Electron-Transfer Reactions on Passive Chromium

Thomas P. Moffat, Hongjun Yang, Fu-Ren F. Fan, and Allen J. Bard

Department of Chemistry, University of Texas, Austin, Texas 78712

ABSTRACT

The kinetics of electron transfer between electrochemically passivated chromium and several outer-sphere redox couples have been investigated as a function of passive-film thickness, $d = 5$ to $25 \text{Å}$, in $1\text{M H}_2\text{SO}_4$. The apparent rate of electron transfer decreased exponentially with increasing thickness of the passivating overlayer. Similarly, during potentiostatic film growth, the electron-transfer rate decreased logarithmically with time, $t$, as a consequence of the film-growth kinetics, since $d$ varies with $\log(t)$. These relationships indicate an electron-tunneling controlled process. However, variations in the film thickness and defects result in electron transfer occurring at distributed sites of enhanced tunneling probability, making a meaningful quantitative analysis difficult.

Chromium plays an essential role in the corrosion resistance of many engineering alloys. Protection results from the formation of a thin, $5-25 \text{Å}$, passivating oxide film. The electrochemical characteristics of this electrode are determined by reactions involving both ions and electrons. The passive film blocks ion-transfer processes associated with metal dissolution. The kinetics of film formation indicate that ion transport across the protective film occurs by a high field mechanism. To sustain the high field condition, the film must be electronically insulating. In contrast, the reversible potential and associated redox kinetics of the Fe$^{2+}$/Fe$^{3+}$ electron-transfer reaction have been readily measured on a passive chromium electrode. The relatively facile nature of this reaction leads to the contradictory suggestion that the passive film is electronically conducting. Theoretical studies address this question of film conductivity by invoking electron tunneling through the thin depleted semiconducting oxide film. Chromium with its native oxide has been used previously to construct solid-state tunneling junctions. Similarly, the tunneling process has been used with varying degrees of rigor, to describe redox reactions occurring on oxidized tin, iron, nickel, chromium, stainless steel, and SnO$_2$. However, no detailed electron-transfer studies have been performed on electrochemically passivated chromium.

Much effort has been expended to resolve the influence of tunneling in heterogeneous electron-transfer reactions. Many of these studies have been hampered by complications arising from the probing redox couple (e.g., O$_2$/H$_2$O on Pt$^{0}$) or ambiguities associated with the tunneling barrier (e.g., pinhole defects in alkylthiol barriers on gold). The influence of the tunneling process should be most evident for films ranging from 5 to 30 Å in thickness. This corresponds precisely to the thickness range of the passivating film found on chromium. The rate of charge transfer across this barrier should reflect the electronic properties of the film as well as its thickness. Here we describe the kinetics of electron transfer between several simple outer-sphere redox couples and a chromium electrode as a function of passive-film thickness.

Overview of the electrochemistry of chromium.—Combined surface analytical and electrochemical studies have generated significant information concerning the passive state of chromium. The characteristic i-E curve for chromium in sulfuric acid is given in Fig. 1. The active-passive transition, associated with a five-orders-of-magnitude decrease in reactivity, is apparent at $\sim -0.439 \text{ V}$. Active dissolution yields chromous ions, while passivation is associated with the formation of the blocking passive layer. A small cathodic current loop, due to proton reduction on the...
passive surface is observed in the region of -0.40 V. The anodic current in the passive regime is almost independent of potential. X-ray and optical spectroscopic studies indicate that the passive film is a hydrated chromic oxy-hydroxide, CrOOH-(H_2O)_x. The thickness of the film is a linear function of potential (-15.5 A/V), while the electrode capacitance is inversely proportional to potential. Therefore, in agreement with high-field growth kinetics, the passive overlayer may be described as a simple dielectric with ε ~ 25. The film is stable against reduction, as long as the potential is not swept into the active regime (i.e., more negative than -0.45 V). At more positive potentials (>0.8 V), transpassive dissolution occurs with the production of soluble chromate. The onset of this reaction also is associated with the generation of higher valent species in the film as revealed by voltammetric measurements.1

**Experimental Procedure**

High-purity chromium was provided by F. A. Schmidt of Ames Laboratory, Ames, Iowa. Mass spectroscope analysis revealed that the arc-melted specimen contained 48 ppm oxygen and was 99.988% pure with respect to metals. The average grain diameter was 0.4 cm. For most thin-film solids, the detailed properties of the passive layer are a distinct function of the formation conditions; consequently, a direct comparison between data sets requires careful specification of these parameters. The following film-growth program was used. Initially the electrode was activated in the test solution at -0.8 V for at least 15 s. The potential then was stepped to the film-growth potential of interest, and after 1 h, the electron-transfer experiments were performed. The potential was increased by 100 mV increments (without reactivating) to grow thicker films for successive experiments. In complementary work, the electron-transfer kinetics were measured as a function of time and temperature for a given potential.

**Electron-transfer kinetics.**—The kinetics of three different outer-sphere redox couples were examined on passivated chromium

\[
\text{Ru(NH}_3)_6^{2+} + e^{-} \rightleftharpoons \text{Ru(NH}_3)_6^{3+} \quad E^{\circ} = -0.234 \text{ V vs. SCE}
\]

\[
\text{Co(phen)}^{2+} + e^{-} \rightleftharpoons \text{Co(phen)}^{3+} \quad E^{\circ} = 0.064 \text{ V vs. SCE}
\]

\[
\text{Os(bpy)}^{3+} + e^{-} \rightleftharpoons \text{Os(bpy)}^{2+} \quad E^{\circ} = 0.553 \text{ V vs. SCE}
\]

where phen represents 1, 10-phenanthroline; bpy, 2,2'-bipyridine. These reactions exhibit well-defined voltammetric behavior on gold. Consequently, gold ultramicroelectrodes were used to measure the intrinsinc rate of these systems using cyclic voltammetry. The heterogeneous kinetics of these reactions are defined by the formal potential, \(E^{\circ}\), standard rate constant, \(k_{\text{on}}\), and transfer coefficient, \(\alpha\). The \(k_{\text{on}}\) for Ru(NH_3)_6^{2+} at 50 \(\mu\)m diameter ultramicroelectrode, was 0.85-5.5 cm/s. Table I lists the experimentally observed peak splitting (\(AE_p\)) values for a variety of sweep rates. These measurements were sensitive to the electrode pretreatment. However, reasonably precise results were obtained if the specified cleaning step was performed prior to each measurement. Voltammetry performed at high sweep rates is systematically distorted by solution resistance and electrode capacitance. Therefore, the upper limit of the rate constant for Ru(NH_3)_6^{2+} corresponded to the sweep rate at which deviation from reversible behavior was first noted, i.e., 400 V/s. The \(k_{\text{on}}\) values listed in Table I agree favorably with those derived from Tafel plot measurements on various metal electrodes, e.g., Au, Ag, Pt, Pd, Cu, and Hg, under turbulent pipe-flow conditions (0.5-1.2 cm/s). The cathodic and anodic transfer coefficients were 0.51 ± 0.05 and 0.41 ± 0.04, respectively.15 The diffusion coefficient, \(D\), of Ru(NH_3)_6^{2+}, determined from the steady-state diffusion-limited current at 50 and 100 \(\mu\)m diameter ultramicroelectrodes, was 1.18 x 10^-5 cm^2/s at 30°C. The temperature dependence of the diffusion coefficient was evaluated by examining the peak current of the reversible voltammograms, between 0°C and 30°C, yielding (with \(T\) in K)

\[
D(T) = 5.3 \times 10^{-5} - 1.3 \times 10^{-2} \left(\frac{1}{T}\right)
\]

Similarly, \(k_{\text{on}}\) for Os(bpy)_3^{2+}, at 30°C, was 0.38-3.2 cm/s, while that for Co(phen)_3^{2+} was 0.066 cm/s. In a similar fashion, the rate of electron transfer on passivated chromium, with varying film thickness, was characterized by an effective standard rate constant, \(k_{\text{on}}\), and transfer coefficient \(\alpha\). These parameters were measured by cyclic voltammetry or steady-state log \(i\) vs. \(E\) (Tafel) analysis.16

**Cyclic voltammetry.**—The kinetics of Ru(NH_3)_6^{2+} and Os(bpy)_3^{2+} on gold and passived chromium were measured by voltammetry performed over a range of potential sweep rates, \(v\), of 0.005-1000 V/s. The effective rate constant and transfer coefficient were evaluated by comparing the data with digital simulations based on the well-developed theory of quasi-reversible one-electron-transfer reactions.15 To expedite this process, theoretical working curves were constructed based on four experimental parameters, \(AE_p = E_p - E_mE_p - E_m = E_m/v,\) and \(\Psi(E)\), vs. the logarithm of the dimensionless parameter \(\Lambda\), where \(E_p\) and \(E_m\) are the cathodic and anodic peak potentials, \(E_m/v\) is the half-peak potential, \(\Psi(E)\) is the current function, defined as

\[
\Psi(E) = \frac{nFACoD^{1/2}}{RT} \left(\frac{nF^{1/2}}{RT}\right)^{1/2} \left(\frac{i}{RT}\right)^{1/2}
\]

and \(\Lambda\) is the dimensionless rate parameter

\[
\Lambda = \frac{k_{\text{on}}}{D^{1/2} \left(\frac{nF}{RT}\right)^{1/2} \left(\frac{i}{RT}\right)^{1/2}}
\]

where \(n\) is the number of equivalents, \(A\) is the geometrical electrode area, and \(C_0\) is the bulk concentration. This was
quasi-reversible one-electron-transfer reaction (curve c) occurring at these potentials. The transformation of the 

crOOH (H2O) dielectric film voltammogram essentially represents the capacitive discharge and charging currents that were not explicitly treated in this analysis.

Tafel analysis.—For [Co(phen)3]3+2−, the rate of electron transfer on passive chromium was much slower than on gold. In this instance k\textsubscript{et} and \alpha\textsubscript{et} were obtained easily from a Tafel plot, log(i) vs. E, assuming that the concentration of redox species near the electrode was unperturbed over the potential range investigated. The best-fit linear slope of the curve gives \alpha\textsubscript{et}

\[
\frac{\partial E}{\partial \log(i)} = -\frac{2.303RT}{\alpha_{et}F}
\]

while the intercept with the potential yields i\textsubscript{e}, the exchange current, and k\textsubscript{et} (cm/s)

\[
k_{et} = \frac{i_{e}}{nFE_{app}}
\]

Results

Passive chromium.—The redox behavior of the as-grown passive film on chromium was investigated by voltammetry. For films grown at potentials less than 0.544 V, the voltammogram essentially represents the capacitive discharge and charging of the CrOOH (H2O) dielectric film (Fig. 2). At higher potentials, E > 0.550 V, the film undergoes further oxidation as shown by a reduction peak on the “negative going” scan. Capacitance and chronoamperometric measurements are consistent with a change in film composition occurring at these potentials.1,2 The transformation may be assigned to either the conversion of Cr\textsuperscript{3+} to Cr\textsuperscript{4+} by electron-proton injection/ejection and/or to the formation of a Cr\textsuperscript{3+}/Cr\textsuperscript{5+} mixed valent oxide.1,2

Ru(NH\textsubscript{3})\textsubscript{3}2+2−.—A typical capacitive voltammogram for chromium passivated at 0.444 V is shown in Fig. 3(b). When the same experiment is performed in a solution containing 1 mM Ru(NH\textsubscript{3})\textsubscript{3}Cl\textsubscript{2}, reduction and oxidation waves for the redox couple appear (Fig. 3(a)). A simulation for a simple quasi-reversible one-electron-transfer reaction (curve c) agrees favorably with the data (curve a). Similar results were obtained for films grown at other potentials. The apparent rate constants, k\textsubscript{app}, were extracted from the voltamograms (Fig. 4). The best fit between experiment and theory was for a transfer coefficient of 0.50 ± 0.05. The effective rate constant, k\textsubscript{et}, decreased exponentially with an increase in the potential of film formation. The k\textsubscript{et} values plotted represent the average obtained from experiments performed at several different scan rates. The whole experiment was repeated four times, and the k\textsubscript{et} values were reproducible to the extent indicated by the error bars in Fig. 4.

Os(bpy)\textsubscript{3}2+2−.—The same experiments were performed with 1 mM Os(bpy)\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2} as the probing redox species. In this instance peak splitting, AE\textsubscript{p}, alone was used to estimate k\textsubscript{app}. The derived rate constant was identical to that measured for Ru(NH\textsubscript{3})\textsubscript{3}2+2− under similar conditions. As shown in Fig. 4, the rate decreased exponentially with increasing film-formation potential. However, k\textsubscript{app} values for this couple, with a more positive E\textsubscript{p}, are not as precise as those for Ru(NH\textsubscript{3})\textsubscript{3}2+2−. The measurement of k\textsubscript{et} for films grown below the formal potential of Os(bpy)\textsubscript{3}2+2− required that the potential be swept in the positive direction where additional film growth may occur. Moreover, the rate constants derived for films grown above the formal potential are complicated by the oxidation of the redox couple during film growth. This perturbs the boundary conditions utilized in the analysis of the voltammetric data. Finally, at potentials greater than 0.55 V the passive film itself exhibits some redox activity. Thus, the rate constants measured in this regime are probing a mixed-valent oxide, while in the case of the Ru(NH\textsubscript{3})\textsubscript{3}2+2− data this mixed valency is removed prior to the electron transfer measurement.

Co(phen)32+2−.—The slower kinetics of the Co(phen)32+2− couple facilitates the simple application of Tafel analysis. The log(i)-E plots for films formed at various potentials in a 1 mM Co(phen)3Cl\textsubscript{2} solution are given in Fig. 5. These data also reveal the redox activity of the passive films formed above +0.55 V. The effective rate constant and transfer coefficient obtained from the Tafel plots are summarized in Fig. 4 and 6. In agreement with the results for the other redox couples, the rate of electron transfer decreased exponentially with increasing film-formation potential. Simultaneously, the apparent cathodic transfer coefficient decreased monotonically from 0.5. This deviation may result from measuring the slope at different over-
Potential of Film Formation, V(SCE)

Fig. 4. The apparent rate constant as a function of the film-growth potential. The error bars pertain to variations of the rate constant for Ru(NH$_3$)$_6^{3+/2+}$, determined from four independent experiments.

Dependence of $k_{et}$ on film thickness. — As noted in Fig. 1, the thickness of the passive film is a monotonic function of the potential of film formation. The thickness data were obtained from a recently published x-ray photoemission (XPS) study. While a degree of uncertainty surrounds the precise value of film thickness used in this study, the favorable comparison between the XPS data and prior ellipsometry data is encouraging. Consequently, the kinetics of electron transfer can be correlated to the passive-film thickness (Fig. 7). This reveals that the electron-transfer rate is exponentially dependent on film thickness,

$$k_{et} = \gamma \exp(-\beta d)$$  \[6\]

with $\beta$ ranging from 0.215 Å$^{-2}$ for Ru(NH$_3$)$_6^{3+/2+}$ and Os(bpy)$_3^{3+/2+}$ to 0.164 Å$^{-1}$ for Co(phen)$_3^{3+/2+}$. For the Ru(NH$_3$)$_6^{3+/2+}$ data, extrapolation of the curve to zero film thickness yields an intrinsic rate constant near that observed on the gold electrode. A similar relationship holds for the Os(bpy)$_3^{3+/2+}$ data, which indicates the dominating influence of film thickness as opposed to differences in the relative energetics of the respective redox couples. The Co(phen)$_3^{3+/2+}$ rate data exhibit a similar dependence on film thickness; however, extrapolation to zero thickness gives a rate constant two orders of magnitude below the value measured for gold. This discrepancy might arise from the differing measurement schemes employed. Specifically, the concept of active area is at issue. In the Tafel analysis (Co(phen)$_3^{3+/2+}$: Cr) the rate constant is explicitly dependent on the electrochemically active area while peak splitting, $\Delta E_p$, which was used predominantly in the analysis of the voltammetric data (Ru(NH$_3$)$_6^{3+/2+}$, Os(bpy)$_3^{3+/2+}$: Cr, Au and Co(phen)$_3^{3+/2+}$: Au) is not a function of the active area.

Rate constant measured during film growth. — The relationship between the kinetics of electron transfer and film potentials, i.e., sampling of Tafel plot curvature as predicted by Marcus theory. In this case the apparent rate constant will be artificially high.
thickness also can be demonstrated by monitoring the redox kinetics during film growth. At a given potential, passive film growth occurs as a logarithmic function of time, i.e., \( d = \log(t) \). Electron-transfer kinetics were measured by interrupting potentialistatic film growth with cyclic voltammograms probing \( \text{Ru(NH}_3)_6^{3+/2-} \) reduction and oxidation. In these experiments, a freshly polished electrode was prepared by first activating at \(-0.8 \text{ V}\) followed by passivation at \(-0.156 \text{ V}\). One hour later the potential was stepped to the value of interest, e.g., \(+0.344 \text{ V}\), and cyclic voltammograms such as those in Fig. 3 were obtained as a function of time. We used a scan rate of 0.1 V/s, although higher temporal resolution could be obtained with a faster scan rate. The rate constant was evaluated by considering peak splitting, \( \Delta E_p \), of the voltammograms. The logarithm of the rate constant was found to decrease linearly with the logarithm of time giving a slope of \(-0.2 \) (Fig. 8). Similar results were obtained for a film grown at 25°C with the electrolyte open to the atmosphere.

**Influence of temperature.**—The effect of temperature on the redox kinetics for \( \text{Ru(NH}_3)_6^{3+/2-} \) was investigated over a range of 35°C using the same electrodes as those used for the film growth study. Typically, the electrode was held at a given potential for \(-20 \text{ h}\) at 30°C to produce an oxide film of given thickness, \( d \). Voltammograms were taken of the electrochemical cell was cooled to \(-60°C\) and brought back to 30°C. Temperatures greater than 30°C (the temperature of film growth) were not examined since additional film growth occurs. The thermal cycle took approximately 1 h to complete. Rate constants were obtained from the \( \Delta E_p \) values (Fig. 9). The precision of these measurements was not great due to a maximum variation in the peak splitting of \(-10 \text{ mV}\) over the temperature range investigated. This difference is the same order of magnitude as the normalization constant (temperature-dependent diffusion coefficient, etc., Eq. 1, 3) used to derive the rate constant \( k_{et} \) from the dimensionless rate parameter \( \Lambda \). Significant scatter is apparent among the three data sets with the activation energy ranging from a maximum of \(0.15\) to \(0.0 \text{ eV}\). The solid line in Fig. 9 is the thermal dependence predicted by the model described in the Discussion section. The slope of this curve corresponds to an activation energy (\(0.15\) eV), while the absolute magnitude of the curve was arbitrarily set for easy comparison with the experimental data.
Fig. 7. The apparent rate constant as a function of passive-film thickness. The line through the Ru(NH₃)₆³⁺/²⁺ data corresponds to β = 0.215 Å⁻¹ while β = 0.164 Å⁻¹ for the Co(phen)₃³⁺/²⁺ data. The intrinsic rate constant on gold is indicated on the film-thickness axis, at d = 0.

Discussion

Qualitatively, the relationship between the rate constant and film thickness (Fig. 7) may be a consequence of electron tunneling through the thin dielectric passive film. However, if there is significant spatial variation in film thickness, the passivated electrode also can be treated as a partially blocked electrode. These two ideas will be developed below.

Electron tunneling.—In the case of elastic tunneling through a homogeneous barrier, the constant β (Eq. 6) defines the blocking character of the film. To develop a quantitative description of β requires a physical model of the passive oxide interface. Figure 10 shows a schematic of the electronic structure of the interface. We used this schematic to generate a simple equation for the electrode kinetics based on the fluctuating energy model that is analogous to the more sophisticated transfer Hamiltonian formalism developed by Schmickler and Ulstrup. We assume that the effective oxide bandedges at the film/solution interface are fixed and determined by the solution pH via OH⁻/H⁺ equilibria. This is equivalent to the potential drop across the Helmholtz layer at the oxide/solution interface being independent of the potential of the passive electrode with respect to the reference electrode, i.e., for the voltammetric experiments a potential change of the metal, with respect to the reference electrode, causes a change in the electric field only within the oxide film. Prior impedance and polarization measurements support this assertion and also demonstrate that the dielectric constant of the film is independent of thickness. Electron transfer proceeds by tunneling between occupied and unoccupied states of equal energy in the metal and the electrolyte. The probability of finding occupied states in the metal electrode is described by the Fermi-Dirac distribution function

\[ F(\varepsilon, \eta) = \frac{1}{1 + \exp \left( \frac{\varepsilon + e\eta}{kT} \right)} \]

where \(\eta\) is the overpotential (\(\eta = E - E^{\text{red}}\)), \(e\) is the electronic charge, and \(\varepsilon\) is the electron energy in the metal relative to the Fermi level of the redox couple. In the electrolyte, the electronic states are localized at the reduced and oxidized species. The energy depends on the configuration of the reactive complex. Thermal fluctuations produce a Gaus-
Fig. 10. A schematic of the electronic structure of the passive electrode for a film grown at 0.6 V.

Fig. 11. An example of a Tafel plot calculation performed for a range of film thickness, for $\epsilon_B = 1.5$ eV and $\eta_m = 0.1$ using Eq. 11. Multiplication of the current function by a pre-exponential constant of 10$^7$ or 10$^4$ and examination of the rate at $\eta = 0$ yields a favorable comparison with the absolute value of the data given in Fig. 4.
coefficient is related to the magnitude of the barrier, and this is a function of the formal potential of the probing redox couple as revealed in Fig. 10.

While reliable independent measurements of either of these parameters are limited, photoelectrochemical studies of the passive film on chromium indicate an optical gap ranging from 2.4 to 3.3 eV depending on the film-formation conditions. Both anodic and cathodic photocurrents were reported. In a similar vein, these parameters are limited, photoelectrochemical studies of the redox couple as revealed in Fig. 10. This is a function of the formal potential of the probing electron.

While tunneling theory and the partly blocked electrode formalism must be combined to treat the data realistically. A tunneling barrier was developed by building up a film through random deposition of atoms. Consequently, the Poisson distribution function was used to describe the variation in film thickness. The thickness, \( d_{\text{average}} \), derived from capacitance measurements was close to that of the mean value, \( d_{\text{average}} \). Thus, the effective tunneling distance, \( d_{\text{tunnel}} \), was found to be equal to one half of that determined by capacitance, \( d_{\text{tunnel}} \). Good agreement was found between this model and experimental data for Al-AlOx-Al tunnel junctions. This problem has been treated theoretically by Chow and Hurch. A tunneling barrier was developed by building up a film through random deposition of atoms. Consequently, the Poisson distribution function was used to describe the variation in film thickness. The thickness, \( d_{\text{average}} \), derived from capacitance measurements was close to that of the mean value, \( d_{\text{average}} \). Thus, the effective tunneling distance, \( d_{\text{tunnel}} \), was found to be equal to one half of that determined by capacitance, \( d_{\text{tunnel}} \). Good agreement was found between this model and experimental data for Al-AlOx-Al tunnel junctions. Thus a revised treatment of the passive interface would involve a tunneling process with appropriate corrections made for the active area and the corresponding film thickness at such sites. Further progress on this issue requires a more direct experimental assessment of the active surface regions. Studies by scanning electrochemical microscopy may provide an approach to this issue.

**Applications.**—The strong dependence of the electron-transfer rate on the conditions of film formation suggests possible applications for the chromium electrode. Currently there is interest in modifying electrodes with Langmuir-Blodgett and self-assembling organic layers. These
films bring an array of unique interfacial properties to electrochemistry. For example, in a manner analogous to passive chromium, the rate of electron transfer across hydroxyl-terminated alkylthiol layers on gold is a function of the length of the alkyl chain. These structures have been proposed for examining high rate constants, as well as for probing the electronic state densities of solvated redox species. Similarly, it is possible to impart novel characteristics to metal oxide surfaces by forming self-assembling monolayers (SAM) by adsorption of appropriate precursors. The ability to form complex, addressable, chemical microstructures also has been demonstrated, e.g., an array of alternating Au and Al/Al2O3 band electrodes with chemically distinct self-assembled organic overlays. The influence of the passive chromium oxide layer on electron-transfer kinetics for a similar interdigitated array of Au and Cr electrodes recently was demonstrated by scanning electrochemical microscopy. Thus, careful pretreatment of the chromium electrode could provide an added degree of freedom in the design of metal/metal oxide/SAM interfaces for electrochemical applications (i.e., give a rate constant for electron transfer which is a function of the passive-film thickness in series with the characteristics of the underlying SAM).

Another possible extension of this study derives from interest in techniques for examining the passivity of metals. During the last fifteen years, significant advances in understanding have been driven by the development of UHV techniques, e.g., x-ray photoelectron spectroscopy. However in many instances the ex situ nature of the UHV experiment perturbs the interface under study leading to artifacts which are difficult to resolve. Studies of the kinetics of electron transfer should provide a sensitive measure of such changes. Thus, redox measurements performed before and after the ex situ UHV experiment should yield an assessment of such changes.

**Conclusion**

The kinetics of electron transfer between electrochemically passivated chromium and several outer-sphere redox couples have been investigated as a function of passive film thickness, d = 5 to 25 Å. The thickness of the dielectric passive overlayer can be defined by using rigorously controlled film-formation conditions. The redox rate decreased exponentially with increasing thickness of the passivating film. Similarly, during potentiostatic film growth, the electron-transfer rate decreases logarithmically with time, and this is correlated with the film-growth kinetics, i.e., d is proportional to log(t). These observations may be attributed to either a homogeneous tunneling barrier or a partly blocked electrode. However these formalisms are highly simplified, and the basic tenets of each model were violated. Nonetheless, a combination of these ideas can explain the experimental results qualitatively, although a meaningful quantitative treatment remains elusive until the precise microstructural nature of the film is defined clearly.

**Acknowledgment**

The support of the Office of Naval Research is gratefully acknowledged. The authors wish to thank D. O. Wipf and D. T. Pierce for helpful discussions.

Manuscript submitted March 9, 1992; revised manuscript received June 1, 1992.

The University of Texas assisted in meeting the publication costs of this article.

**LIST OF SYMBOLS**

- **A**: Electrode area  
- **D**: Tunneling constant  
- **C**: Concentration of redox species  
- **D**: Thickness of passive film  
- **D_ox**: Probability distribution of energy states in the oxidized species  
- **D_red**: Probability distribution of energy states in the reduced species  
- **ΔE_p**: Absolute difference between E_p and E_c  
- **E**: Electrode potential  
- **E^***: Formal potential  
- **E_p**: Potential of anodic voltammetric peak  
- **E_c**: Potential of cathodic voltammetric peak  
- **ε**: Electronic energy  
- **e**: Electric charge of electron  
- **F**: Faraday’s constant  
- **Γ** (n, η): Fermi function; density of occupied states in the solid  
- **h**: Planck’s constant  
- **i_{ex}:** Exchange current  
- **j**: Current density  
- **k**: Rate constant for redox couple on an inert electrode  
- **k^{ref}_{Cr}**: Rate constant for redox couple on passivated chromium  
- **κ**: Tapping coefficient for a redox couple on an inert electrode  
- **κ^{ref}_{Cr}**: Transfer coefficient for a redox couple on passivated Cr  
- **λ**: Reorganization energy of a redox couple  
- **μ**: Free electron mass  
- **n**: Number of electrons or equivalents  
- **F**: Ratio of the effective mass to the free-electron mass, m^*_e/m_e  
- **R**: Gas constant  
- **T**: Temperature  
- **α**: Transfer coefficient for a redox couple on an inert electrode  
- **κ_α**: Pre-exponential factor for the tunneling probability  
- **κ_β**: Tunneling probability  
- **κ_0**: Pre-exponential factor for the tunneling probability  
- **Ψ(E)**: Current function  
- **A**: Dimensionless rate parameter

**REFERENCES**

Corrosion Inhibition of Mild Steel by Cationic and Anionic Polymers in Cooling Water System

I. Sekine,* M. Sanbongi, H. Hagiuota, T. Oshibe, and M. Yuasa

Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, 2641, Yamazaki, Noda, Chiba 278, Japan

Experimental

Materials. —Inhibitors. —The inhibitors used were polyethyleneimine (PEI, Wako Pure Chemical Industries), its derivative (PEID, Diaflo), polyarylamide (PAAm, Nitto Boseki), and polydicyanodiamide derivative (PDCDA, Diaflo) as cationic polymers, and polymaleic acid derivatives (PMAD), polyacrylic acid derivative (PAAD) and polyacrylic acid (PAA) as anionic polymers as shown in Table I. The cationic polymers were commercially purchased, and the anionic polymers were synthesized as follows.

Maleic acid (HOOC—CH=CH—COOH, MA, Wako Pure Chemical Industries) was reacted with α-olefin compounds and 1,4-butadiene. The crude products were purified by reprecipitation and dialysis to give poly(maleic acid-co-α-olefin) and poly(maleic acid-co-1,4-butadiene) (polymaleic acid derivatives, α-olefin type; PMAD-1 and PMAD-2 and 1,4-butadiene type; PMAD-3). Acrylic acid (CH2=CH—COOH, AA, Wako Pure Chemical Industries) was reacted with sodium styrene sulfonate (CH2=CH—CH2—SO3Na, NaSst) in distilled water containing ammonium peroxo-disulfate (Wako Pure Chemical Industries) and sodium hydrogen sulfite (NaHSO3, Wako Pure Chemical Industries) at 55 to 90°C for about 30 min in a nitrogen atmosphere. The crude product