapter 2. This would lead to the formation of only minimal coverage of Cu-DETC complex on the copper surface as little copper ion is expected to be present at -0.600 V. Evidently, the coverage is not complete as oxygen reduction continues albeit at a slower rate, implying less adsorption sites exist to catalyze oxygen reduction. If the surface layer of DETC achieves complete coverage, which is less likely, the properties of the layer formed allow electron transfer or adsorption of oxygen in ways that catalyze oxygen reduction. This is something that chromium (III) layers do not do as shown in Chapter 3. The pitting observed on the sample of AA 2024-T3 may also have been aggravated by the presence of DETC in the corrosion solution. If the "possible Al₂CuMg" phase preferentially dissolves the equilibrium may be shifted by DETC removing Cu²⁺ as a product as it is formed. In fact this may account for the observation visually of a red precipitate after long times in higher concentrations of DETC as noted in initial experiments.

Diazonium salt modified surfaces

The modification of copper electrodes with diazonium salts was confirmed in the present investigation with both nitroazobenzene (NAB) diazonium salt and nitrophenyl (NP) diazonium salt. Modification is a relatively simple process, and as observed in
Figure 4.14 attachment occurred either under potential control or spontaneously for NAB diazonium salt. NP diazonium salt modification shown in Figure 4.16 was accompanied by a control experiment in the absence of NP diazonium salt to ensure the integrity of the modification process. The control experiment showed no evidence of band structure as expected. The spontaneity of the attachment of NAB to the surface is likely due to the open circuit potential of copper. In acetonitrile, copper has an open circuit potential of about -0.1 V (vs. Ag/Ag⁺). The peak of the reduction wave for NAB diazonium salt in a cyclic voltammetry experiment on a glassy carbon electrode appears at about 0 V (Figure 4.3) and many other diazonium reduction waves are in this region.²⁰⁴,²³⁰ p. 86 Thus, the open circuit potential of the electrode drives the reduction of the diazonium salt.

Predictably, the Raman spectrum for the potential controlled deposition (at -0.700 V) has greater intensity than for the spontaneous interaction as the reaction is driven with greater overpotential. The probability that the Raman spectrum from the spontaneously reacted NAB diazonium salt was from adsorption rather than bonding was investigated by sonication treatment. Sonication in an activated carbon slurry in isopropanol has been shown as an effective method to remove physisorbed species from the surface of an electrode.¹²⁸ As shown in Figure 4.15 the intensity of the Raman bands decreased but they were still relatively strong after over 1.5 hours of sonication. Some of the intensity decrease may be due to stripping of bonded NAB from the surface as well as any loosely adsorbed species but the fact remains that the bond between the surface and the modifying layer is strong.
As stated for the diethyldithiocarbamate experiments, the purpose of this investigation is not to completely vibrationally analyze the surface species observed with Raman spectroscopy. However, again some observations are available. The surface species identified here favorably matches spectra for NAB diazonium modification of glassy carbon surfaces presented by Kuo, who has reported a complete vibrational analysis of the modified glassy carbon surface with several diazonium salts.230 p. 142

Based on the vibrational analyses and tenacity of adsorption after sonication, the NAB is deemed to be bonded to the copper surface. The conclusion that NP is bonded to the Cu is also consistent with Kuo’s results of NP bonded to a glassy carbon surface.230 p. 98 The nature of the surface bond is unclear and beyond the scope of this investigation. It could be a Cu-O-C bond or a Cu-C bond as suggested by Adenier et al.219 Though not directly related to the present study, the advantage of investigating metal surfaces as compared to glassy carbon surfaces is that no subtraction of Raman bands due to glassy carbon (at 1360 cm⁻¹ and 1582 cm⁻¹) is necessary when analyzing the data. The resulting spectra have less distortion in these areas.

The observation of spectral bands on the surface of AA 2024-T3 after modification (Figure 4.17) necessarily calls for interrogation via Raman microscopy. As shown in Figure 4.18, bands appear for a spectrum taken on a “possible Al₂CuMg” phase that do not appear (or are present near the limits of detection) on the matrix phase. The reasons for preferential modification by diazonium salts may be different than for selective interaction of DETC species. The modification procedure was performed under potential control and in organic solvent (acetonitrile). At the negative potentials applied,
oxidation of the Al₆Cu(Fe,Mn) and Al₂CuMg phases probably do not occur, as they do under aqueous open circuit conditions. In fact, these areas are the most likely sites for electron transfer to the diazonium salt. The matrix is high in aluminum and has a relatively thick oxide layer that will severely retard electron transfer. Spectra on an Al₆Cu(Fe,Mn) phase were not taken but NAB bonding to this phase is likely due to the presence of reduced Cu. The Raman spectra observed macro- and microscopically (Al₂CuMg) on the AA 2024-T3 surface are compared to the copper modified surface as shown in Figure 4.22. The three spectra compare quite favorably on all the peaks observed although there are differences in relative intensity. Even less intense peaks (1186, 1340, and 1450 cm⁻¹) are almost defined for the Raman microscopic spectrum. The macroscopic spectrum shown has the intensity multiplied by five for clarity. The overall spectral intensity of the AA 2024-T3 surface is about 10% that of the copper surface. This correlates approximately with reports that intermetallic particles occupy ~4% of the surface of the alloy.⁴⁸

Finally, measurements of oxygen reduction on modified copper surfaces indicate that electron transfer kinetics may be slowed somewhat by the presence of a modifying layer, but not to the level of protection of a chromium (III) layer. Hydrodynamic voltammetry showed that oxygen reduction was initially slightly greater than for the bare electrode (Figure 4.19). As the potential was scanned negative, however, surfaces of NAB and n-butyl phenyl (C₄) inhibited the reduction of oxygen while a terphenyl (TP) surface tracked the bare surface almost identically. This is unusual in that the layers formed by these three molecules are each thicker than the layer formed by chromium (III)
Figure 4.22: Comparison of Raman spectra of nitroazobenzene (NAB) modified surfaces. Top spectrum: Raman microscopy of an Al$_2$CuMg intermetallic phase on AA 2024-T3 (from Figure 4.18). Middle spectrum: Copper (from Figure 4.14). Bottom spectrum: AA 2024-T3 macroscopic spectra (5X intensity) (from Figure 4.17). 514.5 nm excitation. Kaiser and Dilor spectrometers.
as discussed in Chapter 3. C4, NAB, and TP are approximately 11.2, 14.3, and 15.1 Å thick for a monolayer, respectively compared to about 4 Å for a Cr\textsuperscript{III} layer (or ~8 Å with a Cr\textsuperscript{VI} layer adsorbed to the Cr\textsuperscript{III} layer). Based on the tunneling probability of electrons through a non-conductive layer as discussed in Chapter 3 and considering only length of molecule (and not barrier height), the order of electron transfer rate (current) - highest to lowest - should be (1) bare electrode, (2) Cr\textsuperscript{III} layer, (3) C4 layer, (4) NAB layer, and (5) TP layer. The observations in the current study are initially (before any crossover of current - potential curves) TP, NAB, C4, bare, and Cr\textsuperscript{III}. As the potential is scanned negative, the order (after all crossovers of current - potential curves) is bare, TP, NAB, C4, and Cr\textsuperscript{III}. Two possibilities may account for this. First, the layer may simply be incompletely covering the electrode surface. The varying current densities obtained may simply be a result of less active surface area. It does not explain the greater reduction current observed for the modified compared to the bare surfaces, however. Another explanation may be linked to recently discovered properties of certain surface modifications to exhibit switching behavior. A recently published report by Solak et al. has shown that certain surface layers can switch into a more conductive state using a dry junction technique.\textsuperscript{232} These layers are proposed to act as molecular wires effectively lessening the tunneling distance for the electron. Molecules that more readily switch into this state include TP and NAB but not C4. This may explain the observation of lower current density for a C4 modified surface than for that modified with TP or NAB.

The modification of copper surfaces with diazonium salts could lead to viable alternatives to inhibition via chromate containing compounds. The ability to retard
oxygen reduction, while not as powerful as chromate treatments, offers possibilities for the development of better surface layers. The diazonium salt is attractive because it is easily modified to yield hundreds if not thousands of different molecules to investigate. The modified electrode itself has been shown to be modifiable. Enzymes were covalently attached to surfaces modified with 4-phenyl acetic acid diazonium salt in an investigation by Bourdillon et al. Alterations to metal-modified surfaces may be possible also.

The spontaneity of NAB diazonium salt attachment to the copper surface (Figures 4.14 and 4.15) also is an attractive property. Current chromate treatments are simple reactions, as discussed for Alodine™ formation of chromate conversion coatings in Chapter 1. Solution-phase chromate itself spontaneously attaches to sites of oxygen reduction as outlined in Chapter 3. Thus far, many potential replacements for chromate treatments require more extensive sample preparation and post-treatment processing. Ease of operation is important in processing procedures. Although the modification procedures performed in the present study used organic solvents, modification in aqueous solvent has been reported. The self-healing property of chromate conversion coatings could also be mimicked if the diazonium salt could be immobilized in its unreacted state and released as defects (bare reduction sites) developed on the substrate.

CONCLUSIONS

The investigation presented in this chapter explored two compound classes as possible alternates to chromate containing corrosion inhibitors - dithiocarbamates and diazonium salts. Interactions with various metal surfaces including AA 2024-T3 were
investigated with Raman spectroscopy. Both identity of compound and selective attachment were confirmed using this technique. Each class of compounds was characterized with electrochemical techniques outlined in earlier chapters.

Specific conclusions are:

- Diethyldithiocarbamate (DETC) species interact with AA 2024-T3 surfaces to form a surface compound.
- The DETC surface compound was identified as being predominantly a Cu-DETC complex.
- The DETC surface compound attaches selectively to active ("possible Al$_2$CuMg") phases of AA 2024-T3 but not to Al$_6$Cu(Fe,Mn) phases or the alloy matrix.
- DETC treatment does not provide adequate corrosion protection probably due to selective interaction with "possible Al$_2$CuMg" phases encouraging their dissolution.
- Nitroazobenzene (NAB) and nitrophenyl (NP) diazonium salt can be bound to copper surfaces via electrochemical or spontaneous interaction.
- The bonding nature is unclear but the interaction is strong - resisting extensive sonication.
- NAB diazonium salt was shown to bind to intermetallic sites of AA 2024-T3.
- Oxygen reduction current on copper was suppressed by diazonium salt modification but to a smaller degree than by chromate treatment. Possible explanations for the weaker inhibition include incomplete monolayer formation or enhanced conductivity of the modified surface.
APPENDIX

CONDUCTANCE SWITCHING OF MODIFIED ELECTRODE SURFACES

While examining diazonium salts as possible replacement inhibitors for chromate (Chapter 4), an interesting observation was made concerning electrochemical activity of electrodes that had been modified with the diazonium salts. Voltammetry of dissolved oxygen in aerated acetonitrile appeared more kinetically active on modified copper surfaces than on copper itself. Given the importance of electrodes in areas such as sensors and fuel cells, the ability to control the reactivity of the electrode is valuable. The idea of a metal electrode with a surface layer that is an organic molecule is itself intriguing. Voltammetry of several different redox systems in acetonitrile after electrode modification revealed increased kinetics of the studied system following excursion to increasingly negative applied potentials. One system (oxygen) even shows faster kinetics for a modified electrode than for a bare electrode under certain conditions. The increase in kinetics remains when voltammetric scans are returned to less-negative values.

Results of ongoing investigations are presented here.

EXPERIMENTAL

\[ C_{10}H_6Fe \text{ (Ferrocene, Sigma), } C_{12}H_4N_4 \text{ (7,7,8,8-tetracyanoquinodimethane or TCNQ, Acros Organics), 1,4-benzoquinone (Aldrich), CH}_3\text{CN (Acetonitrile,} \]
Mallinckrodt), and [CH₃(CH₂)₃]₄NBF₄ (tetrabutylammonium tetrafluoroborate, Aldrich) were reagent grade and used as received. Argon (prepurified, Praxair) was used for deaeration as indicated. For electrochemical roughening of silver Barnstead NanoPure water (18 MΩ-cm resistivity) and Na₂SO₄ (Jenneile Chemical) were used.

Voltammetry was performed using a Bioanalytical Systems BAS100B Electrochemical Analyzer using BAS100W software (version 2.3). Electrodes were commercial glassy carbon (Bioanalytical Systems), platinum (Bioanalytical Systems), or silver rod (5mm diameter, 99.95% Ag, Alfa Aesar). Electrode polishing procedures were described in Chapter 3. A platinum wire was used as the counter electrode. The reference electrode was Ag/Ag⁺ (Bioanalytical Systems) (filling solution: 0.01 M Ag(NO₃)₃ and 0.1M [CH₃(CH₂)₃]₄NBF₄ in CH₃CN). All references quoted are vs Ag/Ag⁺ unless otherwise indicated. All analyte solutions were 0.001 M unless otherwise noted. For aqueous solutions, a Ag/AgCl reference electrode (Bioanalytical Systems) was used.

Synthesis of diazonium salts was performed as indicated for Chapter 4 by members of the McCreery research group. The diazonium salts used in this study were nitroazobenzene diazonium salt and nitrobiphenyl diazonium salt as shown in Figure A.1. Modification of the electrode with diazonium salts was also described in Chapter 4. For platinum and glassy carbon electrodes modification was performed by cyclic voltammetry. Four cycles were used for nitroazobenzene (NAB) diazonium salt and ten cycles were used for nitrobiphenyl diazonium salt. Constant potential injection of diazonium salt as described previously was used to modify silver electrodes. In the case
Figure A.1: Diazonium salts investigated. Diazonium modification reaction shown at top.
of the silver electrode a roughening procedure was used to increase the signal intensity
during Raman spectroscopy via surface enhancement prior to modification with the
diazonium salt. This consisted of 20 cycles between -0.2 V and 0.7 V (vs. Ag/AgCl
reference electrode) at 0.1 V/s in 0.1 M Na₂SO₄ after which the sample was rinsed with
water and dried with a stream of argon.

Raman spectra were taken using a Kaiser Holospec spectrometer as described in
Chapter 4. Electron transfer coefficients were calculated using DigiSim 3.03a cyclic
voltammetry simulator from Bioanalytical Systems, Inc.

RESULTS

Upon observation of seemingly active oxygen reduction kinetics on copper
electrodes modified with NAB diazonium salt, further investigation was warranted. For
ease of use, electrodes made from more electrochemically stable materials were used in
place of copper. Voltammetry using silver, glassy carbon, and platinum electrodes was
performed in acetonitrile open to the atmosphere before and after modification with NAB
diazonium salt in order to observe the reduction-oxidation reactions of dissolved oxygen.
Cyclic voltammograms are shown in Figures A.2 through A.4 comparing bare and NAB
modified electrodes. In each case ΔE_{peak} values for oxygen reduction-oxidation are less
after modification than on the bare electrode. ΔE_{peak} values for oxygen reduction for a
series of different scan rates are shown in Table A.1 and are consistently lower for the
NAB modified electrodes for all scan rates and electrode materials. Raman spectra were
taken of the silver and platinum electrodes after voltammetry to confirm the presence of a
Figure A.2: Cyclic voltammetry of dissolved oxygen on bare and nitroazobenzene (NAB) modified platinum electrodes as indicated. Scan rate: 0.250 V/s. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M [CH₃(CH₂)₃]₄NBF₄.
Figure A.3: Cyclic voltammetry of dissolved oxygen on bare and nitroazobenzene (NAB) modified glassy carbon electrodes as indicated. Scan rate: 0.250 V/s. Solvent: acetonitrile open to atmosphere. Background electrolyte: 0.1M [CH₃(CH₂)₃]₄NBF₄.
Figure A.4: Cyclic voltammetry of dissolved oxygen on bare and nitroazobenzene (NAB) modified silver electrodes as indicated. Scan rate: 0.250 V/s. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M [CH$_3$(CH$_2$)$_3$]$_4$NBF$_4$. 

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NAB modified surface and are shown in Figure A.5 compared with a sample of copper that had been modified with NAB diazonium salt presented in Chapter 4. Raman spectral features are clearly present that closely resemble Raman bands observed on the copper electrode. Modification of glassy carbon surfaces with NAB diazonium salt has been well established, thus spectroscopy was not performed on the glassy carbon electrode.\textsuperscript{207}

In accordance with observed results for switching molecular junctions (see Discussion section), we hypothesized that the NAB surface layer might be exhibiting a switch to a more conductive state.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Surface</th>
<th>100 mV/s</th>
<th>250 mV/s</th>
<th>1000 mV/s</th>
<th>Surface</th>
<th>$k_{mean}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy Carbon</td>
<td>Bare</td>
<td>173</td>
<td>5.00x10^{-3}</td>
<td>223</td>
<td>4.50x10^{-3}</td>
<td>295</td>
</tr>
<tr>
<td></td>
<td>NAB</td>
<td>96</td>
<td>1.90x10^{-2}</td>
<td>123</td>
<td>1.60x10^{-2}</td>
<td>181</td>
</tr>
<tr>
<td>Silver</td>
<td>Bare</td>
<td>835</td>
<td>1.20x10^{-5}</td>
<td>835</td>
<td>1.20x10^{-5}</td>
<td>835</td>
</tr>
<tr>
<td></td>
<td>NAB</td>
<td>218</td>
<td>4.70x10^{-3}</td>
<td>157</td>
<td>9.60x10^{-3}</td>
<td>258</td>
</tr>
<tr>
<td>Platinum</td>
<td>Bare</td>
<td>116</td>
<td>1.20x10^{-2}</td>
<td>157</td>
<td>9.60x10^{-3}</td>
<td>258</td>
</tr>
<tr>
<td></td>
<td>NAB</td>
<td>92</td>
<td>2.10x10^{-2}</td>
<td>103</td>
<td>2.50x10^{-2}</td>
<td>167</td>
</tr>
</tbody>
</table>

Table A.1: Peak separation and rate constants ($k$) for dissolved oxygen voltammetry on bare and modified electrodes as indicated.

\textsuperscript{a} calculated with Digisim 3.03 simulation software assuming $D = 7.05 \times 10^{-5}$ cm$^2$/s (from Wendt and Vasudevan\textsuperscript{234})

The kinetics of oxygen reduction can be quite complex, with catalysis often coming from adsorption processes. Reduction of oxygen in aprotic solvent (e.g. acetonitrile) is generally considered an outer-sphere electron transfer process. However, traces of water in the solvent may mean protonation may take place unless the solvent is thoroughly dried. Since special solvent drying procedures were not followed here, less complex outer-sphere redox systems might serve to simplify the investigation. Also, $E_{1/2}$
Figure A.5: Raman spectra of Ag, Cu, and Pt surfaces after modification with nitroazobenzene diazonium salt. 514.5 nm excitation. Kaiser spectrometer.
for oxygen reduction occurs near -1.1 V for the conditions studied here. If switching of
the modified electrode occurs at a particular negative potential, studying systems with
more positive $E_{1/2}$ values than oxygen may permit observation of both initial and
conductive states. Figure A.6 shows voltammetry of a known outer-sphere redox system,
tetracyanoquinodimethane (TCNQ), on a bare and NAB modified glassy carbon
electrode. Figure A.6(a) shows the voltammetry for the bare glassy carbon electrode and
the trace is continued through the four graphs shown for reference. Two reversible
reduction waves are observable for TCNQ at approximately 0 V and -0.6 V. The kinetics
of both reduction waves appears to be rather fast. Figures A.6(b) through A.6(d) show
voltammetry after the electrode had been derivatized with NAB diazonium salt. Figure
A.6(b) shows the initial voltammogram after NAB modification. The first reduction
wave is kinetically slow compared to that on the bare electrode. The second wave on the
modified electrode is also kinetically slower than on the bare electrode but the current
increases rapidly at about -0.750 V. Upon the reverse scan two waves appear
corresponding to the oxidation of the reduced TCNQ, with the most positive (TCNQ$^-$ $\rightarrow$
TCNQ) almost matching the corresponding wave on the bare electrode. Figure A.6(c)
shows the subsequent voltammogram of TCNQ on the NAB modified electrode. The
first reduction wave (TCNQ $\rightarrow$ TCNQ$^-$) now nearly matches that of the bare electrode
while the second wave (TCNQ$^-$ $\rightarrow$ TCNQ$^{2-}$) is slower than the bare electrode, although
faster than the initial NAB modified voltammogram. By the fifth cycle shown in Figure
A.6(d) the first couple is almost identical to the bare electrode and the second couple
shows faster kinetics, though not as fast as the second couple on the bare electrode. Also
Figure A.6: Cyclic voltammetry of 0.001 M tetracyanoquinodimethane (TCNQ) on bare and nitroazobenzene (NAB) modified glassy carbon electrodes. (a) bare electrode (dashed line on a-d), (b) initial voltammogram after NAB modification, (c) 2nd voltammogram after NAB modification, (d) 5th voltammogram after NAB modification. Scan rate: 0.250 V/s. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M \([\text{CH}_3(\text{CH}_2)_3]_4\text{NBF}_4\).
observed in Figures A.6(b) through A.6(d) is the development of reduction and oxidation features negative of the TCNQ reduction waves, about -1.2 V.

Continuing along the same lines, the modifying species was next changed to nitrobiphenyl (NBP) diazonium salt as it also exhibits switching in a molecular junction (see Discussion). Results of TCNQ voltammetry on glassy carbon and platinum electrodes modified with NBP is shown in Figures A.7 and A.8. The results are qualitatively similar to the results observed for Figure A.6 with the initial TCNQ voltammetry after electrode modification being kinetically slowed and the reversal scan showing signs of oxidation waves corresponding to faster kinetics. Subsequent voltammetric scans showed faster kinetics until the first TCNQ reduction-oxidation couple nearly matches the voltammetry of the bare electrode. The second scan again did not kinetically match the voltammetry of the bare electrode. The development of an additional couple was also observed in the region negative of the TCNQ reduction waves. The major difference between the two electrode materials (glassy carbon and platinum) was in the onset of the “switch”, with the platinum electrode (Figure A.8) exhibiting no current until reaching approximately -1.0 V while the glassy carbon electrode (Figure A.7) showed a current response beginning slightly negative (~ -0.1 V) of that on the bare electrode but kinetically slower. The onset of reduction current on the platinum electrode occurred with a sharp increase in current to a level approximately twice that of the TCNQ reduction waves on the bare electrode possibly indicating a two-electron reduction. Several more voltammetric scans were required (and to a more negative potential, -2 V)
Figure A.7: Cyclic voltammetry of 0.001 M tetracyanoquinodimethane (TCNQ) on bare and nitrobiphenyl (NBP) modified glassy carbon electrodes. (a) bare electrode (dashed line on a-d), (b) initial voltammogram after NBP modification, (c) 2nd voltammogram after NBP modification, (d) 5th voltammogram after NBP modification. Scan rate: 0.250 V/s. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M [CH₃(CH₂)₃]₄NBF₄.

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Figure A.8: Cyclic voltammetry of 0.001 M tetracyanoquinodimethane (TCNQ) on bare and nitrobiphenyl (NBP) modified platinum electrodes. (a) bare electrode (dashed line on a-d), (b) initial voltammogram after NBP modification, (c) 2nd voltammogram after NBP modification, (d) 7th voltammogram after NBP modification (scans 5 through 7 to -2 V). Scan rate: 0.250 V/s. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M [CH₃(CH₂)₃]₄NBF₄.

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for platinum than for glassy carbon to achieve kinetics similar to TCNQ on bare electrodes.

1,4-benzoquinone (BQ) is another outer-sphere redox system that has two reduction waves observed with cyclic voltammetry, with $E_{1/2}$'s of about -0.750 V for the first couple and negative of -1.3 V for the second couple. Voltammetry of BQ on bare and nitrobiphenyl (NBP) modified platinum electrodes is shown in Figure A.9. Again, the results were qualitatively similar to the previously discussed voltammetry (Figures A.6 - A.8) with some notable observations. The voltammetry of BQ on a bare platinum electrode in Figure A.9(a) showed a kinetically fast first wave (BQ $\rightarrow$ BQ$^-$) but the second wave (BQ$^-$ $\rightarrow$ BQ$^{2-}$) is quite slow. The initial voltammetric scan after modification with NBP showed minimal reduction current on a negative scan until about -1 V. At this potential, the current increased to approximately the same height as for the first BQ reduction wave on the bare electrode. As the potential was scanned further negative a second reduction wave appeared at about -1.5 V. The reverse scan showed oxidation waves corresponding to the two reduction waves. The subsequent scan, shown in Figure A.9(c) exhibited first wave kinetics nearly identical to those for the bare electrode. In addition, the second reduction wave was kinetically much faster than for the bare electrode. After further scans, the modified electrode maintained similar current responses to those shown in Figure A.9(c) and are shown in Figure A.9(d).

With the previous results indicating that the modified electrode surface could be made kinetically active, a possibility is that the active electrode could be used to reduce more diazonium salts as well as the other species studied. Reduction of diazonium salts
Figure A.9: Cyclic voltammetry of 0.001 M 1,4-benzoquinone (BQ) on bare and nitrobenzylphenyl (NBP) modified platinum electrodes. (a) bare electrode (dashed line on a-d), (b) initial voltammogram after NBP modification, (c) 2nd voltammogram after NBP modification, (d) 4th voltammogram after NBP modification. Scan rate: 0.250 V/s. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M [CH$_3$(CH$_2$)$_3$]$_4$NBF$_4$. 

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may result in further bonding with the existing surface layer to form multi-layers. To test this possibility the electrode from Figure A.9 was rinsed and replaced into NBP diazonium salt solution and potential scans were performed as for the original modification. Figure A.10 shows results of the initial and second modification voltammetry. The second modification does indeed show a reduction wave for NBP diazonium salt although it is smaller than the initial modification wave. This “double-modified” electrode was returned to 1,4-benzoquinone (BQ) solution and voltammetry was performed as shown in Figure A.11. The results of the initial scan shown in Figure A.11(b) show a delayed current response as observed for the “single” modification from Figure A.9(b) with the delay of current response now until around -1.2 V, slightly more negative than for the “single” modification. A second reduction wave can be observed but the two waves overlap severely. The reverse wave shows some signs of oxidative activity but it seems to be kinetically slow. The subsequent wave does not show fast kinetics but an increase in current occurs that corresponds loosely to the first reduction wave of BQ. The second reduction wave is more well-defined. Reverse waves never developed fast kinetics although drawn out current waves are discernable.

Voltammetry on glassy carbon electrodes modified with NBP diazonium salt was performed for four systems to compare kinetic parameters on active modified electrodes (termed “on” electrodes) and bare electrodes. Voltammetry of the first wave of TCNQ and BQ are shown in Figure A.12 and voltammetry of ferrocene and oxygen are shown in Figure A.13. The data shown compare initial voltammograms with voltammograms after
Figure A.10: First and second modification of platinum electrode with nitrobiphenyl (NBP) diazonium salt. Top: Initial modification. Ten cycles in 0.001 M NBP diazonium salt. Bottom: 2nd modification after electrode activated as indicated in the text. Scan rate: 0.100 V/s. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M [CH₃(CH₂)₃]₄BF₄.
Figure A.11: Cyclic voltammetry of 0.001 M 1,4-benzoquinone (BQ) on bare and nitrobiphenyl (NBP) double-modified platinum electrodes as described in the text. (a) bare electrode (dashed line on a-d), (b) initial voltammogram after 2nd NBP modification, (c) 2nd voltammogram after 2nd NBP modification, (d) 8th voltammogram after 2nd NBP modification. Scan rate: 0.250 V/s. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M [CH₃(CH₂)₃]₄NBF₄.
Figure A.12: Cyclic voltammetry of 0.001 M tetracyanoquinodimethane (TCNQ) (top) and 0.001 M 1,4-benzoquinone (BQ) (bottom) on bare and nitrobiphenyl (NBP) modified glassy carbon electrodes as described in the text. "on" electrodes were subjected to repeated cycles to -2 V until redox response stabilized. Scan rate: 0.500 V/s. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M [CH₃(CH₂)₃]₄NBF₄.
Figure A.13: Cyclic voltammetry of 0.001 M ferrocene (Fc) and dissolved oxygen on bare and nitrobiphenyl (NBP) modified glassy carbon electrodes as described in the text. "on" electrodes were subjected to repeated cycles to -2 V until redox response stabilized. Scan rate: 0.500 V/s. Solvent: deaerated acetonitrile for Fc voltammetry, open to atmosphere for O₂ voltammetry. Background electrolyte: 0.1M [CH₃(CH₂)₃]₄NBF₄.
the electrode was repeatedly scanned to -2 V until peak separation of the redox couple remained constant. The peak separation data is reported in Table A.2.

<table>
<thead>
<tr>
<th>Redox system</th>
<th>( \Delta E_p ) at 500 (mV/s)</th>
<th>( k^a ) (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bare</td>
<td>Initial</td>
</tr>
<tr>
<td>TCNQ</td>
<td>90</td>
<td>284</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>180</td>
<td>291</td>
</tr>
<tr>
<td>Benzoquinone</td>
<td>62</td>
<td>442</td>
</tr>
<tr>
<td>Ferrocene</td>
<td>92</td>
<td>485</td>
</tr>
</tbody>
</table>

Table A.2: Peak separation and rate constants \((k)\) for various redox systems on bare and nitrobenzyl (NBP) modified glassy carbon electrodes as indicated. \(a\) calculated with Digisim 3.03 simulation software assuming \( D_{\text{oxygen}} = 7.05 \times 10^{-5} \) cm\(^2\)/s (from Wendt and Vasudevan\(^{234}\)) all others assume \( D = 1 \times 10^{-5} \).

Finally, triangular-wave alternating-current voltammetry (TACV) in acetonitrile was performed to determine changes in capacitance of a glassy carbon electrode in bare, modified (NBP), and "on" states with the results shown in Figure A.14. The acetonitrile used was dried by passing over activated alumina immediately before the experiment. The modified electrode was also cleaned immediately after derivatization by stirring in a mixture of activated carbon and isopropanol for approximately 20 minutes. The potential was scanned at 0.004 V/s while a triangular wave of 0.050 V peak-to-peak was imposed at 50 Hz. Current response at the positive and negative limits of the triangular potential wave are sampled and the difference taken. In regions of no redox activity the resulting value is due to the capacitance of the electrode-solution interface, which can be calculated directly from the expression

\[
C = \frac{I}{(dV/dt)} \quad (A.1)
\]
Figure A.14: Triangular wave alternating current voltammetry (TACV) of bare and nitrobenzene (NBP) modified glassy carbon electrodes as described in the text. Negative-going scans performed first. Three consecutive cycles were run on the NBP modified electrode as depicted by 1st, 2nd, and 3rd. Scan rate: 0.004 V/s. Frequency: 50 Hz Amplitude: 0.050 V peak-to-peak. Solvent: deaerated acetonitrile. Background electrolyte: 0.1M \( \text{[CH}_3\text{CH}_2\text{]}_4\text{NBFO}_4 \).
where $C$ is capacitance (Farads), $I$ is current (amperes), $t$ is time (s), and $V$ is potential (V). The expression is rearranged for $TACV$ to

$$C = \frac{I}{2}(1/f)(A)$$

(A.2)

where $I$ is observed current difference measured (amperes), $f$ is frequency of alternating potential (Hz or 1/s), and $A$ is amplitude of the alternating potential (V). The conversion has already been performed as presented in Figure A.14 with the results divided by surface area of the electrode. Both forward and reverse scans between 0 and -1.75 V were performed on the bare electrode and several times on the modified electrode. The magnitude of the capacitance of the various sweeps in acetonitrile (with 0.1 M $[\text{CH}_3\text{CH}_2]_4\text{NBF}_4$) at -0.750 V (chosen arbitrarily) in negative and positive scanning directions (negative capacitance shown in Figure A.14 is a result of software convention only) is listed in Table A.3. The NBP modified electrode exhibited an increasing differential current between -1.25 and -1.75 V due to the reduction-oxidation of the NO$_2$ group of the NBP.
Table A.3: Capacitance of bare and nitrobiphenyl (NBP) modified glassy carbon electrodes measured with triangular wave alternating current voltammetry (TACV). Solvent: deaerated acetonitrile. Background electrolyte: 0.1M [CH₃(CH₂)₃]₄NBF₄.

<table>
<thead>
<tr>
<th>Scan</th>
<th>Capacitance @ -0.750 V (μF/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>negative</td>
</tr>
<tr>
<td>Bare electrode</td>
<td>34.6</td>
</tr>
<tr>
<td>1st on NBP</td>
<td>9.0</td>
</tr>
<tr>
<td>2nd on NBP</td>
<td>15.5</td>
</tr>
<tr>
<td>3rd on NBP</td>
<td>17.0</td>
</tr>
</tbody>
</table>

DISCUSSION

The present investigation reveals some interesting observations regarding the switching of the surface layer to a more conductive “on” state. The nitroazobenzene (NAB) and nitrobiphenyl (NBP) modified electrodes appear to turn “on” at potentials negative of those experienced during modification procedures (typically ~ -0.800 V) but positive of the reduction of dissolved oxygen (~ -1.25 V). The initial observations of fast electron transfer for dissolved oxygen on NAB modified electrodes (Figures A.2 - A.4) without scans to more negative potentials implies that the NAB is turned “on” before the O₂ reduction potential is reached. NBP modified electrodes exhibit initially fast kinetics for oxygen reduction after modification that do not increase greatly as the electrode scanned to -2 V (Figure A.13) also implying that the NBP is turned “on” before the O₂ reduction potential is reached. The switch from “off” to “on” states is more pronounced on modified platinum electrodes than on modified glassy carbon electrodes. Comparing different electrodes with the same redox systems (TCNQ redox on NBP modified...
platinum and glassy carbon in Figures A.7 and A.8 and BQ redox on NBP modified platinum and glassy carbon electrodes in Figures A.9 and A.12) shows that platinum electrodes exhibit small reduction currents until the switch occurs on the initial voltammogram after modification. Modified glassy carbon electrodes, on the other hand, show observable reduction but with slow kinetics on initial scans and the switch is less pronounced. It is likely that this is a manifestation of the difference in bonding between the modifying layer and glassy carbon (a C-C bond) or platinum (a Pt-C or Pt-O-C bond).

Kinetically, cyclic voltammetry with modified electrodes in the “on” state using various redox systems indicates electron transfer rates near those observed on bare electrodes. Rate constants calculated using simulation software and presented in Tables A.1 and A.2 support this observation. Included is the observation of faster electron transfer kinetics for dissolved oxygen on a NAB modified electrode compared to a bare electrode (Table A.1). This is highly unusual and indicates a possible adsorption interaction of the NAB layer with dissolved oxygen which accelerates electron transfer. All other systems studied besides oxygen (TCNQ, BQ, Fc) on NAB modified surfaces and all systems studied on NBP modified surfaces (O₂, TCNQ, BQ, Fc) showed electron transfer rates for the first reduction-oxidation couple that approach but do not exceed electron transfer rates on the bare electrode. Without a change in the interaction between a redox species and an electrode the presence of a surface layer cannot make the electron transfer faster than a bare electrode.

The observations presented here are qualitatively consistent with the discovery of conductance switching characteristics in our laboratory for junctions based on carbon -
monolayer - mercury contacts. Diazonium modification of near atomically flat pyrolyzed photoresist films formed a covalently bonded molecular layer which was then brought into contact with mercury to form a dry junction. Current-potential curves show that upon scanning negative (carbon relative to Hg) a sudden current increase and resistance decrease was observed, often by 1 or 2 orders of magnitude. This low resistance state remains until a potential positive (vs. Hg) is reached when the system switched back to a high resistance state. If the switching point (either positive or negative) is not reached the system remains in its state of high or low resistance. A proposed mechanism for switching involves injection of an electron into the surface layer resulting in a structural change in the molecule. The electron injection results in a lower tunneling barrier height for the modifying layer and higher conductivity, based on a simple tunneling mechanism for electron transfer as discussed in Chapter 3 for chromium (III) layers on an electrode. The changes in capacitance observed with TACV before and after the electron injection (Figure A.14 and Table A.3) support the connection between electron injection and conductivity. Prior to the NO₂ group reduction the capacitance is lower indicating a less conductive film. Subsequent scans result in a consistently higher, but stable, capacitance indicating higher conductivity. The “on” capacitance is less than a bare electrode since any film should reduce the capacitance even if highly conductive.

It is important to note that the switch to a more conductive state persists even when the potential of the system is returned to values positive of the “switch”. This implies that the system has changed to a lower energy state whether the mechanism involves electron injection or an ordering of the entire layer. A high destabilization
energy needs to be applied (in the form of positive potential) for the electron to be ejected or for the layer to disorder. For the present investigation, the modified electrode could be switched to a more active state by scans to negative potentials but was unable to be switched off by scans to positive potentials (not shown) before breakdown of the electrode materials occurred.

The inability to turn the “on” electrode “off” may be explained assuming the electron-injection rearrangement hypothesis presented above. After modification the electrode is in an “off” state. Applied potentials create an electric field between the electrode and the solution. When in the “off” state the resistance of the surface layer is high and when “on” the resistance is lower. In a junction (carbon - modifier - mercury) the potential drop across the modifying layer is easily controlled so “on” and “off” switches can be achieved. In a solution, the applied electric field is manifested as potential drops across both the modifying layer and into the solution.\(^{15}\) The potential drop across the modifying layer is large when the electrode is “off” compared to when it is “on”. If this potential drop (electric field) causes the switch to occur then in the “on” state most of the potential drop occurs in the double layer of the solution. Large positive potentials would need to be applied to the overall system to achieve large enough field across the modifying layer to cause a switch to the “off” state to occur. This is depicted graphically in Figure A.15.

Finally, questions inevitably arise concerning the presence of a modified surface at all. Perhaps the negative scans merely detach the layer from the electrode surface rather than cause a change in conductivity of the layer. Several observations support the
Figure A.15: Potential drop profiles for solution-based and molecular junction systems. The four graphics depict the same total difference in potential between the two electrodes pictured. Potential drops in modifying layers depicted as linear only for simplicity.
switching scenario. First, Raman spectral features present (Figure A.5) after switching to an “on” state indicate that the electrode remains covered with a modifying layer. Second, continued observation of voltammetric waves associated with the reduction-oxidation of the NO₂ group after the electrode is turned “on” indicate surface species. Third, the changes in the second wave of BQ and TCNQ voltammetry after modification implies a surface layer perturbing the electron transfer process. Otherwise, the second waves should approach the fast kinetics observed on bare electrodes. This question is also being addressed by testing with voltammetry of dopamine as described in the next section.

FUTURE CONSIDERATIONS

As mentioned earlier, the investigation of conductance switching in the modification layer is currently ongoing. A publication is currently being submitted to report our first observations. Important issues not discussed above are being addressed that will be summarized here.

After modification with diazonium salt, the electrode was originally rinsed with acetonitrile, the solvent. Present experiments are focused towards developing a cleaning procedure following the diazonium modification procedure that will remove any physisorbed species from the surface without damaging the bonded surface layer. Stirring the electrode in a mixture of activated carbon and isopropanol (AC/IPA) in a method similar to Ranganathan, et al. has been tried but carbon residue that may interfere with voltammetry was observed on electrode surfaces using atomic force.
microscopy after the cleaning procedure. Currently filtration of the AC/IPA mixture to obtain a cleaned rinsing solvent is being attempted.

The surface coverage of the modified electrode is a critical issue. If the surface is not completely covered by the modifying layer the bare portions of the bare electrode (often called “pinholes”) can act as microelectrodes. The resulting voltammetry may be due to the increased mass transport observed at the pinhole rather than on the surface layer. Reduction of dopamine in 0.1 M $\text{H}_2\text{SO}_4$ requires adsorption to the electrode surface to be catalyzed.\textsuperscript{237} If a completely modified surface is formed dopamine reduction is completely inhibited. Investigation of the completeness of the surface layer formed is undergoing using the reduction of dopamine as a marker to refine modification procedures. Also, this test is useful in supporting the conclusion that the surface layer remains intact after derivatization.

Conductance switching the electrode to an “on” state has been observed in aprotic solvent (acetonitrile) only. A much wider range of applications may be available if the modified electrode can be switched to a more active state in aqueous solvents and is currently under investigation.

CONCLUSIONS

Preliminary conclusions for the present investigation include:

- Electrode surfaces modified with nitroazobenzene (NAB) and nitrobiphenyl (NBP) diazonium salts exhibit a transition to a higher conductivity state upon exposure to negative potentials that remains when returned to more positive potentials.
• Both glassy carbon and metal modified electrodes exhibit conductance switching.
• The electrode cannot be switched back to a lower conductivity state by positive scans before breakdown of the electrode occurs, possibly due to the large positive potentials required.
• NAB modified surfaces show faster reduction kinetics for dissolved oxygen in acetonitrile than at a bare electrode, implying a change in the mechanism of electron transfer.
REFERENCES


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