ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE STUDY OF CORROSION OF PHASES IN AA2024-T3

A Thesis

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By
Younghoon Baek, B.S.

The Ohio State University
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Master's Examination Committee:
Dr. Gerald S. Frankel, Adviser
Dr. Rudolph G. Buchheit

Approved by
Adviser
Materials Science and Engineering
ABSTRACT

Characterization of electrochemical activity of intermetallic compounds and the Al matrix in AA2024 is critical for understanding the corrosion behavior of this alloy. However, cathodic corrosion of Al and Al alloys makes it very difficult to determine the true cathodic kinetics using only electrochemical techniques. The electrochemical quartz crystal microbalance was used to directly measure the dissolution rate, and thus the cathodic corrosion rate, of thin film analogs in this alloy. The true cathodic reaction rate was calculated from the summation of the net and the oxidation current density. For pure Al and Al-4Cu in unbuffered chloride solution, the oxidation current density was large relative to the net current density, so the true cathodic current density was considerably larger than the measured net current density. The dissolution rate and the cathodic current density were weakly dependent on potential and the presence of dichromate in the solution, even though the net current density showed stronger dependencies. The cathodic current density was almost identical to the net current density for Al$_2$Cu because the anodic dissolution rate was very small compared to the cathodic reaction rate. The presence of dichromate in solution inhibited the oxygen reduction reaction on Al$_2$Cu more effectively than on pure Al and Al-4Cu. Measurements on Au electrodes were used
to study the causes of the decrease in resonant frequency or increase in apparent mass during cathodic polarization of Al$_2$Cu.
TO MY PARENTS AND WIFE
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VITA

July 30, 1972 ......................................................... Born - Seoul, Korea

Aug. 1998 ................................................................ B.S. Materials Science and Engineering, Seoul National University, Seoul, Korea

Sep. 1999 – present .................................................. Graduate Research Associate, Department of Materials Science & Engineering, The Ohio State University, Columbus, Ohio, USA

FIELDS OF STUDY

Major Field: Materials Science and Engineering
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CHAPTER 1

INTRODUCTION

The corrosion behavior of high strength Al alloy 2024 depends strongly on the cathodic activity of Cu-rich intermetallic particles such as θ phase (Al₂Cu), S phase (Al₂CuMg), and Al-Cu-Mn-Fe [1, 2]. These intermetallic compounds (IMCs) can act as anodes or cathodes, or fluctuate between the two states as their composition changes. Oxygen reduction reaction (ORR) at the cathodic sites leads to the development of high pH zones on IMCs and the surrounding Al matrix. The increased local pH promotes dissolution the Al matrix [2], and may also result in dealloying of IMCs themselves.

Chromate effectively inhibits corrosion of Al alloys. For instance, Cr(VI) was found to increase the corrosion resistance of AA2024 by several orders of magnitude [3]. It has been suggested that chromates inhibit the ORR [4]. However, exact determination of the cathodic kinetics on Al and Al alloys is complicated by cathodic corrosion associated the alkalinity generated by hydrogen evolution and oxygen reduction. Even
during cathodic polarization with a net negative current, the Al oxide film dissolves chemically as a result of the local pH increase [5]. Reformation of oxide film involves Al oxidation reactions. The net current is a summation of all of the electrochemical reactions and is less than the true cathodic current if the cathodic corrosion rate is significant in magnitude. This makes it very difficult to determine the cathodic kinetics this alloy using only electrochemical techniques.

The electrochemical quartz crystal microbalance (EQCM) provides sub-monolayer resolution of mass changes occurring at the electrode surface and a separate measure of the dissolution rate. The EQCM actually measures the change in resonant frequency of the quartz crystal, which can be converted into mass change using Sauerbrey’s equation [6]. However, the density and viscosity change of the liquid layer on the electrode, and surface roughness change of the electrode can also influence the resonant frequency [7-9]. The high mass sensitivity and in-situ capability of the EQCM make it a suitable tool for the study of atmospheric corrosion, passivation, and inhibition.

In this study, thin film analogs of pure Al, Al matrix and θ phase in AA2024 were fabricated using the flash evaporation technique. The ORR rates and cathodic corrosion behavior of the analogs have been studied using the EQCM technique. The thin film analogs were potentiostatically polarized at different potentials and in 0.1 M NaCl solution with different concentrations of chromate. The EQCM allows direct determination of the cathodic corrosion rate from the rate of mass change, and the true cathodic reaction rate from the difference between the net current and cathodic corrosion
rate. The effect of chromate on the cathodic corrosion rate and the true cathodic reaction rate was investigated as a function of the applied potential, the bulk solution and the electrode material.
LIST OF REFERENCES


2.1 CORROSION OF ALUMINUM AND ALUMINUM ALLOYS

2.1.1 Corrosion of Al

Aluminum is an active metal that owes its corrosion resistance to the presence of a thin, protective, native oxide film on its surface. The oxide film is spontaneously developed on the aluminum surface in the presence of air and is largely amorphous alumina with the thickness of 2 to 4 nm [1]. In contact with wet environments, the external side of the oxide film hydrolyzes to produce hydrated oxides such as Al₂O₃·H₂O [1]. Its properties depend on the oxidation conditions and its stability is determined by the chemical composition of the aqueous environment to which it is exposed. Figure 2.1 shows the Pourbaix diagram (potential vs pH diagram) of the Al/H₂O system at 25°C [2]. Hydrated alumina is the most stable form in the intermediate pH range between 4 and 8.5, but Al³⁺ and AlO₂⁻ ions are the most stable forms in more acidic and alkaline solutions,
respectively. The Al oxide film shows both minimum solubility and minimum dissolution rate at pH 5 [3]. Therefore, in general, less corrosion occurs in neutral pH solutions than in either acid or alkaline solutions.

The corrosion behavior of aluminum depends on the native oxide film formed on its surface since the bare surface of aluminum is extremely reactive. An oxide film is likely present on Al, even during dissolution in acid or alkaline solutions. In acidic solution, several researchers [4-6] reported that anodic aluminum dissolution occurs under a porous oxide film by the field-assisted direct metal dissolution mechanism. This involves anodic oxidation of aluminum and direct ejection of aluminum ions from the film into the solution by the electrical field. However, since the direct ejection of aluminum ions into alkaline solution is thermodynamically prohibited, the field assisted dissolution process can never occur in alkaline solution. Furthermore, the Al dissolution reaction in alkaline solution was found to be retarded by the applied electric field [7].

The anodic dissolution mechanism of Al in alkaline solutions has been investigated intensively for the development of aluminum/air batteries. A model for anodic Al dissolution in alkaline solution was proposed by Macdonald et al. [8]. That model involves the stepwise addition of hydroxide ions to surface aluminum atoms, culminating in chemical dissolution of Al(OH)$_3$ to form Al(OH)$_4^-$ . Another similar anodic dissolution mechanism, which was suggested by Chu and Savinell [9], includes fast aluminum ionization and hydroxide formation reactions, followed by the slow hydroxide film dissolution reaction by OH$^-$ attack. Both studies suggested indirect metal dissolution
in alkaline solution, which is different from the field-assisted direct dissolution in acid solution. Indirect metal dissolution of aluminum in alkaline solution involves electrochemical Al oxidation, film formation, and chemical dissolution of the surface film. In the alkaline region, corrosion rates of Al increase with increasing pH of the solution. The dissolution rate of Al in the alkaline solution depends on the concentration of hydroxide ions and the presence of aluminate (Al(OH)$_4^-$) ions in the solution [9].

The presence of aggressive anions like Cl$^-$ increases corrosion rates of Al and Al alloys and causes the breakdown of the oxide film. In addition, aluminum is susceptible to pitting corrosion in the presence of Cl$^-$ ions. The effects of chloride ions on the corrosion rate of Al and Al alloys in the wide pH range of solutions have been studied extensively. The chemical reaction of chloride ions adsorbed on the oxide surface with Al cations was proposed to have a significant effect on the overall aluminum dissolution reaction [10]. The addition of Cl$^-$ ions to acidic and neutral solutions increased the aluminum dissolution rate at anodic potentials due to either the additional charge carrier generated by the incorporation of Cl$^-$ ions into the oxide film [11], or to the participation of Cl$^-$ ions in the metal dissolution reaction [12]. However, in alkaline solution, the aluminum dissolution rate at anodic potentials below the pitting potential was reduced by the addition of Cl$^-$ ions due to the formation of resistive insoluble compounds within the surface film [13]. The addition of OH$^-$ into neutral sodium chloride led to increased anodic current density, which resulted from the chemical dissolution of oxide film by the OH$^-$ attack [14].
2.1.2 Corrosion of Cu-containing Al Alloys

The corrosion of Cu-bearing Al alloys is much more complicated than pure aluminum due to the presence of a heterogeneous microstructure, such as is shown in Figure 2.2. The addition of alloying elements (e.g. Cu and Fe) produce high mechanical performance, heat treatable, and low density Al alloys like AA2024, which has numerous applications in aerospace and automotive industries. The intermetallic phases in the Al alloys are either intentionally precipitated to obtain the good mechanical properties or present in the Al alloys as natural impurities. The size of intermetallic particles ranges from several nanometers to as much as 10 micrometers in diameter depending on the alloy composition and manufacturing process [15].

The characterization of the electrochemical behavior of the individual phases, including intermetallic compounds (IMCs) and Al-matrix, in Al alloys has been an important research topic for understanding their corrosion behavior. Since corrosion is an electrochemical phenomenon, the alloys with phases having similar electrochemical potentials are expected to be more corrosion resistant than the alloy with phases having widely different electrochemical potentials. Generally, the phases with noble alloying elements have higher corrosion potentials than the phases with active alloying elements. But the corrosion potential of the compounds containing mixtures of both noble and active elements not only is unpredictable, but also can change with the exposure time to the solution. Buchheit [16] collected the corrosion potential values for intermetallic phases in Al alloys in a literature survey up to 1995. Even though the direct correlation of
the corrosion potential data is impossible due to different quality of bulk intermetallic samples and different time scales of experimental measurements, the compilation makes it possible to predict the galvanic relationships of common intermetallic phases in Al alloys.

The Al alloys with Cu-rich intermetallic particles, such as AA2024, are susceptible to localized corrosion such as intergranular corrosion and pitting corrosion because of different electrochemical activities of the intermetallic particles with respect to the Al matrix. If IMCs like Al$_2$Cu are preferentially formed along the grain boundaries, then a copper depleted zone can be present next to the grain boundaries. Therefore, the grain boundaries become anodic with respect to the grain and show a strong susceptibility to intergranular corrosion. In addition, Cu-rich IMCs form local galvanic cells with the surrounding Al matrix. These intermetallic phases, which are electrochemically more noble than the Al matrix, usually decrease corrosion resistance because they play the role of preferred cathodic sites while the surrounding Al matrix undergoes anodic dissolution. Another aspect of this interaction is that the oxygen reduction reaction (ORR) on the local cathodes increases the local pH of the solution near these intermetallic particles and allows the surrounding Al matrix to dissolve due to OH$^-$ attack [17]. If the Al matrix is an Al-Cu solid solution, this attack will lead to dealloying of Al and surface enrichment of Cu. In AA2024, the active S-phase particles also dealloy and enrich in Cu. This dealloying process results in nanoporous Cu-rich remnants that induce pitting around their periphery [18]. Pit initiation sites are usually found near these cathodic sites, such as
at the periphery of Cu-enriched Al-Cu-Mg (S-phase) particles and Al-Cu-Fe-Mn particles [19, 20]. Metallic Cu, which is redeposited on the alloy surface during the corrosion of Cu-containing Al alloys, enables the surrounding Al matrix to dissolve further by supporting the cathodic reaction more easily. Therefore, the investigation of cathodic activities for the Cu-rich intermetallic phases is important for understanding corrosion behavior of these Al alloys [21].

2.1.2.1 Corrosion of $\text{Al}_2\text{Cu}$ ( $\theta$ Phase )

Extensive studies have been performed on the electrochemical characterization of $\text{Al}_2\text{Cu}$ or $\theta$ phase. The improved strength of Cu-containing Al alloys is derived from the precipitation of $\text{Al}_2\text{Cu}$, which has a tetragonal crystal structure and, in equilibrium, is incoherent with the Al matrix. From the intergranular corrosion behavior study of Al-4%Cu alloys, Galvele and de Micheli [22] found that $\text{Al}_2\text{Cu}$ is more noble than Al matrix (Al-4%Cu) and Cu-depleted zone (Al-0.2%Cu), and the cathodic reaction is kinetically easier on the Cu-rich phase than on pure Al. In the early 1980's, the electrochemical behavior of $\text{Al}_2\text{Cu}$ in sulfate solutions was investigated using a rotating ring disk electrode by Mazurkiewicz and Piotrowski [23]. It was found that the anodic dissolution of this IMC consists of the dissolution of both elements into $\text{Al}^{3+}$ and $\text{Cu}^{2+}$ ions. But the $\text{Cu}^{2+}$ ions are reduced back on the electrode in the range of potentials corresponding to the stability of metallic copper. At anodic potentials, $\text{Al}_2\text{Cu}$ was also found to exhibit a much higher breakdown potential for the passive film than pure Al in NaCl solution.
Scully et al. [24] compared the electrochemical behavior of Al\textsubscript{2}Cu phase to pure Al in inert buffer solutions ranging from pH 2 to 12. Open circuit potential (OCP) measurements showed that the OCP of Al\textsubscript{2}Cu is approximately 750 mV more positive than that of pure Al from pH 2 to 12, and significantly decreases in the more alkaline solutions between pH 9 and 12 like pure Al. The most significant finding is that Al\textsubscript{2}Cu can support the anodic and cathodic electron transfer reactions (ETR), including oxygen reduction reaction, at enhanced rates relative to pure Al due to the presence of metallic copper in the Al-rich oxide film. After corrosion for 1 hr at an anodic potential in 0.1 N NaOH, Rüdiger and Köster [25] found that mixtures of Al\textsubscript{2}O\textsubscript{3} needles and Cu oxide developed on the surface of the intermetallic phase (Figure 2.3).

2.1.2.2 Corrosion of Al\textsubscript{2}CuMg (S-Phase)

Al\textsubscript{2}CuMg or S-phase is the most predominant phase among the secondary phase particles greater than about 0.5 to 0.7 \( \mu \)m in AA2024 [19]. S-phase is known to be electrochemically active with respect to the Al matrix. In chloride solution, the open circuit potential (OCP) of Al\textsubscript{2}CuMg is between −920 to −930 mV\textsubscript{SCE}, which is 300 to 400 mV negative of the OCP observed for AA2024 [19]. However, Schmutz and Frankel [26] used Scanning Kelvin Probe Force Microscopy to show that S-phase particles at the surface of a freshly-polished AA2024 sample in air were noble with respect to the Al matrix. The high potential on Al-Cu-Mg particles was attributed to the presence of a surface oxide film with altered composition compared to the bulk of the particles, and it
decreased with immersion time in solution. After a certain induction time, S-phase showed active dissolution in chloride solution.

At the initial stage of corrosion of AA2024, S-phase particles are unstable to anodic dissolution and are attacked preferentially with respect to the Al matrix. Selective dissolution of Al and Mg results in the formation of Cu-rich remnants. Figure 2.4 shows the increased Cu signals and decreased Al and Mg signals of the S-phase particle as a result of selective dissolution of Al and Mg from the X-ray line scan before and after corrosion of AA2024.

The dealloying of S-phase produces porous Cu-rich remnant particles, which can support faster cathodic reactions. The net cathodic kinetics of S-phase increases as the extent of corrosion increases. By comparing the net cathodic behavior of S-phase after 60 seconds at OCP with the behavior after 60 minutes at $-0.6 \ V_{SCE}$, Ilevbare and Scully [20] found that the kinetics of ORR and HER on S-phase increased with the amount of anodic charge passed. They attributed the increased cathodic kinetics to increased surface area, change of surface pH from pit formation, and increased extent of Cu-enrichment. S-phase with Cu-enriched surface reverses its electrochemical relationship with the Al matrix and acts as a cathode for oxygen reduction reaction. The increased local pH due to oxygen reduction leads to the continued dealloying of Al and Mg from the S-phase and further Cu enrichment of the S-phase surface. The increased cathodic activity of S-phase can also induce pitting corrosion in the Al matrix at their periphery [19]. In addition, in order to reduce surface area, Cu-rich remnants are decomposed into Cu clusters, which then are
detached from the S-phase [21]. The detached metallic Cu cluster can be carried away from the sites of origin, reach their own higher corrosion potential, dissolve into solution, and redeposit on the alloy surface. The redistributed Cu behaves as a Cu cathode and causes the additional pitting corrosion of this alloy [21].

2.1.3 Cathodic Corrosion of Al and Al Alloys

The corrosion of aluminum at negative potentials, even during the passage of a net negative current, is known as cathodic corrosion [27]. Even in neutral solution the corrosion of Al and Al alloys can take place at cathodic potentials due to local pH increase near the electrode surface. During cathodic polarization, the cathodic reactions, such as oxygen reduction and water reduction, lead to hydroxide ion generation at the surface, which results in increased local pH. Cathodic corrosion proceeds by continual chemical dissolution of surface film and anodic reformation of the oxide film. Van De Van and Koelmans [28] showed from weight loss measurements that a significant amount of cathodic corrosion occurs at room temperature with a weak dependence on applied current density.

Several authors [4, 29, 30] discussed the mechanism of cathodic corrosion, which can be summarized as follows. Due to the increased local pH, the Al hydroxide film on the metal surface is dissolved chemically by OH⁻ attack at the oxide/solution interface:

\[ \text{Al(OH)}_3 + \text{OH}^- \rightarrow \text{Al(OH)}_4^- \]  \hspace{1cm} (2-1)

The chemical dissolution of the hydroxide film results in thinning of the surface film and accelerates the reformation of hydroxide film on the surface. The hydroxide ions
are incorporated into the oxide film and then migrate through the oxide film towards the aluminum. At the aluminum/oxide interface, the electrochemical aluminum oxidation and hydroxide film formation reaction occurs as

$$\text{Al} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 + 3e^- \quad (2-2)$$

The total anodic dissolution reaction of aluminum during cathodic corrosion can be obtained by combining electrochemical formation and chemical dissolution of hydroxide film:

$$\text{Al} + 4\text{OH}^- \rightarrow \text{Al(OH)}_4^- + 3\text{e}^- \quad (2-3)$$

The overall anodic reaction results in Al oxidation to $\text{Al}^{3+}$ and generation of 3 electrons per atom. The electrons produced by the anodic reaction are consumed immediately by cathodic reactions. In the case of the presence of dissolved oxygen in the solution, oxygen reduction reaction will be dominant as a partial cathodic reaction.

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

In the other cases, the water reduction reaction, which generates gaseous hydrogen as well as hydroxide ions, will be the main cathodic reaction in neutral and alkaline solutions.

$$\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^- \quad (2-5)$$

The overall cathodic corrosion reaction of pure aluminum in both cases can be obtained by combining Eq. (2-3) with Eq. (2-4) and Eq. (2-5), respectively.

$$4\text{Al} + 4\text{OH}^- + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_4^- \quad (2-6)$$
Cathodic corrosion results in aluminum dissolution as an aluminate ion. The cathodic corrosion rate of Al can be determined by the concentration of hydroxide ions and aluminate ions [28]. During cathodic corrosion of Al, the partial anodic current generated by Al oxidation is directly consumed by partial cathodic reactions. Therefore, the net cathodic current density measured by electrochemical techniques will be reduced by the anodic dissolution rate of Al.

In Cu-containing Al alloys, cathodic reactions take place mainly at local cathodic sites including Cu-rich intermetallic particles such as \( \theta \) phase and Cu-enriched S-phase, and redeposited metallic Cu on the alloy surface. The high pH zones are developed on and near the local cathodes due to their strong cathodic activities. The local solution of increased pH attacks the surrounding Al matrix and intermetallic particles, which results in pitting corrosion at the periphery of local cathodes and dealloying of IMCs.

2.2 ROLE OF CHROMATE IN CORROSION OF Al AND Al ALLOYS

2.2.1 Basics of Chromate in Corrosion

Chromate and chromate conversion coatings have been widely used as corrosion inhibitors to protect Al and Al alloys from localized corrosion like pitting corrosion. Chromate is an ionic species containing hexavalent chromium that can take various forms: chromic acid \( \text{H}_2\text{CrO}_4 \), dichromate \( \text{Cr}_2\text{O}_7^{2-} \), bichromate \( \text{HCrO}_4 \), and chromate \( \text{CrO}_4^{2-} \). The equilibrium state of \( \text{Cr}^{6+} \) depends on the pH of the solution and the
concentration of each species [31]. Figure 2.5 shows the distribution of Cr\(^{6+}\) species for 0.05 M Cr\(^{6+}\) \[^{[31]}\]. Mainly Cr\(_2\)O\(_7^{2-}\) and HCrO\(_4^-\) ions exist in acidic solution, and CrO\(_4^{2-}\) ions are dominant above pH 7. H\(_2\)CrO\(_4\) ions are dominant only below pH 1. At pH 3 solution, 94% of Cr\(^{6+}\) is in the form of Cr\(_2\)O\(_7^{2-}\) for 1 M Cr\(^{6+}\) concentration, while only 1% of Cr\(^{6+}\) is present as Cr\(_2\)O\(_7^{2-}\) for 10\(^{-4}\) M Cr\(^{6+}\) concentration \[^{[31]}\]. Chromate (CrO\(_4^{2-}\)) and dichromate (Cr\(_2\)O\(_7^{2-}\)) are known to be efficient inhibitors of the corrosion of Al and Al alloys, but they are extremely toxic and carcinogenic. Therefore, environment-friendly corrosion inhibitors have been developed to replace chromate, but their effectiveness for corrosion inhibition is not as good as chromate.

Cu-containing Al alloys are often protected by chromate conversion coatings covered by organic paint, which also might contain chromate for further protection. Common processes for chromate conversion coating use an acidic solution of pH 1.5 containing dichromate, ferricyonide, and fluoride ions. The oxidation of Al in the presence of fluoride ions generates electrons, which are used to reduce the hexavalent dichromate ion and form a protective hydrated Cr(OH)\(_3\) film. The overall reaction for chromate conversion coating formation can be written as

\[
\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr(OH)}_3 + \text{H}_2\text{O} \quad (2-8)
\]

Chromate conversion coating also contains a certain amount of soluble Cr\(^{6+}\) species as well as insoluble Cr\(^{3+}\) species due to interaction of Cr\(^{6+}\) ions with the Cr\(^{3+}\) \[^{[32]}\]. The Cr(OH)\(_3\) film serves as a barrier to the aggressive environment and the residual Cr\(^{6+}\) species in the film serves as a source for self-healing by migration to the damaged sites.
and repairing the breaks and defects in the film [32, 33]. Kendig et al. [33] found from X-ray absorption spectra that the ratio of Cr$^{6+}$ to total Cr in conversion coatings on AA2024 was approximately 20%.

### 2.2.2 Role of Chromate in Solution

The influence of chromate on localized corrosion of Al and Al alloys has been investigated for a long time. However, recent studies have shed new insight on the exact mechanism.

The corrosion inhibition mechanism of chromate has been attributed by some to anodic inhibition, the prevention of pitting corrosion by the adsorption and/or reduction of chromate on Al surface. Pride and Scully [34] found that a small amount of chromate addition into chloride containing solution can dramatically reduce the metastable pit nucleation of Al at a given potential and Cl$^-$ concentration. They suggested that the competitive adsorption of chromate with Cl$^-$ ions might be responsible for decrease in pit growth rates by chromate. In contrast, Sehgal et al. [35] showed that the inhibition of pit growth by chromate occurred only in solutions with a relatively large ratio of dichromate to chloride for anodic potentiostatic conditions.

Recently, chromate has been proposed as a cathodic inhibitor from several experimental studies. Akiyama et al. [36] investigated the growth kinetics for pits and crevices in Al 1100 and the effect of dichromate ions by using artificial crevice electrodes. The active dissolution of Al was not suppressed by the addition of dichromate ions into 0.1 M NaCl, while an increase in the relative amount of local cathodic reactions
on Al due to dichromate reduction was found. Their results indicated that the chromate inhibition mechanism might be something other than anodic inhibition of Al dissolution. In a pit growth study in Al 2024, Sehgal et al. [37] found that small amounts of dichromate can effectively inhibited pitting corrosion at open circuit. In addition, dichromate addition had a large effect on polarization curves of AA2024 only in the cathodic region. These findings indicate that chromate or the chromate reduction product acts as a cathodic inhibitor, which suppresses the activity of the intermetallic phases and reduces the currents available for the localized corrosion by inhibiting the oxygen reduction reaction.

Schmutz et al. [38] performed atomic force microscopy (AFM) scratching experiments on pure Al. At open circuit, scratching of pure Al in stagnant 0.5 M NaCl solution containing $10^{-4}$ M dichromate led to localized breakdown of the surface, resulting in the development of pits. In contrast, scratching of pure Al after 3 hours dipping in the same solution did not show the localized breakdown behavior due to the surface film formed by Cr$^{6+}$ reduction. These results indicate that chromate can act as either a corrosion inhibitor by forming protective films or an aggressive oxidizing agent by adding cathodic reaction, under different circumstances.

Leblanc and Frankel [39] exposed small areas of the AA2024 microstructure to solutions by opening up windows in a protective organic coating. They showed that the strongly protective chromate film formed on Cu-rich intermetallic particles in AA2024 can prevent both cathodic reactions and anodic dissolution. When a window containing
dichromate pretreated Al2CuMg particles and matrix was immersed in 0.5 M NaCl in the presence of another window on an Al-Cu-Fe-Mn particle, no attack was observed. In addition, when a window containing dichromate pretreated Al-Cu-Fe-Mn particles was exposed to chloride solution along with a window of only untreated matrix and S-phase particles, no attack was found again. Both results indicate that chromate film on AA2024 acts as a protective barrier for anodic dissolution of S-phase and Al matrix and cathodic inhibitor at local cathodes.

2.3 OXYGEN REDUCTION REACTION ON AL AND AL ALLOYS

2.3.1 Basics of Oxygen Reduction Reaction

Oxygen reduction is an important electrocatalytic reaction and a very complex process. Extensive investigations of this reaction have been made over several decades due to the importance of oxygen reduction in electrochemical energy conversion [40, 41]. In aqueous solutions, oxygen reduction can occur via two-electron reduction to H2O2, or four electron reduction to H2O, depending on the electrode material and surface modification. The oxygen reduction reaction (ORR) depends on the chemisorption of O2 or its reduction product, and by the chemisorbed anions [40]. Oxygen reduction also has strong dependence on the pH of the solution. In neutral and alkaline solution, direct four electron reduction can be written as Eq. (2-4) and two electron reduction involving HO2− as an intermediate is [40]:

\[ O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \]  \hspace{1cm} (2-9)
This reaction is followed by further two-electron reduction or by decomposition.

\[ \text{HO}_2^- + \text{H}_2\text{O} + 2e^- \rightarrow 3\text{OH}^- \]  
(2-10)

\[ 2\text{HO}_2^- \rightarrow \text{O}_2 + 2\text{OH}^- \]  
(2-11)

Peroxide is the final reduction product on some less active surfaces that support two-electron reduction [40]. Two and four electron reduction can occur in parallel on some surfaces. Since the outer-sphere reduction mechanism of oxygen is kinetically slow, catalysis via O\(_2\) adsorption to the electrode surface is usually involved [42]. Various catalysts including metal and organic components have been used to promote the disproportionation of H\(_2\)O\(_2\) or HO\(_2^-\) or to facilitate four electron reduction [41]. For Au electrodes, Adzic et al. [43] found that the OH\(^-\) adsorption on the surface promoted four electron reduction. In the absence of OH\(^-\) adsorption, for pHs below 6, oxygen reduction started as a two electron process, and then turned into a four electron process due to the increase in local pH during the process. For pHs above 6, oxygen reduction began as a four electron process in the presence of OH\(^-\) adsorption. In summary, even though there has been a consensus on the importance of oxygen reduction, the complexity of its mechanism and its slow kinetics make it difficult to determine the detailed reaction mechanism on various electrode materials. Therefore, oxygen reduction continues to be a challenging topic for electrochemical energy conversion and corrosion studies.

2.3.2 Oxygen Reduction Reaction on Al and Al Alloys

The oxygen reduction reaction is a dominant cathodic partial reaction in aqueous solution exposed to ambient air. Hydrogen reduction can also be dominant, but occurs
mainly in well-established actively corroding pits with very low local pH [44]. The kinetics of ORR are slow on pure Al due to the difficulty in electron transfer through the insulating surface oxide film. ORR rates on Al were found to decrease with increasing oxide thickness, which indicates that electron transfer at oxide/solution interface limits the mass-transport-limited current density on Al [20]. The estimated steady-state current density on a planar electrode was much larger than the measured limiting current density on Al [45]. In addition, the exchange current density for hydrogen evolution reaction (HER) is so low on Al oxide that mass-transport-limited ORR is the dominant cathodic reaction on pure Al at potentials as low as $-1.5 \ V_{\text{SCE}}$ [20].

In the corrosion of AA2024, Cu-rich intermetallic particles serve as preferential sites for oxygen reduction due to their higher open circuit potential compared the Al matrix. They can support enhanced ORR rates because the conductivity of the mixed oxide film covering them is higher than that of the passive film on pure Al [18]. Furthermore, dealloying of S-phase, occupying 60% of the particle population, results in the formation of highly catalytic nano-structure cathode for oxygen reduction [17]. Dissolution and redistribution of metallic Cu from the Cu-rich intermetallics also forms Cu cathodes for oxygen reduction on this alloy [21]. In addition, dissolution of Al matrix can also develop a surface enriched in Cu. These catalytic metallic Cu or Cu-rich surfaces can support higher oxygen reduction reaction rate due to high conductivity associated with the large Cu content and increased surface area. The higher ORR rate leads to local pH increase, which results in further dissolution and dealloying of this alloy. Therefore,
the increased cathodic activity of these catalytic sites for oxygen reduction is detrimental to the corrosion of this alloy.

2.3.3 Effect of Chromate on Oxygen Reduction Reaction

Chromate has been known to inhibit the corrosion of AA2024 for a long time, but studies of cathodic inhibition by chromate have been made only recently [20, 42, 46-48]. Chromate has been proposed as a cathodic inhibitor because dichromate addition had a large effect on polarization curves of AA2024 only in the cathodic region [37]. Scully et al. [20, 46] investigated the ORR kinetics on Cu-containing IMCs in AA2024 in the presence of chromate conversion coating or in chromate-containing solutions. They observed the reduced ORR kinetics both for chromate coated electrode and by chromate in solution, but their explanations about the mechanism of oxygen reduction inhibition by chromate conversion coating and chromate were unclear. Clark et al. [48] also observed the strong inhibition of the ORR on Cu and AA2024 electrodes by dilute chromate solution, and persistence of inhibition effect after removal of Cr$^{6+}$ from the solution. In their later study with Cu, Pt, and glassy carbon electrodes, the mechanism of inhibition was attributed to the reduction of Cr$^{6+}$ and irreversible adsorption of Cr$^{3+}$ to the surface of the electrode to block sites of O$_2$ adsorption [42]. The protective Cr$^{3+}$ film was found to form in about mono-layer quantities and also inhibited further chromate reduction. The absorbed Cr$^{3+}$ film was non-conductive so that it also decreased the electron transfer rate. However, since a Cu electrode was used as a model for Cu-containing IMCs and
redistributed Cu, the exact effect and mechanism of inhibition by chromate on the real IMCs could be somewhat different.

2.4 ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE (EQCM)

2.4.1 Basics of Quartz Crystal Microbalance

The quartz crystal microbalance (QCM) is a piezoelectric device capable of in-situ measurement of mass changes on a metal electrode with extremely high sensitivity. Most applications of QCM are in vacuum and gaseous environments as an ultra-sensitive mass measuring sensor.

The inverse piezoelectric effect is a key factor to the operation of QCM devices. When an alternating potential is applied across a quartz crystal using electrodes deposited on both sides, an oscillatory motion of the quartz crystal results due to the piezoelectric effect. The vibration motion of the quartz crystal causes a transverse acoustic wave that propagates back and forth across the thickness of the crystal as shown in Figure 2.6 [49]. If the acoustic wavelength ($\lambda$) is equal to twice the combined thickness of the crystal and electrodes, a standing-wave condition can be established in the quartz resonator. The resonant frequency $f_0$ of the acoustic wave in the fundamental mode is given by [49]:

$$f_0 = \frac{\nu_u}{2t_q} = \frac{N}{t_q} \quad (2-12)$$
where \( v_r \) is the transverse velocity of sound in quartz \((3.34 \times 10^4 \text{ m s}^{-1})\), \( t_q \) is the resonator thickness, and \( N \) is the frequency constant. The resonator thickness is related to its mass by

\[
t_q = \frac{M}{\rho_q A} \tag{2-13}
\]

where \( \rho_q \) is the density of quartz \((2.648 \text{ g cm}^{-3})\), \( A \) is the piezoelectric active area, and \( M \) is the mass of the resonator. Combining Eq. 2-12 and 2-13 yields

\[
f_0 = \frac{\rho_q N}{m} \tag{2-14}
\]

where \( m = M/A \) \((\text{g cm}^{-2})\). A thin rigid solid layer attached on the electrode surface causes changes in the resonant frequency by \( \Delta f \) in the same way as a quartz layer of the same mass. If a foreign mass, \( \Delta M \), is attached uniformly to one of the electrode area \( A \), and \( \Delta m = \Delta M/A \), then,

\[
f_0 + \Delta f = \frac{\rho_q N}{m + \Delta m} \tag{2-15}
\]

The frequency change accompanying the attachment of the foreign mass is

\[
\Delta f = -\left(\frac{f_0^2}{\rho_q N}\right) \left(\frac{\Delta m}{1 + \Delta m/m}\right) \tag{2-16}
\]

With appropriate substitution, Eq. 2-16 yields (when \( m \ll \Delta m \))

\[
\Delta f = -\frac{2f_0^2 \Delta m}{A \sqrt{\mu_q \rho_q}} = -C_f \Delta m \tag{2-17}
\]
where $\mu_q$ is the shear modulus of quartz ($2.947 \times 10^{11}$ dyn cm$^{-2}$) and $C_r$ is the sensitivity factor. This equation was first obtained by Sauerbrey [50] in 1959. According to the Sauerbrey equation, a decrease in the resonant frequency is linearly proportional to an increase in mass on electrode surface. This equation applies only when the added mass, $\Delta m$, is rigidly attached to the electrode surface, and the thickness of the deposited layer is less than 2% of the thickness of quartz crystal due to the assumptions made to derive this equation.

The resonant frequency of the quartz crystal also depends on the orientation of the crystal with respect to its large surface. In general, AT-cut quartz crystals are used for QCM because the temperature dependence is negligible in a wide range of temperature for any practical purpose. AT-cut quartz crystals are fabricated by slicing through a quartz rod at an angle of approximately $35^\circ$ 15' with respect to the crystallographic x axis [49]. For an AT-cut quartz with $f_0 = 10$ MHz, the sensitivity factor $C_r$ is $2.26 \times 10^6$ Hz cm$^2$ g$^{-1}$.

2.4.2 Electrochemical Quartz Crystal Microbalance

Recently, QCM has been combined with the electrochemical cell to simultaneously measure current, potential, and mass changes occurring at the electrode surface in the solution. The first application of QCM to the study of electrochemistry was made by Nomura and co-workers [51, 52] for the electrodeposition of copper and silver in the early 1980's. Figure 2.6 shows a schematic representation of the electrochemical quartz crystal microbalance (EQCM) system. In the electrochemical application, one side
of the quartz crystal is exposed to the solution as a working electrode, while the other is exposed to air.

When the quartz resonator is placed in an aqueous solution, the density and viscosity of the solution alter the characteristics of the resonator. The density of the solution effectively adds to the mass of the resonator, while viscosity provides additional energy damping. Several researchers [53-55] investigated the resonant frequency dependence of quartz crystals on liquid properties and found a square root dependence of the resonant frequency on the density and viscosity of liquid. According to Bruckenstein and Shay [55], the oscillating quartz crystal generates an oscillating liquid boundary layer at the QCM-liquid interface. From dimensional analysis and analogy with the ac polarographic diffusion layer thickness, the thickness of this layer, $L$, is given by

$$L = \left( \frac{v}{f_L} \right)^{1/2}$$  \hspace{1cm} (2-18)

where $v$ (cm$^2$s$^{-1}$) is the kinematic viscosity of the liquid and $f_L$ (Hz) is the resonant frequency of the quartz crystal in the liquid. The effective additional liquid mass per unit area, $\Delta m_L$, is

$$\Delta m_L = \rho_L \left( \frac{v}{f_L} \right)^{1/2} = \left( \frac{\eta_L \rho_L}{f_L} \right)^{1/2}$$  \hspace{1cm} (2-19)

where $\eta$ is the conventional viscosity of the liquid. Provided $f_L = f_0$, substitution of Eq. 2-19 into Eq. 2-17 yields

$$\Delta f = -C_f \left( \frac{\eta_L \rho_L}{f_0} \right)^{1/2}$$  \hspace{1cm} (2-20)
Bruckenstein and Shay [55] experimentally proved that the frequency varies as the square root of the solution viscosity, which is predicted by Eq. 2-20. The effect of contact of the quartz crystal with a liquid corresponds to attaching a liquid layer whose thickness is a function of the solution viscosity, density and the frequency of crystal oscillation.

There are other factors, such as surface roughness, liquid conductivity, temperature, and total pressure, which can affect the resonant frequency of quartz crystal [56-58]. For instance, even though AT-cut quartz crystals have negligible temperature dependence, a strong temperature dependency of the resonant frequency was predicted as a result of the temperature coefficient of viscosity of liquid [49]. Usually, these factors can be maintained constant during the measurement or their effects on the resonant frequency are so small that they can be neglected.

2.4.3 Applications of EQCM in Corrosion Studies

EQCM has advantages over conventional electrochemical methods due to its high sensitivity to mass changes at the electrode surface and its in situ capability. The possibility of recording simultaneously the mass changes of the metal electrode and the corresponding potential and current behavior have led to a number of applications of the EQCM technique. Since the capabilities of the EQCM provide a unique approach for examining electrode dissolution that are important in processes such as corrosion, the EQCM has recently been applied into the study of corrosion and corrosion inhibition.
Significant information about corrosion mechanisms has been obtained from the EQCM analysis. In late 1980’s, the EQCM was used to investigate the anodic dissolution of nickel and nickel-phosphorous film. The potential dependence of dissolution of the different NiH\textsubscript{x} phases was found from the frequency-potential plot and the presence of the two different Ni-P compositions was proved from the frequency-charge analysis [49]. Schumacher et al. [59] studied the mechanism of electrochemical dissolution of copper in oxygenated sulfuric acid. They revealed the copper dissolution rate is linearly proportional to the concentration of O\textsubscript{2} and H\textsuperscript{+} in the solution and concluded a heterogeneous surface reaction is operative with the in-situ EQCM measurement. Schmutz and Landolt [60, 61] applied the EQCM technique to the study of the transient passivation response of iron-chromium alloys. Mass change associated with passive film dissolution and growth were monitored along with current during potential step experiments in acid and alkaline solutions. A formalism was successfully developed to explain the mass and current transients observed with binary alloys in the passive state.

The EQCM was also used in corrosion inhibitor studies. Pickering et al. [62] investigated copper corrosion in acid solution in the absence or presence of various inhibitors. They could show the effect of various inhibitors on the copper corrosion due to the high sensitivity of the EQCM technique.

In several studies, aluminum electrodes were used for the EQCM study. Lin et al. [63] applied the EQCM technique to investigate the changes in electrical conduction behavior of surface films on Al. In their study, conductive properties of surface film could
be inferred by measuring the variation of current flow with film mass changes during its
growth. Yang et al. [64] investigated the corrosion of aluminum in the electrolytes for Li
batteries. The protective film reformation behavior after scratching or abrading were
compared in the various electrolytes and their mechanisms were suggested using the
EQCM analysis.

2.5 GOALS OF THIS THESIS

The corrosion behavior of high strength Al alloy 2024 depends strongly on the
cathodic activity of Cu-rich intermetallic particles such as S phase (Al$_2$CuMg) and θ
phase (Al$_2$Cu). These IMCs can act as anodes or cathodes, or fluctuate between the two
states as their composition changes. Oxygen reduction at the cathodic sites leads to the
development of high pH zones on IMCs and the surrounding Al matrix. The increased
local pH promotes dissolution the Al matrix, and may also result in dealloying of IMCs
themselves. This makes it very difficult to determine the true cathodic kinetics of IMCs
and Al matrix using only electrochemical techniques.

The EQCM provides sub-monolayer resolution of mass change occurring at
electrode surface. This non-electrochemical method provides a separate measure of mass
loss rate, which can be converted into an anodic dissolution rate. On the other hand, the
EQCM requires samples in the form of thin films, which can have similar compositions
as bulk phases, but might have different structures.
The purpose of this work is to investigate the electrochemical activities of phases in AA2024 at cathodic potentials and the effect of chromates on their corrosion behavior. This is done using the EQCM technique, which allows to measure mass changes on the electrode surface as well as current and potential. Thin film analogs of pure Al, Al matrix, and ϑ phase, prepared by the flash evaporation technique, are studied. True anodic and cathodic reaction rates are simultaneously obtained from the measured mass loss and net current density. The true anodic and cathodic reaction rates at cathodic potentials in limiting oxygen reduction region are determined as a function of alloy composition, applied potential, and dichromate concentration in sodium chloride solution. As a summary, cathodic behaviors of each phase in AA2024 and effects of chromate on them are discussed.
LIST OF REFERENCES


Figure 2.1. Potential versus pH diagram for Al/H₂O system at 25 °C [2].
Figure 2.2. Scanning Electron Microscope image of a heterogeneous microstructure of AA2024-T3. Particles labeled 1-4 are Al-Cu-(Fe-Mn) phases, and particles labeled A-C are Al-Cu-Mg phases [26].

Figure 2.3. Mixture of Al₂O₃ needles and Cu oxide developed after 1 hour polarization of Al₂Cu in 0.1 N NaOH solution at 480 mVₜₜ [25].
Figure 2.4. X-ray line profiles across an Al$_2$CuMg particle (a) before (b) after dealloying of Al and Mg. The Mg signal for (b) has been multiplied by a factor of 10 [19].
Figure 2.5. The distribution of Cr(VI) species in aqueous solution with 0.05M Cr(VI) as function of pH [31].

(a) \( \lambda / 2 = t_q \)

(b) \( \lambda / 2 = t_q + \Delta t \)

Figure 2.6. Schematic representation of the transverse shear wave in a quartz crystal with thin film electrodes (a) without and (b) with a thin layer of a foreign material [49].
Figure 2.7. Schematic representation of typical EQCM system [49].
CHAPTER 3

EXPERIMENTAL

3.1 PREPARATION OF MATERIALS

3.1.1 Thin Film Analogs

Thin films of pure Al and thin film analogs of intermetallic compounds (Al$_2$Cu) and Al matrix (Al-4Cu) were deposited onto quartz crystal substrates by flash evaporation using the unit in the Fontana Corrosion Center at The Ohio State University. In the flash evaporation technique, metallic powder is slowly fed onto a heated boat, which is hot enough to evaporate all the powder immediately [1]. Since there is no accumulation of powder in the boat, the vapor flux has the same stoichiometry as the powder fed onto the boat. Figure 3.1 is a schematic drawing of the flash evaporation unit.

Quartz crystals (International Crystal Manufacturing Co, Inc) were used as substrates. These quartz crystals were 0.55" in diameter and had a resonant frequency of 10 MHz. AT-cut crystals were used due to their frequency stability over a wide range of
temperature. Before the flash evaporation, the quartz crystals were rinsed with distilled water and dried with Ar gas to clean the surfaces. A stainless steel mask was used to mount a quartz crystal onto the substrate stand of the flash evaporation unit and make a metal electrode of a keyhole shape as shown in Figure 3.2. The circular parts of the keyhole shape on the two sides of electrodes were overlapped at the center of the quartz crystal and the current leads on both sides of the electrode were positioned in opposite directions. Samples deposited on Si wafers were used for potentiodynamic polarization experiments.

For the deposition of pure Al, 99.999% pure Al pellets were directly placed into the tungsten boat without using the feeder. For the deposition of θ phase and Al matrix, alloy ingots were prepared from 99.99% pure Al and Cu pellets. These were weighed separately and combined in an alumina crucible to obtain the desired composition of the intermetallic compounds and Al matrix. The crucible was loaded into a quartz tube, which was then evacuated, backfilled with 0.25 atm of Ar and sealed. The encapsulated quartz tube was heated to 1150 °C, held for 20 min, and furnace cooled to room temperature. The obtained alloy was multiphase, but overall had the desired composition. It was crushed into powder form, which was used as the starting material for flash evaporation. Crushed alloy powder was preferred over mixed elemental powders because the crushed powder resulted in films of lower oxygen content in the thin film analogs. A tungsten boat and a feeder were used to evaporate those powders. The average deposition rate was about 1 nm/s and the average thickness of the analog films was 450-500 nm for
quartz crystal substrates and 750 nm for Si wafer substrates. Since the Sauerbrey equation is applicable when the thickness of the deposited layer is less than 2% of the thickness of quartz crystal, the thickness of the metal electrodes was controlled to be less than 0.5 µm on each side of the quartz crystal. The base pressure of the chamber prior to evaporation was $6 \times 10^{-8}$ Torr and the operating pressure was less than $2-3 \times 10^{-7}$ Torr.

3.1.2 Electrolytes

Solutions were prepared using certified A.C.S. grade chemicals, most in the form of solid crystals. They were weighed using a Sartorius BP210D Balance with an accuracy of 20 µg. The deionized water for preparing the solutions were produced by an ultra-pure water purification system (Milli-RO Plus/Milli-Q Plus, Millipore), with an output water conductivity of $18.2 \, \text{M} \Omega^{-1}\text{cm}^{-1}$. Solutions were typically prepared in 1 L or 2 L volumes and then used within 24 h to avoid contamination from the ambient air. The pH values of all solutions were also recorded using a Beckman Φ32 pH Meter with an accuracy of 0.01 pH units.

Solutions of 0.1 M NaCl (pH=6.2) were used as a base solution. Different concentrations of Na$_2$Cr$_2$O$_7$ were added into the base solution and the pH of dichromate solutions were adjusted to 6.2 by the addition of $10^{-2}$ M NaOH. Some experiments were performed in borate buffer solutions and sodium sulfate (Na$_2$SO$_4$) solutions. The pH of borate buffer solutions was controlled by using the different ratios of boric acid (H$_3$BO$_3$) and sodium borate (Na$_2$B$_4$O$_7$). For the calibration of EQCM system, 0.05 M CuSO$_4$ + 0.05 M H$_2$SO$_4$ solution was used.
3.2 ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE SETUP

3.2.1 EQCM System

A commercial electrochemical quartz crystal microbalance system was used for the electrochemical and mass change measurements. The EQCM system consists of a potentiostat (PS-605, Elchema), frequency scanner (EQCN 906, Elchema) and electrochemical microbalance (EQCN-900, Elchema). Quartz crystals with metal electrode films were fixed in a teflon holder. The metal electrode consisted of the circular part and current lead part. The circular part had an area of 0.196 cm\(^2\), which was used for the active area of the quartz crystal microbalance. The total area of metal electrode including the circular part and current lead part, was 0.256 cm\(^2\), which was used for the current density calculation. The electrical contact of the metal electrodes to the crystal holder was made with colloidal silver paint and was isolated from the solution by silicone resin.

The crystal holder mounted with the quartz crystal was placed vertically or horizontally into electrochemical cell made of plexiglass. Teflon tape was used to prevent the cell from leaking. A Pt electrode mesh was used as a counter electrode. A saturated calomel electrode (SCE) or a mercurus sulfate electrode (MSE) was used as a reference electrode to complete the three-electrode cell.

All EQCM measurements were made in a Faraday cage to minimize electromagnetic interference from the surroundings. The frequency difference between
the working quartz crystal in the solution and a reference quartz crystal with gold electrodes in the Faraday cage, was measured with EQCN 900 system and converted to a mass change by the Sauerbrey equation [2]. The VOLTASCAN program provided by Elchema was used for the experimental data acquisition and the IGOR software was used for the data processing and evaluation.

The solution volume in the cell was controlled at 150 ml. Unless otherwise specified, the solutions were open to ambient air and stagnant. Deaerated solution was prepared by purging the solution with prepurified argon before experiments for 24 h and during experiments. All experiments were conducted at room temperature.

3.2.2 Calibration of EQCM System

The calibration of the EQCM system was performed by electrochemical deposition of Cu on an Au electrode from 0.05 M CuSO₄ + 0.05 M H₂SO₄ solution. The crystal holder mounted with the quartz crystal was placed vertically into the cell containing 0.05 M Cu²⁺ ions. The potential was held at 0.0 V_MSE for 30 seconds to clean the surface and then decreased to -1.0 V_MSE for 60 seconds for Cu electrodeposition.

Figure 3.3 shows the measured current density and mass change on the gold electrode in the solution. At the potential of 0.0 V_MSE (initial 30 s), the current density and the mass change remained constant. After the potential was decreased to -1.0 V_MSE, mass increase was observed due to the electrochemical deposition of Cu on the Au surface. As the current density became constant, the mass change showed a linear behavior, indicating that the amount of charge passing the metal/solution interface was
directly related with the mass increase. From Faraday's law, the theoretical value of the ratio of mass change to current density for Cu deposition from cupric ion (n=2) is \( \frac{dm}{dt}/i = 329 \text{ ng mA}^{-1} \text{ s}^{-1} \). Experimentally, a value of 316 ng mA\(^{-1}\)s\(^{-1}\) was observed, which is within 5% of the theoretical value. The linear relationship between the amount of charge and the mass change indicates that the EQCM system was properly calibrated and could be used for the direct measurement of mass changes on the electrode surface.

3.3 ELECTROCHEMICAL TESTS

3.3.1 Open Circuit Measurements

Potential and mass change for pure Al were measured at open circuit in 0.01 M Na\(_2\)B\(_4\)O\(_7\) + 0.5 M Na\(_2\)SO\(_4\) (pH=9.2) with different concentrations of dichromate. The crystal holder mounted with the quartz crystal was placed vertically into the cell and the measurement started right after immersion of the sample into solution. The sample was left at open circuit for 1 hour, and mass change and potential were measured by the EQCN 900 system.

3.3.2 Potentiodynamic Polarization Measurements

Potentiodynamic polarization experiments were performed in 0.1 M NaCl solution with 0, 10\(^{-4}\) or 10\(^{-2}\) M dichromate concentration. For the thin film analogs on Si wafer substrate and bulk AA2024-T3 samples, the samples were positioned horizontally and immersed in the stagnant solution exposed to ambient air for 30 min at open circuit until the corrosion potential stabilized, and then the potential was scanned at 1 mV/sec in
the negative direction from 50 mV above the open circuit potential. The potential and current values were recorded by the EQCN 900 system. The range of potential scan was limited by the amount of material in the thin film analogs. The minimum possible potential and maximum current density for the experimental setup were \(-1.8 \text{ V}_{\text{SCE}}\) and \(-2 \text{ mA/cm}^2\), respectively.

For the potentiodynamic polarization of Au electrodes on quartz crystal substrates, the samples were held at 400 mV\text{SCE} in 0.1 M NaCl for 3 minutes, and then scanned negatively at the scan rate of 5 mV/sec.

3.3.3 Potentiostatic Polarization Measurements

Potentiostatic polarization experiments were performed with the thin film analogs and Au electrodes on quartz crystal substrates. For the thin film electrodes on the quartz crystals, the crystal holder was placed horizontally into a electrochemical cell to simulate the high pH zones developed during corrosion of Al alloys. The samples were held in the stagnant 0.1 M NaCl solution with 0, \(10^{-4}\) or \(10^{-2}\) M dichromate concentration for less than 3-5 min. to minimize the material loss at open circuit, and then the potential was decreased to a cathodic potential in the oxygen reduction reaction region, which was chosen from potentodynamic polarization experiments. The potential was held at the cathodic potential for about 30 min and the mass changes as well as potential and current were measured as a function of time by the EQCN 900 system. The measuring time was also limited by the amount of material in the thin films.
3.3.4 Cycle Polarization Measurements

Cyclic polarization experiments were performed with Au electrodes on quartz crystals. The samples were positioned horizontally and were immersed in the solution at open circuit for 3 min, and then the potential was increased to 500 mV_{SCE} for 3 min until the background current was minimized. The potential was scanned from 500 mV_{SCE} to -500 mV_{SCE} at a rate of 10 mV/sec. After making four cycles between 500 mV_{SCE} and -500 mV_{SCE}, the potential scan ended at -500 mV_{SCE}. The mass changes as well as potential and current were measured by the EQCN 900 system. For some experiments, 1 mL of 3 mM dichromate was also injected into 150 mL of 0.1M NaCl solution after the first scan to result in a dichromate concentration of $2 \times 10^{-5}$ M.

3.4 CHARACTERIZATION TECHNIQUES

3.4.1 Characterization of Liquid Viscosity and Density

The viscosity and density of sodium chloride solutions with different concentrations of sodium hydroxide were measured to see their effects on the measured resonant frequency of the quartz crystal. A viscometer of the capillary type, designed by Cannon and Fenske, was used for the viscosity measurement of each solution. The basic operation of this viscometer is to load the bulbs above the capillary with the test solution and then allow it to flow through the capillary while accurately measuring the period of the passage of the meniscus between the two etched marks [3]. The relative viscosity of each solution to distilled water was calculated from the ratio of the passing time of each
solution to the passing time of distilled water. The viscosity of distilled water was taken as 0.8913 cP \([3]\) and then the viscosity of each solution was calculated from the relative viscosity. The density of the solutions were determined from the mass of 100 mL of each solution.

Figure 3.4 shows the measured viscosity and density of 0.1 M NaCl solutions with different pH. The density of 0.1 M NaCl solution increased slightly with increasing pH. The viscosity slightly increased with increasing pH up to pH 12, and then showed a dramatic increase with pH above 12. The effects of the measured viscosity and density changes on the resonant frequency and apparent mass were estimated by the Bruckenstein and Shay equations \([4]\) (Eqns. 2-19 and 2-20) and are shown in Figure 3.5. The resonant frequency is expected to decrease and the apparent mass expected to increase as pH is increased. The resonant frequency and apparent mass are expected to change dramatically above pH 12.

3.4.2 Scanning Electron Microscopy / Energy Dispersive Spectroscopy

Scanning electron microscopy (SEM) and combined energy dispersive spectroscopy (EDS) (XL-30 Field Emission Gun, Philips), were used to analyze the surface and chemical composition of samples. The chemical composition of each thin film analog was measured by EDS after the flash evaporation. The oxygen content of thin film analogs was also checked in order to make sure it was low. SEM was used mainly for imaging of surfaces after electrochemical experiments.
3.4.3 Atomic Force Microscopy

Digital Instruments MMAFM-2 Atomic Force Microscope (AFM) was used to analyze the uniformity of surface potential as well as the topology of the thin film analogs. An area of 1 μm$^2$ was selected for scanning of the probe and Ni was used as a reference for Volta potential measurements [5]. The root mean square values of surface roughness and Volta potential distribution were obtained for the whole area of 1 μm$^2$. 
LIST OF REFERENCES


Figure 3.1. Schematic representation of the flash evaporation unit.
Figure 3.2. Schematic representation of quartz crystal with working electrode (a) front view (b) side view.

Figure 3.3. Calibration curve of the EQCM system from the electrodeposition of Cu on Au electrode in 0.05 M CuSO₄ + 0.05 M H₂SO₄ solution.
Figure 3.4. Measured viscosity and density versus pH of 0.1 M NaCl solutions with different concentrations of NaOH.

Figure 3.5. Estimated changes in resonant frequency and apparent mass with pH of 0.1 M NaCl solutions with different concentrations of NaOH by the using Bruckenstein and Shay equation [4].
CHAPTER 4

RESULTS

4.1 CHARACTERIZATION OF ANALOG THIN FILMS

The compositions of thin film analogs can be easily and uniformly controlled by using the flash evaporation technique. Energy dispersive spectroscopy (EDS) characterization was conducted on analog thin films of pure Al, Al matrix, and $\theta$ phase, which were deposited on quartz crystal substrates. Table 4.1 shows the composition of each thin film analog by weight percent (wt%) of each element. EDS analysis showed the composition of thin films was well controlled and in good agreement with the compositions of the same phases in bulk Al alloy. The content of oxygen was controlled to less than 1% by using crushed powder from a cast ingot and maintaining a low chamber pressure during the evaporation process. It has been reported that Al thin films deposited with a base pressure of $2\times10^{-7}$ Torr or better behave very similarly to the bulk material [1]. In addition, a thin film analog of Mg(Zn,Cu,Al)$_2$ was successfully used for
investigation of electrochemical behaviors of this intermetallic compound [2]. Assuming that the influence of any structural difference is small and chemical composition is dominant in electrochemical behavior, it is reasonable to expect that the behaviors of these analog films would be representative of those of the intermetallic phase and Al matrix of the same composition found in Cu-bearing Al alloys.

The surface roughness and the surface uniformity of electrochemical activity were analyzed by atomic force microscopy (AFM). Figure 4.1 shows AFM images of the thin film analog of Al$_2$Cu phase. The topography of the film and the Volta potential map of the surface are shown on a 1 µm scale. The analog thin film of Al$_2$Cu was relatively flat and had a surface roughness of less than 2 nm. It can clearly be seen that there is little potential contrast in this region. Both indicate that the film is homogenous.

4.2 ALUMINUM DISSOLUTION AT OPEN CIRCUIT

4.2.1 Open Circuit Behavior of Pure Al in Alkaline Solution

Electrochemical quartz crystal microbalance (EQCM) measurements at open circuit were performed with pure Al under alkaline conditions where Al oxide/hydroxide is not the most stable form in the Pourbaix diagram anymore. Open circuit potential and mass change behaviors, obtained from pure Al thin films in 0.01 M Na$_2$B$_4$O$_7$ + 0.5 M Na$_2$SO$_4$ (pH=9.18), are shown in Figure 4.2. The open circuit potential stabilized after about 1 hour at -1.69 V$_{MSE}$. The mass increased at the beginning, perhaps due to hydration of the oxide film, and then decreased with time due to oxide film dissolution.
In alkaline solutions, the aluminum oxide/hydroxide film is dissolved chemically by OH\(^-\) attack at the oxide/solution interface, which is followed by reformation of Al oxide at the metal/oxide interface by an Al oxidation process. A steady-state with a constant mass loss rate developed. The mass loss rate at open circuit can be calculated from the slope of mass change vs. time, and then can be converted into a current density associated with Al oxidation and oxide film dissolution, \(i_{\text{diss}}\), using Faraday's Law:

\[
\frac{\text{d}m}{\text{d}t} = \frac{nF}{M} \left( \frac{\text{d}m}{\text{d}t} \right)
\]  

(4-1)

where \(n\) for Al is 3 equiv/mol, \(F\) (96,487 C/equiv) is Faraday’s constant, \(M\) is the atomic mass for Al (27 g/mol), and \(\frac{\text{d}m}{\text{d}t}\) is a mass loss rate in g/sec. The mass loss rate was 0.323 ng cm\(^{-2}\)s\(^{-1}\) after 1000 sec and then increased to 0.681 ng cm\(^{-2}\)s\(^{-1}\), which corresponds to a thickness loss of 9.05 nm/hour, as the potential became stable at 1 hour.

At open circuit, the anodic reaction is balanced by the cathodic reaction, resulting in zero net current. The dissolution rate calculated from mass loss rate was 7.3 µA/cm\(^2\) at 1 hour, indicating that cathodic reaction rate on pure Al also was 7.3 µA/cm\(^2\) at 1 hour in this borate and sulfate solution.

### 4.3.2 Effect of Chromate at Open Circuit

Figure 4.3 shows open circuit potential and mass change in 0.01 M Na\(_2\)B\(_4\)O\(_7\) + 0.5 M Na\(_2\)SO\(_4\) + 10\(^{-3}\) M Na\(_2\)CrO\(_4\) (pH =9.15). The stabilized open circuit potential increased to -1.49 V\(_{\text{MSE}}\) in the presence of dichromate in the solution and the dissolution rate at open circuit decreased to 0.145 ng cm\(^{-2}\)s\(^{-1}\), which corresponds to the anodic reaction rate...
of 1.6 $\mu$A/cm$^2$. With a higher concentration of dichromate ($10^{-2}$ M Na$_2$CrO$_4$, pH =9.12), the open circuit potential was further increased to $-1.41$ V$_{\text{MSE}}$ and the dissolution rate at open circuit was further decreased to 0.085 ng cm$^{-2}$s$^{-1}$ or 0.94 $\mu$A/cm$^2$ as shown in Figure 4.4. With increasing dichromate concentration, the values of open circuit potential were observed to increase and the dissolution rates at open circuit decreased. The decrease in dissolution rates at open circuit indicates the loss of electrochemical activity of pure Al due to the formation of Cr(III) oxide, resulting in the decrease in cathodic reaction rates.

4.3 CATHODIC POLARIZATION OF ANALOG THIN FILMS

4.3.1 Potentiodynamic Polarization of Analog Thin Films

Potentiodynamic polarization experiments were performed with pure Al, Al-4Cu, 0 phase and AA2024-T3 in 0.1 M NaCl solution. Cathodic polarization curves are shown in Figure 4.5. The potential was scanned negatively from 50 mV above the open circuit potential (OCP) at a scan rate of 1 mV/sec and the solution was exposed to air during the measurements. The open circuit potential was higher for Al$_2$Cu phase, and lower for pure Al and Al-4Cu compared to AA2024-T3, which confirmed the OCP values of these phases from the literature [3]. The OCP in 0.1 M NaCl was -1.2 V$_{\text{SCE}}$ for pure Al and OCP's were significantly increased as the content of Cu in the analogs increased from zero to 53.5 wt%.

The net current density in the mass transport limited oxygen reduction reaction (ORR) region was very low, less than 5 $\mu$A/cm$^2$, for pure Al even though the potential
was as low as -1.5 \text{ V}_{\text{SCE}}. \text{ Hydrogen evolution reaction started to occur below -1.6 V}_{\text{SCE}}. On the other hand, the net current density was higher for Al\textsubscript{2}Cu phase than for pure Al and Al-4Cu and the mass transport limited ORR region for Al\textsubscript{2}Cu phase was found at higher potentials between -550 mV\textsubscript{SCE} and -950 mV\textsubscript{SCE}. The net current densities increased in the mass transport limited ORR region as the content of Cu in the analogs increased. Bulk AA2024-T3 showed a rapid increase in net current density below the OCP and a broader mass transport limited ORR region.

The exchange current densities for hydrogen evolution increased with Cu content so that the onset of hydrogen evolution occurred at higher potentials. The overpotential for cathodic reaction was about 0.31 V less on Al-4Cu than on pure Al in 0.1 NaCl. Even though only 4.0 wt\%, corresponding to 1.74 atomic percent (at\%), of copper was added into pure Al, the OCP's and ORR rates for Al-4Cu were significantly higher than those for pure Al.

4.3.2 Potentiostatic Polarization of Analog Thin Films

Potentiostatic polarization experiments were conducted with the EQCM, simultaneously measuring mass changes of the electrode as well as current and potential. Figure 4.6 shows net current and mass as a function of time for pure Al in 0.1 M NaCl at different potentials in the mass transport limited ORR region. Even though the net or measured current was cathodic or negative, the mass decreased rapidly at the beginning of cathodic polarization and then reached a slower constant rate of decrease. As described in Chapter 2, cathodic corrosion of Al occurs due to a local pH increase near the electrode.
surface resulting from oxygen reduction and/or hydrogen evolution. As occurred at open
circuit in the alkaline solution, the aluminum oxide/hydroxide film was dissolved
chemically by OH⁻ attack at the oxide/solution interface, which was followed by
reformation of Al oxide at the metal/oxide interface by an Al oxidation process. The net
current density was also large at the beginning of polarization, and then became smaller
and constant at longer times. A steady state with constant mass loss rate and net current
density was developed in which the rate of chemical dissolution of oxide film was
balanced by the rate of oxide film formation. While the mass loss of pure Al showed
weak dependence on applied potential, the net current density showed strong dependence
on applied potential.

The net current and mass curves of Al-4Cu during potentiostatic polarization in
the mass transport limited ORR region in 0.1 M NaCl are shown in Figure 4.7. As for the
case of pure Al, the current decreased, reaching steady state values after several minutes.
The current density exhibited a weaker potential dependence than for pure Al. The net
current density was higher for Al-4Cu than for pure Al; notice that higher potentials were
examined. For instance, the steady-state net current density at -1200 mV_{SCE} was about -3
to -4 \mu A/cm² for Al-4Cu, and only 0.4 \mu A/cm² for pure Al. The mass showed the same
trend as pure Al. It decreased at a constant rate after an initial transient period. In general,
the mass loss was higher for Al-4Cu than for pure Al. The increased cathodic reactivity
and resultant mass loss of Al-4Cu compared to pure Al can be explained by the presence
of copper in the thin film analog. The cathodic reaction, oxygen reduction, can be
enhanced not only by the addition of Cu into the alloy, but also by the increase in exposed copper area on the surface due to selective dissolution of Al oxide. During cathodic polarization, hydroxide ions generated by cathodic reactions promote Al oxide dissolution to expose more metallic copper on the surface, which results in increased cathodic reactivity with time.

Figure 4.8 shows the current and mass curves of Al$_2$Cu during potentiostatic polarization in the mass transport limited ORR region in 0.1 M NaCl. The net current density was much higher for Al$_2$Cu than for pure Al and Al-4Cu even at higher potentials. The mass increased rapidly at the beginning of the polarization, and then decreased slowly at longer times. In order to understand this increase in apparent mass during the initial transient period of cathodic polarization of Al$_2$Cu, experiments were performed on Au electrodes. The results of those experiments and a detailed discussion are given in Appendix A. In summary, cathodic polarization of Au in chloride solutions below a potential of about 0.0 V$_{SCE}$ results in an increase in apparent mass, similar to what is seen in Figure 4.8 for Al$_2$Cu. As discussed in Appendix A, the increase in apparent mass for Au is associated with changes in the structure and composition of the adsorbed film and double layer and perhaps changes in the electrolyte near the surface. It is likely that the apparent mass increase after cathodic polarization of Al$_2$Cu is due to similar effects.

4.3.3 Calculation of Anodic and Cathodic Reaction Rates

The true dissolution and cathodic reaction rates can be calculated from the measured mass loss and net current density. The mass loss rate at steady-state, which is
obtained by differentiating the mass curves, can be converted into a current density, \( i_{\text{diss}} \), associated with Al oxidation and dissolution using Eq. (4-1). At steady-state, the rate of chemical dissolution of the oxide film is balanced by the rate of oxide film formation. Assuming the thickness of oxide film is constant at steady-state region, the mass loss rate can be directly related to the Al oxidation reaction rate.

The net current density, \( i_{\text{net}} \), measured by the potentiostat is a sum of all of the reactions occurring on the surface:

\[
i_{\text{net}} = i_{\text{cat}} + i_{\text{diss}} = i_{\text{O}_2} + i_{\text{H}_2} + i_{\text{diss}}
\]

(4-2)

where \( i_{\text{cat}} \) is the total cathodic current density, and \( i_{\text{O}_2} \) and \( i_{\text{H}_2} \) are the cathodic current densities associated with oxygen reduction and hydrogen evolution, respectively. It can be assumed that the current associated with hydrogen evolution is small in comparison to oxygen reduction in aerated neutral solution at potentials above those where water reduction is observed. For Cu containing samples, nonfaradaic release of metallic Cu and electrochemical redeposition of Cu ions might contribute cathodic current density. It is known that metallic Cu clusters can be detached from the electrode surface [4, 5]. These nonfaradaically released metallic Cu clusters are isolated from the electrode and directly oxidized by oxygen in the solution to Cu ions, which subsequently deposit on the electrode surface. This process generates reduction current from electrochemical redeposition of Cu ions. There is no net mass change associated with this process if all of the released Cu is subsequently deposited back on the surface. This Cu release and redeposition process might occur for Al-4Cu and Al\(_2\)Cu. However, since the Cu release
from Al-Cu alloys was observed be on the order of 1% of the total dissolution current and decrease with exposure time [6], the magnitude of the Cu ion reduction current is expected to be much smaller than oxygen reduction. Therefore, the cathodic current associated with oxygen reduction is dominant in the limiting ORR region and can be written as

\[ i_{o} \approx i_{net} - i_{diss} \]  

(4-3)

4.3.4 Cathodic Kinetics in Sodium Chloride Solution

The dissolution rate and cathodic current densities for pure Al in 0.1 M NaCl calculated from the net current and mass change during the potentiostatic polarization experiments in the steady state region (at 1000 sec) are shown in Figure 4.9. The dissolution rate, or cathodic corrosion rate on cathodically polarized pure Al is about 4 \( \mu \)A/cm\(^2\) in 0.1 M NaCl. The dissolution rate is seen to be high relative to the net current density, so the measured cathodic current density is much less than the actual cathodic current density in this case. These dissolution and cathodic reaction rates are almost independent of the applied cathodic potential in the ORR region, which is similar to what has been found from conventional weight loss experiments [7]. This is reasonable because the cathodic corrosion rate depends not on applied potential, but on the concentration of hydroxide ions. Since the net current density is determined by the difference in the cathodic current density and dissolution rate, which are close in magnitude, it exhibits a stronger dependence on applied potential.
The calculated dissolution rate and cathodic current densities of Al-4Cu in 0.1 M NaCl are shown in Figure 4.10. The dissolution rate for Al-4Cu was almost the same as pure Al but the cathodic current densities were higher for Al-4Cu than for pure Al, even in higher potential ranges. The dependence of the dissolution rate and cathodic current densities on the applied potentials was also weak. The measured net current density was much higher for Al-4Cu than for pure Al because the difference between the cathodic current density and dissolution rate was large for Al-4Cu.

For pure Al and Al-4Cu, the dissolution rates were similar in magnitude to calculated cathodic current densities. The measured net current density was much lower than the true cathodic reaction rate because the current generated by Al oxidation was directly consumed by cathodic reaction without being measured by the potentiostat. This indicates that the measured net current density can sometimes be misleading.

Figure 4.11 shows the calculated dissolution rate and cathodic current densities of Al₂Cu in 0.1 M NaCl. It was assumed that the change in resonant frequency during the initial transient period for Al₂Cu was caused by changes in the double layer structure and composition and changes in the viscosity and density of the electrolyte near the surface. It was also assumed that there was little further effect of these factors on the resonant frequency so that the steady state decrease in mass at longer times was caused by dissolution of the electrode. The dissolution rate or cathodic corrosion rate in 0.1 M NaCl was calculated from the slope at 1500 sec, which is well after the initial transient period. The dissolution rate was much lower for Al₂Cu than for pure Al, but the cathodic current
density for Al₂Cu was higher than for pure Al and Al-4Cu. The calculated cathodic current density was similar to the measured net current density for Al₂Cu because the dissolution rate was so small compared to the cathodic current density.

4.4 EFFECTS OF CHROMATE ON CATHODIC KINETICS

4.4.1 Effect on Potentiodynamic and Potentiostatic Polarization Curves

The effects of dichromate on cathodic kinetics for pure Al, Al-4Cu and Al₂Cu were measured in 0.1 M NaCl solution with 10⁻⁴ M or 10⁻² M Na₂Cr₂O₇. The initial pH of the solutions was adjusted to 6.2 by the addition of NaOH. Potentiodynamic polarization curves of pure Al in 0.1 M NaCl solution with different concentrations of dichromate are shown in Figure 4.12. The open circuit potential was higher in the presence of 10⁻⁴ M dichromate than in blank sodium chloride solution. With higher concentration of dichromate (10⁻² M), the open circuit potential was further increased to -760 mV SCE. The increase in the open circuit potential with increasing dichromate concentration suggests either that the chromate acts as an oxidizing agent by providing an extra cathodic reaction or that the anodic kinetics are inhibited. In the presence of the smaller amount of dichromate (10⁻⁴ M) in 0.1 M NaCl, the net cathodic current density decreased in the mass transport limited oxygen reduction reaction (ORR) region. This net current was slightly higher with 10⁻² M dichromate due to the additional cathodic current for Cr(VI) reduction so dichromate apparently has several effects.
The potentiodynamic polarization curves for Al-4Cu and Al<sub>2</sub>Cu in 0.1 M NaCl with 0, 10<sup>-4</sup> and 10<sup>-2</sup> M dichromate ions are shown in Figures 4.13 and 4.14. They exhibited the same trends as found for pure Al. The OCP’s increased as the dichromate concentration increased. The measured net current density decreased in the mass transport limited ORR region in the presence of dichromate in the solution. The effects were smaller for Al<sub>2</sub>Cu.

Figure 4.15 and 4.16 show net current and mass curves for pure Al during potentiostatic polarization at different potentials in the ORR region in 0.1 M NaCl with 10<sup>-4</sup> M or 10<sup>-2</sup> M dichromate, respectively. The net current densities in the presence of dichromate were lower than in the blank sodium chloride solution. The mass showed a rapid decrease at the beginning of cathodic polarization and then decreased at a constant rate, similar to what was found in the blank sodium chloride solution. With dichromate in the solution, a mass increase associated with the formation of at least a monolayer of Cr(III) oxide/hydroxide on the Al surface, is predicted [8]. This might occur immediately upon immersion in the dichromate-containing solution and thus not be recorded by the EQCM. In the dichromate solutions, a steady state but lower mass loss region than blank sodium chloride solution was also observed.

The net current and mass curves of Al-4Cu and Al<sub>2</sub>Cu during potentiostatic polarization in 0.1 M NaCl solution with 10<sup>-2</sup> M or 10<sup>-4</sup> M dichromate are shown in Figures 4.17-4.20. The net current density for Al-4Cu and Al<sub>2</sub>Cu showed the same trend as pure Al. The net current densities decreased slightly in the presence of dichromate. The
magnitude of mass loss of Al-4Cu decreased with dichromate concentration, but was slightly larger than the mass loss of pure Al in the same solution. Al$_2$Cu phase showed similar mass change as in 0.1 M NaCl solution. Mass also increased at the beginning of polarization, and then was almost constant due to low mass loss rates. Initial mass increase in dichromate solution was slightly larger at -500 mV$_{SCE}$ and slightly lower at -900 mV$_{SCE}$ compared to that in the blank sodium chloride solution.

4.4.2 Effect of Chromate on Cathodic Kinetics

The calculated dissolution rate and cathodic current densities of pure Al in 0.1 M NaCl with $10^{-4}$ M or $10^{-2}$ M dichromate are shown in Figures 4.21 and 4.22. Chromate reduction associated with the formation of Cr(III) species might take place during cathodic polarization. Therefore, the cathodic current density associated with chromate reduction, $i_{Cr^{6+}}$, must be considered in Eq. (4-2).

$$i_{net} = i_{cat} + i_{diss} = i_{O_2} + i_{H_2} + i_{Cr^{6+}} + i_{diss}$$ (4-4)

However, since the net charge associated with this layer formation passes at the beginning of cathodic polarization and is small [9], the contribution of chromate reduction to the cathodic current can be neglected at long times.

The addition of dichromate into the NaCl solution decreases the dissolution rate of pure Al from 4 µA/cm$^2$ to 1-2 µA/cm$^2$. Since the cathodic dissolution rate of Al is determined by the concentration of hydroxide ions or pH change, the slight reduction of dissolution rate might result from the pH buffering capacity of dichromate. Even though
the effect was small compared to the decrease in the net current density, dissolution rate and true cathodic current density were reduced by the addition of dichromate.

Al-4Cu shows the same trend as pure Al in dichromate solutions (Figures 4.23 and 4.24). The addition of dichromate ions into 0.1 M NaCl decreased the dissolution rates and cathodic current densities. The dissolution rate was reduced from 4 µA/cm$^2$ to less than 2µA/cm$^2$, and the cathodic current density decreased from 6 µA/cm$^2$ to 3 µA/cm$^2$. The presence of dichromate suppressed cathodic reaction rate more than dissolution rate, but the reduced dissolution of Al-4Cu can also have an effect on the cathodic reaction rate kinetics by the decreases in Cu-enrichment process and surface roughness on the surface.

The calculated dissolution rate and cathodic current densities of Al$_2$Cu in 0.1 M NaCl with $10^{-4}$ M or $10^{-2}$ M dichromate are shown in Figures 4.25 and 4.26. The dissolution rate decreased to 0.3 µA/cm$^2$ in the presence of $10^{-4}$ dichromate, and became negligible at the higher dichromate concentration. The maximum dissolution rate found in $10^{-2}$ M dichromate solution during the 30 min polarization was less than 0.05 µA/cm$^2$, which is very small compared with the dissolution rates in 0.1 M NaCl. The cathodic current density decreased from 12 µA/cm$^2$ to 4 µA/cm$^2$ in the presence of dichromate. The measured net current densities were almost identical with the calculated cathodic reaction rates for Al$_2$Cu.

In the presence of dichromate in the solution, the formation of Cr(III) oxide/hydroxide on the pure Al, Al-4Cu, and Al$_2$Cu surface is formed as follows.
\[ \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr(OH)}_3 + \text{H}_2\text{O} \quad E^\circ = 0.991 \text{V}_{\text{SCE}} \]  \hspace{1cm} (4-5)

In a $10^{-3}$ M dichromate solution with pH 6.2, the equilibrium potential for Eq (4-5) can be estimated to be $0.473$ V\textsubscript{SCE}. Since the equilibrium potential for Cr(VI) reduction is much higher than OCP of Al and Al-4Cu in the solution with dilute dichromate concentration and neutral pH, there is a strong driving force for Cr(VI) reduction and it might occur immediately upon immersion in the dichromate-containing solution or at the beginning of cathodic polarization. However, OCP of $\theta$ phase and Au is relatively close to the equilibrium potential for Cr(VI) reduction. Therefore, the formation of Cr(III) oxide could give the additional mass increase on Al\textsubscript{2}Cu in dichromate solution at the beginning of polarization.
LIST OF REFERENCES


6. R. K. Boger, in Department of Materials Science and Engineering, The Ohio State University, Columbus, 2001, p. 124.


<table>
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<tr>
<th>Phases</th>
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Table 4.1. Weight and atomic percentages of thin film analogs of Al-4Cu and Al<sub>2</sub>Cu.
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CHAPTER 5

DISCUSSION

5.1 CORROSION OF ALUMINUM IN ALKALINE SOLUTION

In alkaline solution, surface oxide/hydroxide films on Al dissolve chemically as aluminate (Al(OH)$_4^-$) ions due to their solubility. In a borate/sulfate solution at pH 9.2, the open circuit corrosion rate of Al was found to be equivalent to a current density of about 7.5 $\mu$A/cm$^2$. Open circuit measurements of pure Al in this borate/sulfate solution containing $0$, $10^{-3}$, or $10^{-2}$ M dichromate indicate that the corrosion potential increases and the corrosion rate decreases with increasing dichromate concentration, as shown in Figure 5.1. The increase in open circuit potential (OCP) can be caused by an increase in the rate of the cathodic reactions or a decrease in the rate of the anodic reactions. Dichromate may act as an aggressive oxidizing agent by providing extra cathodic current due to its reduction reaction, thereby supporting additional Al oxidation reaction [1]. However, since the Al dissolution rate decreased significantly from 7.3 to 0.94 $\mu$A/cm$^2$ in
the pH 9.12 solution containing $10^{-2}$ M chromate, the increase in OCP after 1 hour can be attributed primarily to the inhibition effect of chromate in solution or a Cr(III) oxide film on the anodic dissolution kinetics of Al. A faster OCP increase in dichromate-containing solutions after the guillotining of an Al electrode was also attributed to the accelerated repassivation effect of chromate [2].

Dichromate ions are usually added to solutions to increase the corrosion resistance. They are reduced on the electrode surface to form a protective Cr(III) oxide film. This increases the thickness of surface oxide films on Al, which can be thinned by alkaline solutions, and retards the dissolution of Al oxide films by blocking direct contact to the aggressive OH⁻ ions.

5.2 CATHODIC ACTIVITY OF ALUMINUM, Al MATRIX, AND 0 PHASE

5.2.1 Cathodic Polarization in Sodium Chloride Solution

Even in neutral solution, the local pH of solutions near cathodically polarized electrodes can increase to pH 9 and higher due to the alkalinity generated by the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) [3]. The increased local pH attacks oxide films on Al and Al alloys, similar to the case of open circuit exposure to alkaline solution. This leads to Al oxidation and oxide reformation, even under cathodic conditions, which is called cathodic corrosion. Cathodic corrosion makes it difficult to determine the exact cathodic kinetics of Al and Al alloys in aerated neutral solutions. This difficulty was overcome in this work by using the electrochemical quartz crystal
microbalance (EQCM), which can measure mass loss as well as potential and net current. The true cathodic reaction rate, or ORR rate, of pure Al, Al matrix, and θ phase were obtained by summing the measured the net cathodic current density and the mass loss, which can be converted into the current density associated with Al oxidation and oxide film dissolution under cathodic polarization.

The OCP's and net current densities at potentials in the mass transport limited oxygen reduction region are summarized in Table 5.1 and 5.2, respectively, for pure Al, Al-4Cu, Al2Cu, and AA2024-T3 in 0.1 M NaCl during potentiodynamic polarization. The OCP of AA2024-T3 was between those of Al-4Cu and Al2Cu, but the mass transport limited net current density was higher than those of the other phases. The ORR rate was significantly enhanced on the Al-4Cu compared to that on pure Al, resulting from the addition of only 4 wt% Cu in the solid solution. As the content of Cu increased from 0 to 53.5 weight percent (wt%) in Al-Cu binary alloy system, the OCP and net current density at cathodic potentials in 0.1 M NaCl solution increased significantly and the onset of hydrogen evolution occurred at higher potentials. The ORR limiting rates are clearly not the mass transport limited rate on these Al alloys because such a rate would not depend on the electrode material. This has been observed by others and attributed to kinetic limitations imposed by the oxide film [4, 5]. This result indicates that the cathodic activity of Al-Cu alloy strongly depends on the content of Cu in the alloy.

Figure 5.2 summarizes the measured net current density, the cathodic corrosion current density determined from weight loss, and the true cathodic current density for
pure Al, Al-4Cu, and Al$_2$Cu in 0.1 M NaCl with $0, 10^{-4},$ and $10^{-2}$ M dichromate during potentiostatic polarization at the indicated potentials in the middle of the limiting current region. For pure Al and Al-4Cu in 0.1 M NaCl, the dissolution or cathodic corrosion occurred at a rate of about 3-4 $\mu$A/cm$^2$ in the mass transport limited ORR region and the true cathodic current density ranged between 4-6 $\mu$A/cm$^2$, which was of the same order of magnitude as the dissolution rate. As a result, the true ORR rate was much larger than the measured net current density measured by the potentiostat, which does not reflect the true cathodic reaction rate for pure Al and Al-4Cu.

For Al$_2$Cu or $\theta$ phase, the true cathodic reaction rate was much higher, about 12 $\mu$A/cm$^2$, than that for pure Al and Al matrix in 0.1 M NaCl, showing the effect of Cu content on the relative order of the ORR rates: $\theta$ phase $>$ Al-4Cu $>$ pure Al. The true cathodic current density was similar to the measured net current density for Al$_2$Cu because the dissolution rate was so small compared to the net current density. The cathodic corrosion rate for $\theta$ phase, about 1 $\mu$A/cm$^2$, was lower than those for pure Al and Al-4Cu. It should be noted that current density values are at different potentials for the different materials. At the same potential, the true cathodic reaction rate increased with the Cu content in the alloy, indicating that the cathodic reaction is kinetically easier as the Cu content in the alloys increases.

5.2.2 Implications for Cathodic Corrosion

A considerable amount of cathodic corrosion occurred on cathodically polarized pure Al and Al-4Cu, which exhibited true cathodic reaction rates on the same order of
magnitude. Cathodic corrosion was almost independent of applied potential, suggesting that it is a chemical dissolution reaction, which depends on the concentration of OH\textsuperscript{-} generated by oxygen reaction. In the pure chloride solution, the cathodic corrosion rate on Al-4Cu was slightly higher than that on pure Al due to the increased ORR rate. However, even though the ORR rate was much larger on Al\textsubscript{2}Cu, less cathodic corrosion occurred.

During cathodic corrosion, the electrons generated by Al oxidation are directly consumed by the oxygen reduction reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$  \hspace{1cm} (5-1)

while the hydroxide ions resulting from oxygen reduction are also consumed by cathodic corrosion process:

$$Al + 4OH^- \rightarrow Al(OH)_4^- + 3 e^-$$  \hspace{1cm} (5-2)

When this occurs (for pure Al and Al-4Cu), the net current density, corresponding to the difference between cathodic current density and dissolution rate, is much smaller than the true oxygen reduction rate. The consumption of hydroxide ions by the cathodic corrosion reduces the concentration OH\textsuperscript{-} ions on the electrode, which promotes additional oxygen reduction if the current density is not limited by mass transport of oxygen. Therefore, extra attention must be paid in the study of the cathodic kinetics of Al and Al alloys, on which relatively low ORR rate and high rate of cathodic corrosion occurs.

5.2.3 Implications for Cathodic Activity of pure Al, Al-4Cu and \(\theta\) Phase

Assuming diffusion limited oxygen reduction on a planar electrode, the diffusion limited steady-state current density \((i_L)\) can be given by the following equation.
\[ i_L = \frac{nFDC_{\text{bulk}}}{\delta} \quad (5-3) \]

where \( n \) for oxygen reduction is 4 equiv/mol, \( F (96,487 \text{ C/equiv}) \) is Faraday's constant, \( D \) is the diffusion coefficient of \( \text{O}_2 \), \( C_{\text{bulk}} \) is the concentration of dissolved oxygen in the bulk solution, and \( \delta \) is the thickness of the diffusion boundary layer at the electrode surface. The mass transport limiting current density estimated from Eq. 5-3 is 10-100 \( \mu \text{A/cm}^2 \). In this estimate, \( D \) is assumed to be \( 10^{-5} \text{ cm}^2/\text{s} \), \( C_{\text{bulk}} \) is taken to be \( 2.5 \times 10^{-4} \text{ mol/L} \) [6], and \( \delta \) is assumed to range from 0.01 to 0.1 cm. The estimated limiting current density is larger than the true cathodic current density, or ORR rate for pure Al and Al-4Cu.

The lower ORR rate on pure Al and Al-4Cu suggests that electron transfer reaction (ETR) through the insulating Al oxide is the limiting step for the ORR on Al. ETR's on this Al oxide are not well supported and the kinetics of ORR decreases with increasing Al oxide thickness [7]. During cathodic polarization, even though Al oxide film was already thinned by cathodic corrosion, the kinetics of ORR on pure Al and Al-4Cu was still controlled by electron transfer through the Al oxide.

On the other hand, the high oxygen reduction rates on \( \theta \) phase can be attributed to the Cu content of the surface oxide. Since mixed oxides consisting of \( \text{Cu}_2\text{O} \) and \( \text{Al}_2\text{O}_3 \) are formed on \( \theta \) phase, it supports faster ETR than pure Al and Al matrix [4, 5]. The presence of conducting metallic \( \text{Cu}^0 \) in Al-rich native oxide was detected on Al-2Cu and Al-2CuMg [7-9]. This metallic \( \text{Cu}^0 \) in the Al oxide changes the conductivity of the oxide film on
Al$_2$Cu, and enhances the kinetics of ORR on this phase. The ORR rate on Al$_2$Cu was about 12 $\mu$A/cm$^2$, which is in the range predicted from Eq. (5-3). This indicates that the limiting step of this phase was not electron transfer through oxide film, but mass transport limited O$_2$ reduction. In addition, Al oxide dissolution due to the increased local pH leads to the enrichment of Cu content on the surface during cathodic corrosion, which makes the surface more catalytic and accelerates oxygen reduction further.

5.3 EFFECT OF DICHLROMATE ON CATHODIC ACTIVITIES

5.3.1 Cathodic Polarization in Dichromate Containing Solution

During potentiodynamic polarization, net current densities were reduced in the solution containing only $10^{-4}$ M dichromate, but net current densities were slightly higher in the solution containing $10^{-2}$ M dichromate perhaps owing to the extra current density of Cr(VI) reduction (Table 5.2). Dichromate lowered the potentials at which the onset of hydrogen evolution occurred, indicating a decrease in the catalytic properties of the surface.

The effect of dichromate concentration on the dissolution rate and cathodic current density in current limited cathodic region was investigated in 0.1 M NaCl containing $10^{-4}$ M or $10^{-2}$ M dichromate as shown in Figure 5.2. The addition of $10^{-4}$ M dichromate decreased the dissolution rate, or cathodic corrosion rate, for pure Al and Al-4Cu to about 50% of that in blank sodium chloride solution. A further decrease in dissolution rate for pure Al was observed in the presence of $10^{-2}$ M dichromate. The
dissolution rate for Al$_2$Cu, which was smaller than that for pure Al and Al-4Cu in the pure chloride solution, became negligible, less than 0.3 μA/cm$^2$, in the presence of dichromate. Therefore, the net current density for Al$_2$Cu was almost identical to the true cathodic reaction rate in dichromate containing solutions.

The true cathodic reaction rates, or ORR rates, for pure Al and Al-4Cu in dichromate solution were also reduced compared with the blank sodium chloride solution. A larger decrease in ORR rate was observed for θ phase, which supported faster ORR rate in 0.1 M NaCl. The true cathodic reaction rate for Al$_2$Cu decreased from 12 to 4 μA/cm$^2$ in the presence of dichromate and was only slightly higher than those for pure Al and Al-4Cu in the same solution.

5.3.2 Implications for Effect of Dichromate on Cathodic Corrosion

The presence of dichromate in 0.1 M NaCl decreases oxide dissolution rate or cathodic corrosion rate for pure Al, Al-4Cu and Al$_2$Cu during cathodic polarization. Since the OCP's of pure Al, Al-4Cu, and Al$_2$Cu in 0.1 M NaCl with dilute dichromate concentration and neutral pH are much lower than the equilibrium potential for Cr(III) hydroxide formation, at least a Cr(III) mono-layer is formed on the electrode surface according to the following reaction, accompanied by Al dissolution:

$$\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr(OH)}_3 + \text{H}_2\text{O}$$  \hspace{1cm} (5 - 4)

There is a strong driving force for Cr(VI) reduction and it might occur immediately upon immersion at open circuit or at the beginning of cathodic polarization in the dichromate-containing solution, depending on the OCP and surface activity of the samples, as was
described for Au electrodes in dichromate solution in Chapter 4. This explains why the monolayer formation was not detected by EQCM measurements during potentiostatic polarization.

This Cr(III) oxide film can act as a physical barrier for cathodic corrosion, which is mainly caused by chemical attack of OH⁻ ions. The formation of an insoluble Cr(III) oxide layer on top of the Al oxide film could block direct contact of the Al oxide with the alkalinity generated by oxygen reduction. However, it should be noted that cathodic corrosion still occurred in dichromate containing solutions. So the Cr(III) oxide was not perfectly protective and allowed cathodic corrosion around it. It should also be noted that, since dichromate has buffering ability, the presence of dichromate in solution can retard local pH change on the electrode surface, resulting in less chemical dissolution by OH⁻ ions.

5.3.3 Implications for Effect of Dichromate on Cathodic Activity

The Cr(III) oxide film and dichromate in solution also reduced the cathodic reaction rates, or ORR rates on pure Al, Al matrix, and θ phase. The decrease in ORR rate in dichromate solution can be attributed to several characteristics of a Cr(III) oxide layer on electrode surface.

The Cr(III) oxide film is electrically non-conductive so it can reduce the ORR rate by decreasing the conductivity of surface oxide films. The efficiency of the dichromate inhibition of oxygen reduction was not so high for pure Al and Al-4Cu, which already have a relatively insulating Al oxide on the surface. However, dichromate showed higher
efficiency of cathodic inhibition for Al₂Cu, which can support faster oxygen reduction rate due to more conductive surface oxide film than pure Al and Al matrix. A non-conductive Cr(III) oxide layer formed on Al₂Cu by chromate reduction makes ETR’s on θ phase more difficult by changing the conductivity of the surface oxide [4, 5]. Therefore, a greater decrease in oxygen reduction rate is expected in phases with a conductive oxide than on phases with an insulating oxide.

The Cr(III) oxide film formed on the electrode surface can inhibit oxygen reduction by occupying the active sites for oxygen chemisorption [10]. Since the outer-sphere reduction mechanism of oxygen is kinetically slow, catalysis via O₂ adsorption to the electrode surface is usually involved. The reduction of Cr(VI) and irreversible adsorption of Cr(III) to the electrode surface blocks sites of O₂ adsorption.

The effect of dichromate as an oxidizer and Cr(III) oxide layer also can reduce cathodic reaction rate by thickening oxide film on the surface. Scully et al. [4] found from EIS measurements that chromate thickened oxide films on Cu and Al₂₀Cu₂(MnFe)₃, resulting in an increase in corrosion resistance. The reduced cathodic corrosion also can have an effect on the reduced oxygen reduction rate on Cu-rich intermetallic particles because it prevents further exposure of catalytic metallic Cu on the surface.

5.4 IMPLICATIONS FOR CORROSION OF AA2024

During the corrosion of AA2024, Cu-containing intermetallic compounds (IMCs) act as preferred cathodic sites for oxygen reduction and the Al matrix and S-phase
particles act as the anodic site [11]. Due to the ORR, high pH zones are developed on and near the cathodic sites, which then attack the surrounding Al matrix, causing localized attack at the periphery of Cu-containing intermetallic particles.

Chromate can inhibit the corrosion of AA2024 by forming a protective Cr(III) oxide film. The Cr(III) oxide/hydroxide formed on Cu-containing intermetallic phases act as a physical barrier for oxygen reduction reaction. This film diminishes the ORR rate by reducing the active sites for oxygen reduction on the surface and increasing the thickness of the oxide film, which decreases the ORR rate. The poor conductivity of the Cr(III) oxide/hydroxide makes it a more efficient inhibitor for Cu containing intermetallic phases with more conductive oxide film. This reduces the galvanic interaction by suppressing fast cathodic ETR on Cu-rich IMCs. The reduced oxygen reduction makes it difficult to develop high pH zones expanding into the surrounding Al matrix.

The Cr(III) oxide film and chromate in the solution also protect the Al matrix from anodic dissolution. Even though it cannot be directly derived from this study, the OCP increase in dichromate containing solution implies anodic inhibition of Al. The Cr(III) oxide film reduces Al oxide dissolution and subsequent Al oxidation by preventing direct contact of OH⁻ ions with the high pH zones. The buffering ability of chromate in solution also reduces the concentration of OH⁻ on the alloy surface. The reduced anodic dissolution of the Al matrix limits the Cu-enrichment process on surface, which would otherwise generate active catalytic Cu sites for oxygen reduction.
These effects of chromate on dissolution and cathodic reaction kinetics can be combined together, which makes chromate a superior corrosion inhibitor. The decrease in cathodic reaction rate results in the reduced anodic reaction rate and vice versa. Chromate decreases the net current density more for AA2024 than that for θ phase. Table 5.3 summarizes the effects of chromate on the net current densities for AA2024 and Cu-containing IMCs in AA2024 reported in the corrosion literature [4, 12, 13] and from this study. Comparison of these data is complicated by the fact that the data were collected in different solutions and experimental conditions. Nonetheless, they demonstrate that the corrosion rate of AA2024 is inhibited more effectively by chromate than is the cathodic rate on θ phase. Chromate is more effective at decreasing the net cathodic current densities on the more active phases such as Cu and Al₂₀Cu₂(MnFe)₃, making them less than several µA/cm². It also decreases the anodic reaction rate on Al₂CuMg, which is about 60% of second-phase particles in AA2024 [14]. The reduced oxygen reduction reactions on θ phase and Al-Cu-Fe-Mn phase by chromate generates less hydroxide ions, which attack the surrounding Al matrix and IMCs themselves, so it suppresses further development of active cathodic sites from Cu-redistribution and exposition of catalytic Cu on the alloy surface. S phase particles, which can provide a Cu source for Cu-redistribution after it is dealloyed and thus generate more active cathodic sites for ORR [14, 15], are anodically inhibited. This further decreases the active cathodic sites for oxygen reduction. These combined effects make chromate a more efficient oxygen
reduction inhibitor and subsequently corrosion inhibitor for AA2024 than for Al$_2$Cu or Al-4Cu individually.
LIST OF REFERENCES


Table 5.1. The open circuit potentials (mV<sub>SCE</sub>) for pure Al, Al-4Cu, Al<sub>2</sub>Cu, and AA2024 in 0.1 M NaCl (pH=6.2) with different concentrations of dichromate.

<table>
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<th>Pure Al</th>
<th>Al-4Cu</th>
<th>Al&lt;sub&gt;2&lt;/sub&gt;Cu</th>
<th>AA2024-T3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M NaCl</td>
<td>-1198</td>
<td>-887</td>
<td>-485</td>
<td>-645</td>
</tr>
<tr>
<td>0.1 M NaCl + 10&lt;sup&gt;-4&lt;/sup&gt; M Na&lt;sub&gt;2&lt;/sub&gt;Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>-925</td>
<td>-781</td>
<td>-470</td>
<td>-632</td>
</tr>
<tr>
<td>0.1 M NaCl + 10&lt;sup&gt;-2&lt;/sup&gt; M Na&lt;sub&gt;2&lt;/sub&gt;Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>-743</td>
<td>-692</td>
<td>-449</td>
<td>-608</td>
</tr>
</tbody>
</table>

Table 5.2. The ORR limiting net current densities (µA/cm<sup>2</sup>) for pure Al, Al-4Cu, Al<sub>2</sub>Cu, and AA2024 in 0.1 M NaCl (pH=6.2) with different concentrations of dichromate. The potentials of the measurements were in the middle of the transport-limited region between the corrosion potential and the hydrogen evolution potential, and are given in the parentheses.

<table>
<thead>
<tr>
<th></th>
<th>Pure Al (-1300 mV&lt;sub&gt;SCE&lt;/sub&gt;)</th>
<th>Al-4Cu (-1100 mV&lt;sub&gt;SCE&lt;/sub&gt;)</th>
<th>Al&lt;sub&gt;2&lt;/sub&gt;Cu (-900 mV&lt;sub&gt;SCE&lt;/sub&gt;)</th>
<th>AA2024-T3 (-900 mV&lt;sub&gt;SCE&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M NaCl</td>
<td>3.36</td>
<td>8.50</td>
<td>17.97</td>
<td>25.61</td>
</tr>
<tr>
<td>0.1 M NaCl + 10&lt;sup&gt;-4&lt;/sup&gt; M Na&lt;sub&gt;2&lt;/sub&gt;Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>0.811</td>
<td>2.01</td>
<td>10.01</td>
<td>-6.62</td>
</tr>
<tr>
<td>0.1 M NaCl + 10&lt;sup&gt;-2&lt;/sup&gt; M Na&lt;sub&gt;2&lt;/sub&gt;Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>2.03</td>
<td>2.57</td>
<td>9.27</td>
<td>-6.41</td>
</tr>
<tr>
<td>Electrode</td>
<td>Solution</td>
<td>pH</td>
<td>c. d. w/o Cr(VI)</td>
<td>c. d. w/ Cr(VI)</td>
</tr>
<tr>
<td>------------------</td>
<td>----------------------------</td>
<td>-----</td>
<td>------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>AA2024 (cathodic)</td>
<td>0.1M Na$_2$SO$_4$+ 0.005M NaCl</td>
<td>6.0</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1 M NaCl</td>
<td>-</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.1M NaCl</td>
<td>6.2</td>
<td>11</td>
<td>1.4</td>
</tr>
<tr>
<td>Al$_2$Cu (cathodic)</td>
<td>0.1M Na$_2$SO$_4$+ 0.005M NaCl</td>
<td>6.0</td>
<td>21</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>0.1M NaCl</td>
<td>6.2</td>
<td>10.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Al$_{20}$Cu$_2$(MnFe)$_3$ (Cathodic)</td>
<td>0.1M Na$_2$SO$_4$+ 0.005M NaCl</td>
<td>6.0</td>
<td>21</td>
<td>0.5</td>
</tr>
<tr>
<td>Al$_2$CuMg (anodic)</td>
<td>0.1M Na$_2$SO$_4$+ 0.005M NaCl</td>
<td>6.0</td>
<td>2000</td>
<td>55</td>
</tr>
<tr>
<td>Cu (cathodic)</td>
<td>5%NaCl</td>
<td>6.1</td>
<td>95</td>
<td>3</td>
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</tbody>
</table>

Table 5.3. The net current densities ($\mu$A/cm$^2$) at -700 mV$_{SCE}$ for AA2024-T3 and intermetallic compounds in AA2024 without and with the presence of Cr(VI) in the solutions.
Figure 5.1. Corrosion potential and corrosion rate for pure Al in 0.01 M Na₂B₄O₇ + 0.5 M Na₂SO₄ (pH=9.18) with different concentrations of dichromate.
Figure 5.2. The measured net current density, the cathodic corrosion current density, and the true cathodic current density for (a) pure Al, (b) Al-4Cu, and (c) Al₂Cu at indicated potentials as a function of dichromate concentration at 1000 sec. The solutions are all adjusted to pH 6.2.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

- The electrochemical quartz crystal microbalance with thin film analogs of phases in AA2024 provides a unique method for study of the true cathodic activities of individual phases in this alloy, which are complicated by cathodic corrosion of Al.

- As Cu content in Al-Cu binary alloy system increases, open circuit potential and net current density at cathodic potentials increase and the onset of hydrogen evolution occurs at higher potentials in 0.1 M NaCl solution.

- For pure Al and Al-4Cu in 0.1M NaCl solution, a considerable amount of cathodic corrosion, ranging up to several μA/cm², occurs at cathodic potentials, which is on the same order of magnitude as the true cathodic reaction rates.
Cathodic corrosion rate for Al₂Cu in 0.1 M NaCl is about 1 µA/cm² in the mass transport limited oxygen reduction region, but is much smaller than the true cathodic reaction rate.

The true cathodic current density is much different from the measured net current density for pure Al and Al-4Cu, while it is almost equal to the measured net current density for Al₂Cu.

In 0.1M NaCl solution containing chromate, the open circuit potential increases, and both cathodic corrosion rate and oxygen reduction rate decrease for pure Al, Al-4Cu, and Al₂Cu.

The decrease in the cathodic corrosion rate may result from either the buffering ability of chromate or the Cr(III) oxide film formed on surface.

The decreased oxygen reduction reaction in chromate solution can be attributed to a Cr(III) oxide film, which is non-conductive and blocks active sites for oxygen reduction, and its oxidizing effect, which thickens the oxide film on surface.

A larger decrease in oxygen reduction rate on Al₂Cu, which can support faster electron transfer through its oxide film, is observed than those on pure Al and Al-4Cu, which have more insulating Al oxide films.
Chromate concentration and applied cathodic potential have little effect on the cathodic corrosion rates and the oxygen reduction rates in mass transport limited oxygen reduction reaction region, while the net current density has relatively stronger dependencies on them.

For the corrosion of AA2024, effects of chromate on both dissolution and cathodic reaction rates can be combined, which makes chromate a more efficient corrosion inhibitor for AA2024 than for individual phases in this alloy.

6.2 FUTURE WORK

6.2.1 Fabrication and Characterization of Thin Film Analogs

The other thin film analogs such as Al$_2$CuMg and Al-Cu-Fe-Mn phases in AA2024 can be developed using the flash evaporation technique. Electrochemical characterization of them with the results in this work will provide better understanding of cathodic activity of each phase in AA2024 and effects of chromate.

The surface characterization of thin film analogs using scanning electron microscopy and Auger electron spectroscopy is needed to better understand the properties of Cr(VI) reduction product on surface and its effect on cathodic reaction kinetics.
6.2.2 Electrochemical Quartz Crystal Microbalance Technique

- Since the EQCM and its thin film approach limits experimental conditions, for instance, uniform corrosion and less aggressive solutions, electrochemical system, which is best suited to the EQCM measurement, needs to be investigated.

- Other electrochemical or non-electrochemical techniques need to be combined to better understand the complicated EQCM results and separate unexpected effect on the EQCM measurement.
Appendix A

EQCM STUDIES ON GOLD

A.1 Cathodic Polarization of Au

In order to understand the initial mass increase observed on the Al₂Cu analog, experiments were performed with Au electrodes, which do not exhibit extensive oxide film formation or dissolution. The electrolytes used were 0.1 M NaCl containing 0, 10⁻⁴, or 10⁻² M dichromate, as well as 0.05 M Na₂SO₄, 0.1 M KCl, and borate buffer solution (pH = 6.8). Other experimental details were identical to those used for Al, Al-4Cu, and Al₂Cu.

Figure A.1 shows that potentiostatic polarization of Au films at -700 mV_{SCE} resulted in a decrease in frequency, or an apparent increase in mass, similar to that observed for Al₂Cu. In 0.1 M NaCl, the mass curve exhibited a large increase initially and then a constant rate of mass increase for times up to 1 h. In borate buffer solution, however, the apparent mass was constant after the initial increase. As discussed in section
3.4.1, the resonant frequency changes with the pH because of changes in solution viscosity and density. During cathodic polarization of Au in NaCl solution, the solution pH near the electrode surface will increase as a result of the generation of hydroxyl. It is possible that part of the increase in apparent mass is associated with a change in the electrolyte. The buffering capacity of the borate buffer solution would minimize the pH changes. Comparison of the behavior in the chloride and borate buffer solution suggests that the constant rate of apparent mass increase at longer times in chloride solution is related to a continued increase in pH, viscosity, and density of solution near the electrode. The initial increase in apparent mass seems to be related to something other than pH changes near the electrode. This will be discussed below.

Potentiodynamic polarization (Figure A.2) and cyclic polarization (Figure A.3) experiments with Au electrodes in 0.1 M NaCl solution showed a step increase in mass of 0.8-1.0 µg/cm² as the potential went below 0.0 V_sce in the negative scan. The cyclic polarization experiment (Figure A.3) showed that the mass increase was reversible with a hysteresis. During the positive scan, the mass decreased to a value within 0.1 µg/cm² of the original mass at 0.1 V_sce, suggesting that potential-dependent adsorption and desorption occur on the Au electrode surface. The cyclic polarization experiment was also performed in deaerated 0.1 M NaCl solutions in order to see the effect of dissolved oxygen on the mass increase on Au electrodes (Figure A.4). The mass change was much less in the deaerated solution. Reduction and oxidation current peaks were observed at potentials corresponding the reversible increase and decrease in mass, respectively. Since
the current densities associated with the peaks were less than 2 µA/cm², they might be present in solutions exposed to ambient air, but were not visible due to the large background current density. These results suggest that adsorption and desorption of ionic species are related to the mass increase of Au and Al₂Cu.

Cyclic polarization experiments were performed in 0.1 M KCl and 0.05 M Na₂SO₄ solutions in order to see the effect of varying cationic and anionic species on the mass change of Au electrodes. The mass behavior and magnitude of limited oxygen reduction current density in 0.1 M KCl solution were similar to those in 0.1 M NaCl (Figure A.5). However, in 0.05 M Na₂SO₄ solution, the mass increase at 0.0 V SCE became negligible and oxygen reduction reaction rate was smaller than that in chloride containing solution (Figures A.6). When sulfate was injected into a 0.1 M NaCl solution after one potential cycle to result in a final solution of 5 x 10⁻³ M Na₂SO₄ + 0.1 M NaCl, the mass at higher potentials increased by 0.15 µg/cm² the mass increase at lower potential decreased with the number of cycles (Figure A.7).

A.2 Chromate Reduction on Au

The formation of Cr(III) oxide and subsequent mass increase by chromate reduction was investigated with EQCM in 0.1 M NaCl with and without dichromate ions. During potentiostatic and potentiodynamic polarization experiments, the mass showed a larger increase on Au in 0.1 M NaCl containing dichromate ions than in the blank sodium chloride solution (Figures A.1 and A.2). A Cr(VI) reduction peak was seen in the
dichromate solution at 0.1 \(V_{\text{SCE}}\) and mass also started to increase only in dichromate solution around that potential (Figure A.2). The magnitude of the additional mass increase in dichromate solution was 0.3-0.4 \(\mu g/cm^2\), suggesting the formation of a Cr(III) oxide/hydroxide monolayer on Au electrode surface [1].

Cyclic polarization experiments showed that the Cr(III) oxide formed irreversibly on the Au electrode. In the presence of \(2 \times 10^{-5}\) M dichromate, injected after the first scan, the mass started to increase right below 0.1 \(V_{\text{SCE}}\) and showed larger increase at 0.0 \(V_{\text{SCE}}\) than in blank sodium chloride solution (Figure A.8). The increased mass rapidly decreased at 0.1 \(V_{\text{SCE}}\) during the positive scan, but did not drop below 0.4 \(\mu g/cm^2\). For the following cycles, the magnitude of mass increase at 0.0 \(V_{\text{SCE}}\) was reduced with the number of cycles, but the mass values at higher potentials remained at 0.4 \(\mu g/cm^2\). A similar result was obtained in a solution containing \(10^{-2}\) M dichromate from the beginning (Figure A.9). In this case, chromate reduction peak was found at 0.2 \(V_{\text{SCE}}\) only at the first negative scan and the mass started to increase at 0.2 \(V_{\text{SCE}}\) as chromate reduction reaction reached a maximum. The mass increase by Cr reduction was combined with the frequency decrease associated with adsorption and desorption of ionic species at 0.0 \(V_{\text{SCE}}\). This mass increase did not recover to its original value when the potential was cycled back to high values. After the first cycle, the mass at high potentials was 0.3-0.4 \(\mu g/cm^2\) higher than the original mass, and this value was attained at subsequent cycles. These results also indicate the irreversible formation of Cr(III) oxide/hydroxide on the Au electrode. The value of mass increase at low potentials decreased incrementally with
subsequent cycles to low potentials. The Cr(III) oxide formed during the first scan seemed to block the formation of an adsorbed film and further Cr(VI) reduction reaction for the following cycles. Net current density also decreased dramatically after the formation of Cr(III) oxide, indicating that the Cr layer also blocked the oxygen reduction reaction on Au.

A.3 Discussion on Mass Change and Chromate Reduction on Au

Due to the extremely high sensitivity of the electrochemical quartz crystal microbalance (EQCM) technique, the formation of an absorbed film at monolayer or submonolayer amounts can be monitored [2]. However, the frequency change might not obey the linear relationship between mass change and frequency change predicted by the Sauerbrey equation [3] because of changes in the electrolyte viscosity and density near the electrode and charging of the electrochemical double layer at the electrode surface.

Apparent mass increases associated with frequency decreases were observed on the thin film Au electrode in 0.1 M NaCl and 0.1 M KCl during cathodic polarization. The magnitude of mass increases was about 0.8 $\mu$g/cm$^2$ in aerated solutions containing chloride ions. Partially, these mass increases can be attributed to the increases in viscosity and density of the electrolyte solution due to the generation of hydroxide during oxygen reduction as predicted by the Bruckenstein and Shay equation [4]. However, the presence of reversible mass changes during cyclic polarization, even in deaerated 0.1 M NaCl solution, suggests that the adsorption and desorption of ionic species and subsequent
changes in double layer structure and composition of the electrode surface cause the frequency change or apparent mass change.

Adsorption of both ions and solvent may occur at the electrode surface and the extent of their adsorption and other interfacial properties may strongly depend on electrode potential. The decrease in electrode potential from the open circuit potential (OCP) to cathodic potentials makes the surface more negatively charged, which tends to result in repulsion of anions from the surface and attraction of cations to the surface. At potentials higher than the potential of zero charge (PZC) where no net charge exists in the double layer [5], the electrode surface is positively charged and a higher density of anionic species is expected in the double layer. If the potential is switched to a value lower than the PZC, anions in double layer will be replaced by solvated cations. The replacement of anions by cations during polarization below the PZC might result in changes in resonant frequency or apparent mass. It should be noted that the EQCM only measures changes in mass from some initial condition.

Polarization of the Au electrode below 0.0 V_{SCE} in deaerated solutions containing Cl^- and Na^+ ions resulted in a decrease in resonant frequency or increase in mass, as shown in Figure A.4. The data suggest that the PZC for Au is about 0.0 V_{SCE} which is similar to the PZC value reported for Au in 0.02 N Na_2SO_4 [6] and that the frequency increase is associated with a rearrangement of the double layer structure by replacement of anions with cations. The increase was larger when oxygen was dissolved in solution (Figure A.3). It is not clear how oxygen interacts with the ions to change the structure of
the double layer. Oxygen might decrease the mass at high potentials or increase the mass at low potentials.

For potentiostatic experiments, the mass increases resulting from the adsorption and desorption and subsequent changes in double layer composition and structure might occur and be dominant at the beginning of polarization. This might give a large and rapid mass increase at the beginning of polarization. However, once the double layer is stabilized with time, the contribution of pH increase from continued oxygen reduction to the mass increase is expected to be dominant. But the increasing rate of local pH near the electrode is expected to be small after the initial transient period since the hydroxide ions generated on the electrode surface by oxygen reduction are balanced by the amount of hydroxide ions lost by ion diffusion and solution convection. Therefore, the slow mass increases with time after the initial transient period can be attributed to the local pH increase near the electrodes.

A similar increase in the apparent mass could occur for pure Al, Al-4Cu, and Al$_2$Cu electrodes if the potential were decreased from above to below their PZCs. For Al in 0.01 N KCl and Cu in 0.02 N Na$_2$SO$_4$, the PZC values were found to be $-0.75$ V$_{SCE}$ and $-0.20$ V$_{SCE}$, respectively [6]. The values of the PZCs for Al-4Cu and Al$_2$Cu phases in 0.1 M NaCl solution are not known. They are probably different than those of pure Al and Cu and different for each material. The PZCs of Al-4Cu and Al$_2$Cu are expected to be between those of the pure materials. The OCPs of pure Al and Al-4Cu in 0.1 M NaCl were $-1.20$ V$_{SCE}$ and $-0.89$ V$_{SCE}$, respectively, which are lower than the PZC of pure Al.
Al$_2$Cu had the OCP value of $-0.49$ V$_{SCE}$, which is approximately in the middle of the PZCs of pure Al and Cu. Therefore, it is reasonable that the OCPs of pure Al and Al-4Cu were below their PZCs so there was no structural change in the double layer during cathodic polarization. However, if the PZC for Al$_2$Cu was below its OCP, cathodic polarization could force the potential across the PZC and subsequent structural changes in double layer. This could explain the increase in mass seen immediately upon cathodic polarization of the Al$_2$Cu.

For the Au electrode in the sulfate solution (Figure A.6), cathodic polarization resulted in very small changes in resonant frequency. It is possible that this results from a difference in the sulfate rich double layer formed at high potentials compared to the chloride double layer. Since an adsorbed film of sulfate was found to be irreversibly formed at open circuit and remain at lower potentials [7, 8], it is possible that the sulfate anions are chemisorbed and are not displaced at lower potentials. Cathodic polarization of Au in the presence of sulfate injected in 0.1 M NaCl (Figure A.7) also suggested that sulfate increased mass at higher potential by the difference in mass values between chloride rich double layer and sulfate rich double layer, and reduced mass increase at low potentials by irreversible adsorption of sulfate on the electrode surface.

The formation of Cr(III) oxide by Cr(VI) reduction was also investigated by the EQCM technique. Comparing the magnitude of the mass increases in dichromate containing solution to that without dichromate, the additional mass increase of 0.3-0.4 µg/cm$^2$ was observed in dichromate containing solutions. This value of the mass
increases is very close to the surface density of hydroxylated Cr$_2$O$_3$ films [9], indicating that the formation of a mono-layer of Cr(III) oxide/hydroxide on electrode occurs during cathodic polarization. The surface density of hydroxylated Cr$_2$O$_3$ films was found to contain $1.9 \times 10^{15}$ atoms/cm$^2$ of Cr(III), $0.8 \times 10^{15}$ atoms/cm$^2$ of O$^{2-}$, and $1.6 \times 10^{15}$ atoms/cm$^2$ of OH$^-$ [9]. Converting these values to grams gives a total weight density of the Cr monolayer as 0.24 µg/cm$^2$. Considering the surface roughness factor of thin film samples, this value is very close to the difference in mass measured by the EQCM for the solution with dichromate compared to that without dichromate.

The Cr(III) oxide film started to form at about 0.15 V$_{SCE}$ and remained on the surface even at higher potentials than its formation. The Cr(III) oxide irreversibly formed on electrode blocked not only the formation of the adsorbed film of cations and further Cr(VI) reduction reaction, but also the oxygen reduction reaction on electrode surface.
LIST OF REFERENCES

Figure A.1. (a) Net current density and (b) Mass change for Au during potentiostatic polarization at -700 mV_{SCE} in 0.1 M NaCl + x M Cr_{2}O_{7}^{2-} and borate buffer solution (pH =6.8).
Figure A.2. Net current density and mass change for Au during potentiodynamic polarization in 0.1 M NaCl without and with $10^{-4}$ M Cr$_2$O$_7^{2-}$ starting at 400 mV$_{SCE}$ and scanning downward at a rate of 5 mV/sec.

Figure A.3. Net current density and mass change for Au during cyclic polarization in 0.1 M NaCl (pH =6.2) at a scan rate of 10 mV/sec.
Figure A.4. Net current density and mass change for Au during cyclic polarization in deaerated 0.1 M NaCl (pH=6.2) at a scan rate of 10 mV/sec.

Figure A.5. Net current density and mass change for Au during cyclic polarization in 0.1 M KCl at a scan rate of 10 mV/sec.
Figure A.6. Net current density and mass change for Au during cyclic polarization in 0.05 M Na$_2$SO$_4$ at a scan rate of 10 mV/sec.

Figure A.7. Net current density and mass change for Au during cyclic polarization in 0.1 M NaCl (pH=6.2) with injected 5 x10$^{-3}$ M SO$_4^{2-}$ after the first cycle at a scan rate of 10 mV/sec.
Figure A.8. Net current density and mass change for Au during cyclic polarization in 0.1 M NaCl (pH=6.2) with injected $2 \times 10^{-5}$ M Cr$_2$O$_7^{2-}$ after the first cycle at a scan rate of 10 mV/sec.

Figure A.9. Net current density and mass change for Au during cyclic polarization in 0.1 M NaCl $+ 10^{-2}$ M Cr$_2$O$_7^{2-}$ at a scan rate of 10 mV/sec.
The local pH near the electrode surface can be estimated by equating the observed limiting oxygen reduction current density ($i_L$) to the diffusion current for OH$^-$ away from the electrode surface [1].

$$i_L = \frac{nF D_{OH^-} [(C_{OH^-})_{surf} - (C_{OH^-})_{bulk}]}{\delta} \quad (B-1)$$

$$C_{OH^-}^{surf} = C_{OH^-}^{bulk} + \frac{i_t \delta}{nF D_{OH^-}} \quad (B-2)$$

where $n$ for oxygen reduction is 4 equiv/mol, $F$ (96,487 C/equiv) is Faraday’s constant, $D_{OH^-}$ is the diffusion coefficient of OH$^-$, $(C_{OH^-})_{surf}$ and $(C_{OH^-})_{bulk}$ are the concentration of OH$^-$ in mol/L at electrode surface and bulk solution, and $\delta$ is the thickness of the diffusion boundary layer at the electrode surface. The diffusion boundary layer thickness, $\delta$, increases with time and can be assumed as a $(D_{OH^-} t)^{1/2}$. Therefore, the concentration of OH$^-$ ions on the electrode surface shows the square root dependence on time. From the
measured limiting ORR current density and the initial pH of bulk solution, the pH on the electrode surface during cathodic polarization can be estimated. For the limiting oxygen reduction current density of 30 µA/cm², the estimated pH on the electrode surface at the beginning (1 sec) is 12.0 assuming D_{OH}⁻ as 5.3 x 10⁻⁵ cm²/s. This pH value increases to 13.0 after 100 seconds and then increases much slowly to 13.8 after 1 hour. As the diffusion boundary layer expands into the bulk solution, the pH of a liquid layer, which has an effect on the resonant frequency, also increases with time, but at a slower rate than the increase in the pH of the electrode surface. When the diffusion boundary layer δ is much larger than the liquid layer, the pH changes in the liquid layer becomes small and negligible. This might make a sharp decrease in the resonant frequency according to Bruckenstein and Shay equation [2] and a sharp increase in apparent mass calculated from the changes in the resonant frequency of quartz crystal. In buffer solution, this behavior may become complex due to the buffer reaction to correct pH change from oxygen reduction. In the presence of strong buffering species, buffering effect retard the development of high pH zone near the electrode, resulting in constant mass during cathodic polarization.
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