Inhibition of Corrosion-Related Reduction Processes via Chromium Monolayer Formation

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The oxygen reduction reaction (ORR) was examined on copper, platinum, and glassy carbon electrodes, with regard to its inhibition by exposure of the electrode to chromate ion (Cr VI) in NaCl solution. All three electrode materials exhibited a mass transport limited current for the ORR at sufficiently negative potentials, but this current was strongly inhibited in the presence of Cr VI. Inhibition persisted in Cr VI-free solution after the electrode was rinsed thoroughly, indicating that Cr VI formed an irreversibly adsorbed inhibiting layer. A reduction peak observed in Cr VI solution had an area of 1.1-2.5 mC/cm², and the area varied little with Cr VI concentration, electrode material, and potential in the range of +0.2 to −0.6 V vs. Ag/AgCl. This reduction peak is attributed to Cr III formation, and corresponds to formation of approximately a monolayer of Cr III oxyhydroxide. Once formed, this Cr III monolayer inhibits both O₂ reduction and further reduction of Cr VI. The onset of monolayer formation at about +0.25 V vs. Ag/AgCl is the same as the potential of the onset of ORR inhibition in dilute Cr VI. The monolayer also decreases the electron transfer rate to ferrocene and Ru(NH₃)₆³⁺, which are known to be outer sphere redox systems that do not require adsorption to the electrode surface. The results indicate that the adsorbed Cr III film formed by Cr VI reduction is a powerful inhibitor of oxygen reduction, due both to occupation of active chemisorption sites and to inhibition of electron transfer. In the context of corrosion protection, Cr VI acts as a “site-directed” irreversible inhibitor which migrates to active sites for the ORR, then is reduced to Cr III, and forms a permanent inhibiting monolayer.

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oxidation of ferrocene (in organic solvent), a system that does not require adsorption to the electrode for electron transfer to occur.

The reduction of oxygen, like chromium, is a very complex process and has been studied extensively.\(^1\) The reduction can occur via two or four electrons and has a strong pH dependence. The outer-sphere reduction mechanism (not involving an adsorption step) is kinetically slow, thus catalysis via adsorption to the electrode surface is usually involved. Studies on glassy carbon (GC) electrodes have illustrated one example of how adsorption sites can be blocked and the outer-sphere process observed.\(^1\) For aluminum alloys, oxygen reduction is the primary cathodic reaction that occurs. H\(^+\) reduction can also be an important reaction, but occurs mainly in well-established actively corroding pits having very low local pH.\(^2\) An important question to answer regarding the inhibition of oxygen reduction is whether the mechanism involves blockage of adsorption sites or if the electron-transfer process itself is inhibited.

It is not the purpose of the present investigation to provide a detailed mechanism for either Cr\(^{VI}\) or O\(_2\) reduction. Rather, we sought to determine the relationship between the reactions of Cr\(^{VI}\) and the cathodic inhibition of the ORR under common field conditions encountered by AA2024-T3. The effects of Cr\(^{VI}\) on the ORR were examined, initially using Cu electrodes as models of Cu-containing intermetallic compounds and redistributed Cu. In addition, Cr\(^{VI}\) reduction was examined on Pt and GC electrodes to permit a wider potential range than possible with Cu.

**Experimental**

Barnstead NanoPure water with a resistivity of 18 MΩ cm was used for rinsing and solution preparation in all cases. NaCl (Fisher Scientific), K\(_2\)Cr\(_2\)O\(_7\) (Alfa Aesar), Ru(NH\(_3\))\(_6\)Cl\(_3\) (Aldrich), Na\(_2\)BO\(_3\) (Fisher Scientific), NaOH (Mallinckrodt), HCl (Fisher Scientific), CH\(_3\)CN (Mallinckrodt), and [CH\(_3\)(CH\(_2\))\(_3\)]BF\(_4\) (Aldrich) were reagent grade and used as received. Electrodes were commercial Pt or GC (Bioanalytical Systems) or were made from 0.5 mm diam copper wire (99.9% Cu, Aldrich). Copper wire electrodes were attached to standard copper electrical wire with silver epoxy resin (SPI Supplies/Structure Probe Inc.), and embedded in epoxy (Buehler). They were mechanically polished with successively finer Si:C papers (Buehler: 240, 400, 600, 800, 1200 grit), rinsed with water, and dried under a stream of hot air. Prior to each experiment, all electrodes were polished using Al\(_2\)O\(_3\) slurries (Buehler: 1.0, 0.3, and 0.05 μm) and rinsed with water.

Hydrodynamic and potentiostatic electrochemical measurements were performed using a Gamry Instruments PC/300 potentiostat/galvanostat/zero resistance ammeter with Framework (Version 3.11) and DC105 dc corrosion measurement software. Cyclic voltammetry was performed using a Bioanalytical Systems BAS100B electrochemical analyzer using BAS100W software. Experiments were performed using a standard three-electrode electrochemical cell. Experiments in water utilized Ag/AgCl as the reference electrode (potential = 0.197 V vs. normal hydrogen electrode, NHE) and all potentials quoted are with respect to this reference. Experiments in acetonitrile used Ag/Ag\(^+\) (filling solution: 0.1 M [CH\(_3\)(CH\(_2\))\(_3\)]BF\(_4\) in CH\(_3\)CN) as the reference electrode. Pt wire was used as the counter electrode. Unless otherwise noted, 0.1 M NaCl served as the background electrolyte for aqueous solutions and 0.1 M [CH\(_3\)(CH\(_2\))\(_3\)]BF\(_4\) for acetonitrile. Aerated refers to stirred solutions open to air and deaerated refers to solutions purged with purified argon for >15 min. Where noted, solutions were also saturated with extra O\(_2\). Solution additions were made using 0.05 M K\(_2\)Cr\(_2\)O\(_7\) (0.1 M total Cr\(^{VI}\)) in 0.1 M NaCl, and 10 mM Ru(NH\(_3\))\(_6\)Cl\(_3\) as noted in the text and figures. Unless stated otherwise, Cr\(^{VI}\) concentrations are stated as total [Cr\(^{VI}\)] in the form of HCrO\(_4\), CrO\(_4^{2-}\), CrO\(_2^{2-}\), etc. Unless noted, solutions were unbuffered except by Cr\(^{VI}\) itself, resulting in a pH of ~6.

Electrochemical experiments were performed as follows.

**Constant potential with Cr\(^{VI}\) injection.**—The solution was stirred with a magnetic stir bar and aerated or deaerated as noted. The electrode was held at −1.500 V for 60 s to reduce surface oxides before setting to the desired experimental potential. At a specified time an aliquot of analyte was injected into the solution. If the solution was deaerated the injection aliquot was deaerated also. The current response was monitored as a function of time.

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

**Potential step.**—The solution was stirred and aerated or deaerated as noted. The electrode was held at −1.000 V for 60 s to reduce surface oxides. The potential was then held at +0.750 V for a specified time period. Analyte species were added during this step if desired. The potential was then stepped to a specified value and held for a fixed time. The current response was monitored as a function of time. If the electrode was to be used in a subsequent experiment without additional polishing it was removed from the solution under potential control while being rinsed with water.

**Cyclic voltammetry.**—Experiments were performed in both aqueous and organic media. For aqueous media, the solution was quiescent and oxygenated. The potential was cycled from 0.000 V to either +1.000 or −1.000 V in pH 11 buffer (0.1 M BO\(_3^{-}\)/0.9 M NaCl) at 200 mV/s while observing current response. In some cases, the electrode was pretreated with Cr\(^{VI}\) as described in the Results section. For organic media experiments, the solution was quiescent and deaerated. The potential was cycled between −1.000 and +1.000 V at 1000 mV/s while observing current response.

**Results**

Figures 1 and 2 show results of constant/potential hydrodynamic experiments using a copper electrode held at −0.550 V. This potential was chosen due to its proximity to the OCP for AA2024-T3.
examined in the previous study. In Fig. 1 both aerated and deaerated solutions of 0.1 M NaCl are shown. The higher current density before chromate injection for the aerated solution is attributed to the reduction of dissolved oxygen. Upon injection of chromate (to \(-10 \text{ mM total Cr}^{VI}\)) the current immediately increases and then rapidly decreases for both solutions. The current density of each solution after chromate addition falls to less than 3% of its value prior to Cr VI addition. The inset in Fig. 1 shows the cathodic current spike more clearly and indicates that it occurs for both aerated and deaerated solutions, with approximately equal peak area. Table I lists the more clearly and indicates that it occurs for both aerated and deaerated solutions, with approximately equal peak area. Table I lists the lowest Cr VI additions, 0.5 and 0.05 M NaCl. At the indicated time Cr VI was injected to 0.1 M NaCl as shown. The higher current density of each solution may be caused by measurement difficulty rather than a trend. The decrease in current following the spike has two implications. First, the cathodic processes occurring on the Cu electrode before Cr VI addition are greatly inhibited by Cr VI or its reduction products. Second, the continuing reduction of Cr VI is inhibited after the current spike, so that a steady-state reduction current for Cr VI is not observed. Based on the known redox chemistry of Cr III and previous reports on electrochemical Cr VI reduction, we tentatively attribute the cathodic spike to reduction of solution Cr VI to an adsorbed film of Cr III oxyhydroxide. Figure 2 provides additional evidence for the presence of an irreversibly adsorbed species on the copper electrode. Run 1 shows the current spike and rapid inhibition upon addition of Cr VI to deaerated 0.1 M NaCl as observed in Fig. 1. Following this experiment the electrode was rinsed with water, replaced in fresh deaerated electrolyte, and monitored potentiostatically to yield run 2 in Fig. 3. The current is greatly decreased compared to run 1 (\(<0.01 \text{ vs. } \sim0.17 \text{ mA/cm}^2\)) despite the absence of Cr VI in solution. Upon injection of Cr VI, only a minute current spike is observed (spike height \(<0.02 \text{ mA/cm}^2\)) compared to a freshly polished electrode (spike height \(-2.5 \text{ mA/cm}^2\)). The results indicate that an adsorbed layer is formed upon the initial injection of Cr VI that remains after rinsing the electrode. Since the current spike observed upon Cr VI injection occurred immediately prior to the inhibition of reduction currents, the events taking place during the spike must be critical to the inhibition mechanism. A series of constant potential experiments were conducted to examine the spike area dependence upon potential, with the results presented in Table II. The applied potential has little effect on the spike area over the range studied for Cu electrodes. The average spike area from 26 injection experiments for the potential range of \(-0.200 \text{ to } -1.000 \text{ V} = 1.2 \times 10^{-3} \pm 0.61 \times 10^{-3} \text{ C/cm}^2\).

The potential dependence of O2 reduction was examined with hydrodynamic voltammetry, shown in Fig. 4 for copper, platinum, and GC electrodes. Platinum and GC electrodes offer wider potential ranges than Cu, particularly for positive potentials. Although the current densities for O2 reduction differ for the three electrodes, the potentials observed for O2 and Cr VI reduction follow similar trends as expected from thermodynamic considerations. In aerated Cr VI-free solutions, the O2 reduction current begins to increase be-

### Table I. Concentration dependence of Cr VI reduction spike on Cu electrode.

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Cr VI (M)</th>
<th>Spike area (C/cm²)</th>
<th>Cr reduced (nmol/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.600</td>
<td>5 \times 10^{-3}</td>
<td>2.2 \times 10^{-3}</td>
<td>7.5</td>
</tr>
<tr>
<td>-0.600</td>
<td>5 \times 10^{-4}</td>
<td>1.4 \times 10^{-3}</td>
<td>4.9</td>
</tr>
<tr>
<td>-0.600</td>
<td>5 \times 10^{-5}</td>
<td>1.6 \times 10^{-3}</td>
<td>5.5</td>
</tr>
</tbody>
</table>

* Final concentration of total Cr VI after injection into deaerated 0.1 M NaCl.

b Mean ± standard deviation for first four columns.
between −0.200 and −0.400 V on Cu (Fig. 4a). With constant stirring, the current increases as the potential is scanned negative, then levels off to a mass transported limited value. The same experiment in deaerated electrolyte yields little current until very negative potentials (negative of −1.2 V). The experiments were repeated (both aerated and deaerated) in the presence of 5 mM Cr$^{VI}$ with the results...
shown in Fig. 1 is observed, the current for the ORR is greatly
Cr VI -containing solutions, showing little current attributable to oxy-
However, Cr VI exposure has the
The area under these peaks in the potential range of +0.4 to +0.2 V are
approximately 2.8 × 10⁻³ C/cm² for GC and 6.5 × 10⁻⁴ C/cm² for Pt.
Cyclic voltammetry was used to examine the reversibility of the adsorption process and its effect on oxygen reduction current. The results are shown in Fig. 6. Scans A and B show the current response of a GC electrode in an oxygenated pH 11 buffer solution when scanned in both positive and negative directions. A wave corresponding to the reduction of oxygen is observed on the negative scan (scan B) at about −0.600 V. The electrode was then treated with Cr VI by scanning between 1.000 and −0.750 V (ending at the negative potential) in chromate ([Cr VI ] = 5 mM). After the GC electrode was removed, rinsed, and replaced in Cr-free electrolyte, negligible O₂ reduction current was observed on a negative scan (scan C). An anodic stripping peak was observed at about +0.600 V vs. Ag/AgCl on a subsequent positive scan (scan D), with an approximate area of 3.8 × 10⁻⁴ C/cm². After stripping, the O₂ reduction wave returned (scan E) with nearly identical current/potential response to the background scan (scan B).

The reduction peak in Fig. 5a was examined more closely using potential step experiments on GC electrodes. Figure 7 shows the results of potential steps from +0.750 V to the indicated potentials in 5 mM Cr VI , with the hydrodynamic voltammogram of Fig. 5a shown for comparison. The insets show current transients when the potential is stepped, and the arrows indicate the potential to which the step was made. If the potential was stepped to a value more positive than the Cr VI reduction peak of the voltammogram, no current spike was observed. When the potential was stepped to values negative of the hydrodynamic peak the current spike appears, with a shape that depends on potential. As the step becomes more negative the spike becomes narrower and the height increases. The area of the spikes shown in Fig. 7 are plotted in Fig. 8 (open squares) and listed in Table II. Despite significant variation in peak height, the area is fairly constant with potential in the range +200 to −400 mV. This limiting value corresponds to 8.1 × 10⁻⁴ C/cm² of reduction for seven potential steps in the range of +0.250 to −0.400 V.

The GC electrodes used in the potential step experiments of Fig. 7 were removed (under potential control), rinsed, and replaced in fresh aerated 0.1 M NaCl. They were then held at −1.000 V for 60 s to reduce any surface species. Following this pretreatment, the
potential was scanned from the OCP to $-1.300 \text{ V}$ at 5 mV/s with aeration and stirring. Figure 8 (solid circles) shows a plot of the current density at $-0.600 \text{ V}$ (from the hydrodynamic voltammetry) vs. the size of the potential step used to construct Fig. 7. Based on Fig. 4c, the current at $-0.60 \text{ V}$ in aerated, Cr-free electrolyte corresponds to O$_2$ reduction. Figure 8 shows a strong inverse correlation between the observed current spike area in Cr$_{VI}$ solution and the O$_2$ reduction current following Cr$_{VI}$ exposure. Stated differently, the Cr$_{VI}$ reduction spike area (Fig. 8) and Cr$_{VI}$ reduction peak (Fig. 5a) correspond directly to the onset of O$_2$ reduction inhibition. The results also indicate that Cr$_{VI}$ does not adsorb strongly enough at potentials positive of the reduction peak to remain on the electrode after rinsing. If it did, the constant/potential pretreatment before hydrodynamic voltammetry should reduce the adsorbed Cr$_{VI}$ layer to Cr$_{III}$ and some inhibition should have been observed.

Given the well-established electrocatalysis of O$_2$ reduction by chemisorption,$^{18}$ it is likely that part of the mechanism of ORR inhibition by chromate is blockage of adsorption sites by a Cr$_{III}$ layer. A Cr$_{III}$ layer may also be an effective barrier to electron transfer, even if chemisorption is not involved. To investigate this possibility, the reduction of Ru(NH$_3$)$_6$$^{3+}$ was studied on both copper and GC electrodes, and the oxidation of ferrocene in acetonitrile was examined on GC. Both systems are well-known examples of outer-sphere redox processes, in which adsorption to the electrode is not involved in the electron transfer.$^{21-23}$ Figure 9 shows the steady-state current for a GC electrode in a stirred solution of 1 mM Ru(NH$_3$)$_6$$^{3+}$ (in 0.1 M NaCl) at an initial potential of $+750 \text{ mV}$. When the potential is stepped to $-600 \text{ mV}$ at 200 s, the mass transport limited reduction of Ru(NH$_3$)$_6$$^{3+}$ produces a current density of $\sim0.7 \text{ mA/cm}^2$. At $t = 500 \text{ s}$, Cr$_{VI}$ was injected to a level of 5 mM, producing a current spike similar to those shown in Fig. 1. After this spike, the Ru(NH$_3$)$_6$$^{3+}$ reduction current decreased to 0.54% of its mass transport limited value. Ru(NH$_3$)$_6$$^{3+}$ reduction was inhibited on a copper electrode in a similar fashion (not shown). The reduction current for a stirred solution containing 0.5 mM Ru(NH$_3$)$_6$$^{3+}$ in the absence of Cr$_{VI}$ was $\sim0.8 \text{ mA/cm}^2$ at $-600 \text{ V}$ on a Cu electrode. After pretreatment with 5 mM Cr$_{VI}$ at a constant potential of $-600 \text{ V}$, the electrode was removed, rinsed, and replaced in fresh 0.5 mM Ru(NH$_3$)$_6$$^{3+}$ in the absence of Cr$_{VI}$. The Ru(NH$_3$)$_6$$^{3+}$ reduction current at $-0.60 \text{ V}$ decreased to $\sim3\%$ of its previous value. Figure 10 shows a cyclic voltammogram on a GC electrode in 1 mM ferrocene in acetonitrile (with 0.1 M tetrabutylammonium tetrafluoroborate background electrolyte), and for the same electrode after pretreatment with 5 mM Cr$_{VI}$ at a constant potential of $-600 \text{ V}$. The oxidation and reduction waves of ferrocene are clearly apparent for the untreated electrode but current on the treated electrode is nearly absent.

**Discussion**

Known chemistry of Cr$_{VI}$ leads to the conclusion that the product of Cr$_{VI}$ reduction at the electrode surface leads to Cr$_{III}$. Cr$_V$ (as CrO$_{2}^{2-}$) and Cr$_{IV}$ have been reported in pulse radiolysis experiments, but their lifetimes are in the submillisecond region in aqueous solutions.$^{24}$ They rapidly disproportionate to form Cr$_{VI}$ and Cr$_{III}$ but they have been characterized as transient species. Once Cr$_{III}$ has been formed, presumably as a hydrated Cr$^{3+}$ ion, it polymerizes to yield an insoluble Cr$_{III}$ oxyhydroxide.$^{8,25}$ The rate of the Cr$_{III}$ polymerization is strongly dependent on both Cr$_{III}$ concentration and pH, and it is not clear from the present experiments how fast the oxyhydroxide film forms after Cr$_{VI}$ reduction. However, it is clear that the resulting film is irreversibly adsorbed on the electrode surface, and is removed only at quite positive potentials ($>$0.5 V vs. Ag/AgCl).

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**Figure 7.** Potential-step experiments using GC electrodes in stirred, deaerated 0.1 M NaCl with 5 mM Cr$_{VI}$. The potential was held at $+0.750 \text{ V}$ and stepped to potentials indicated by the arrows. Insets show current response vs. time at the moment the potential was changed overlayed onto Fig. 5a. The vertical scale bar represents 0.6 mA/cm$^2$ for all insets, and each inset covers 60 s on the time axis.

**Figure 8.** Correlation between onset of Cr$_{VI}$ reduction spike and inhibition of oxygen reduction on GC electrodes. The Cr$_{VI}$ reduction spike area (○) is for potential step experiments from $+0.750 \text{ V}$ to the indicated value in 5 mM Cr$_{VI}$ (as in Fig. 7). The current density (●) value is taken at $-0.600 \text{ V}$ from a hydrodynamic voltammogram (as in Fig. 4) in aerated 0.1 M NaCl following the step to the indicated potential.

**Figure 9.** Current response of a GC electrode vs. time for stirred, deaerated 0.1 M NaCl containing 1 mM Ru(NH$_3$)$_6$$^{3+}$/0.1 M NaCl. At 200 s, the potential was stepped from $+0.750$ to $-0.600 \text{ V}$. At 500 s Cr$_{VI}$ was injected (to $-5 \text{ mM}$).
monolayer until the potential is negative of $-0.8 \text{ V vs. Ag/AgCl}$. Thus the Cr$_{III}$ layer causes more than 1.0 V of kinetic overpotential, shifting the Cr$_{VI}$ reduction from $+0.3$ to $-0.8 \text{ V vs. Ag/AgCl}$. This large shift is presumably what stops Cr$_{III}$ formation at one monolayer unless the electrode potential is very negative. It is important that the OCP of AA2024-T3 is sufficiently negative to form a monolayer, but not so negative that reduction continues past a monolayer. This property permits Cr$_{III}$ monolayer formation, but prevents bulk reduction of Cr$_{VI}$ in the CCC or primer layers.

The self-inhibition of Cr$_{VI}$ reduction by a Cr$_{III}$ film is apparently inconsistent with the formation of a thick (several micrometers) Cr$_{III}$-Cr$_{VI}$ mixed oxide film during CCC formation. For example, the Alodine 1200 process subjects AA2024-T3 to a solution containing $\sim 40 \text{ mM Cr}_{VI}$ plus F$^-$ ion and ferricyanide, and chromate film formation proceeds far beyond a monolayer to a thickness of 1-5 $\mu$m. However, the conditions for CCC formation are very different from those studied here, or those anticipated in the field. The high Cr$_{VI}$ concentration and Fe(CN)$_6^{3-}$ “accelerator” generate a high Cr$_{III}$ concentration at the alloy surface, which polymerizes to a Cr$_{III}$ oxyhydroxide. F$^-$ etching will continue to expose fresh Al and provide reducing sites for further Cr$_{VI}$ reduction, and the low pH in Alodine 1200 will retard Cr$_{III}$ polymerization. Furthermore, the present work dealt with Cu surfaces as models of Cu-rich phases in AA2024-T3. Raman and infrared microscopy have revealed that the CCC is significantly thinner over Cu-rich phases, compared to the Al matrix. Inhibition of Fe(CN)$_6^{3-}$ redox mediation or of Cr$_{VI}$ reduction by a Cr$_{III}$ film on Cu-rich phases would account for slow CCC formation on Cu, and is consistent with the present observations.

Figure 8 indicates a strong correlation between Cr$_{III}$ film formation and O$_2$ reduction inhibition. It is tempting to conclude that the Cr$_{III}$ film is acting as a “barrier” to the electrolyte, thus preventing O$_2$ reduction or alloy dissolution. However, a hydrated monolayer would be an imperfect barrier, and would permit electron tunneling and probably permeation by O$_2$. The results permit identification of some more definite properties of the barrier film that are important to inhibition of the ORR. First, the Cr$_{III}$ film should block sites for O$_2$ chemisorption, thus greatly reducing the electrocatalytic activity of the surface. Without chemisorption, slow kinetics decreases the effective O$_2$ reduction potential from approximately $+0.8 \text{ V (vs. NHE)}$ down to the outer sphere reduction potential of about $-0.5 \text{ V (vs. NHE)}$. At the outer sphere reduction potential, O$_2$ is reduced to superoxide, which disproportionates in solution to eventually form HO$_2$ or H$_2$O$_2$. With chemisorption, the catalytically inactive surface significantly decreases the driving force for O$_2$ reduction, resulting in partial or complete ORR inhibition.

Since Cr$_{VI}$ is itself an oxidizing agent, it may react with the same surface sites as O$_2$. As shown in Fig. 4, Cr$_{VI}$ reduction is slow in the absence of adsorption. It is quite likely that both O$_2$ and Cr$_{VI}$ adsorb to similar sites on Cu, presumably bare copper atoms. The difference is that O$_2$ is reduced and eventually desorbed, while Cr$_{VI}$ reduction leads to permanent occupation of the site. Since Cr$_{III}$ is substitution inert, the Cr$_{III}$ oxyhydroxide film is quite stable, and blocks O$_2$ adsorption indefinitely.

In addition to occupation of catalytic sites, a Cr$_{III}$ monolayer can also inhibit electron transfer. Numerous reports have shown that electrons can tunnel through nonconducting monolayers, with an exponential dependence of tunneling rate on monolayer thickness. For example, electron transfer through an aliphatic hydrocarbon monolayer yields a linear plot of the log of the electron transfer rate vs. layer thickness, with a slope of $-1 \text{ Å}^{-1}$. In other words, each Å of monolayer thickness causes a 1/e decrease in electron tunneling rate. A Cr$_{III}$ oxyhydroxide made under ultrahigh vacuum conditions is $\sim 4 \text{ Å thick}$.

By itself, such a monolayer would decrease the electron tunneling rate by $e^{-4}$ or to $\sim 2\%$ of the rate without the monolayer. However, the Cr$_{III}$ film may adsorb a layer of Cr$_{VI}$ to
form a Cr\textsuperscript{III}-Cr\textsuperscript{VI} mixed oxide.\textsuperscript{8} Such a bilayer would decrease the tunneling rate by at least another factor of e\textsuperscript{-3}. The strong inhibition of electron transfer to Ru(NH\textsubscript{3})\textsubscript{6} and from ferrocene apparent in Fig. 9 and 10 is consistent with decreased tunneling rates to outer sphere redox systems (presumably including O\textsubscript{2}/O\textsubscript{2-}), but the present results permit only a semiquantitative estimate of the magnitude of the effect.

The present conclusions add significantly to the emerging understanding of the origin of the un paralleled performance of chromate-based anticorrosion coatings. Past reports identified the storage and release of Cr\textsuperscript{VI} in conversion coatings and chromated primers as essential prerequisites for the “self healing” observed in chromate coatings. The release and migration of active Cr\textsuperscript{VI} species from a chromate coating to a newly formed defect appears to be essential for the long effective lifetimes of chromate coatings. The present results address the fate of Cr\textsuperscript{VI} once it migrates to a corroding defect. It is clear that reduction of Cr\textsuperscript{VI} leads to a stable, insoluble Cr\textsuperscript{III} film, which apparently does not grow beyond a monolayer in dilute, neutral aqueous solutions. The Cr\textsuperscript{VI} is a “site-directed” inhibitor in that it is adsorbed to an active site, then is reduced to permanently block the site. We stress ORR inhibition as a principal target of the inhibition effect. It is clear that reduction of Cr\textsuperscript{VI} leads to a stable, insoluble Cr\textsuperscript{III} film, which apparently does not grow beyond a monolayer in dilute, neutral aqueous solutions. The Cr\textsuperscript{VI} is a “site-directed” inhibitor in that it is adsorbed to an active site, then is reduced to permanently block the site. We stress ORR inhibition as a principal target of the inhibition mechanism. The unusual combination of storage, release, reduction, and inhibition by Cr\textsuperscript{VI} inhibitors make them outstanding agents for corrosion protection. During the search for environmentally benign alternatives, these properties should be duplicated as much as possible.

Conclusions

1. Cr\textsuperscript{VI} inhibits reduction of oxygen under conditions relevant to corrosion.
2. The mechanism of inhibition involves a reduction and irreversible adsorption of Cr\textsuperscript{III} to the surface of the electrode to block sites of adsorption. Once adsorption sites are blocked, O\textsubscript{2} chemisorption is prevented and O\textsubscript{2} becomes a much weaker oxidizing agent.
3. The Cr\textsuperscript{III} film is formed in near-monolayer quantities.
4. The Cr\textsuperscript{III} film is nonconductive and inhibits outer-sphere redox processes.
5. The Cr\textsuperscript{III} film formed inhibits further Cr\textsuperscript{VI} reduction until very negative potentials can drive outer sphere electron transfer.

6. The reduction of Cr\textsuperscript{VI} and inhibition of O\textsubscript{2} reduction occur over the entire potential range relevant to corrosion of AA2024-T3 alloys.

Acknowledgments

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