Variable-Amplitude Galvanostatically Modulated Impedance Spectroscopy as a Tool for Assessing Reactivity at the Corrosion Potential Without Distorting Temporal Evolution of the System

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ABSTRACT
An algorithm was developed in which galvanostatic regulation of electrochemical impedance measurements is conducted with an amplitude of current perturbation that is adjusted at each frequency to yield a desired variation in potential. Measurements of three previous frequencies are used to estimate the value of the impedance at the target frequency. The algorithm was implemented using a graphically based general interfacing software on a personal computer. Experimental results illustrated artifacts that can arise as a result of galvanostatic measurement with a fixed current amplitude or as a result of potentiostatic measurements for systems with a changing corrosion potential. A demonstration was presented of the use of variable-amplitude galvanostatically modulated impedance spectroscopy to monitor corrosion of copper in synthetic seawater.

KEY WORDS: copper, corrosion potential, current, impedance, linearity, potentiostatic testing, variable-amplitude galvanostatically modulated impedance spectroscopy

INTRODUCTION
Electrochemical impedance measurements usually are performed under potentiostatic regulation. In these measurements, the potential is a fixed value with a superimposed (often sinusoidal) perturbation of fixed amplitude. This approach is attractive because linearity in electrochemical systems is controlled by potential. For example, a Taylor series expansion for current density at the open-circuit condition using the Butler-Volmer equation:

$$i = i_0 \left( e^{\alpha_a F \eta_s / RT} - e^{-\alpha_c F \eta_s / RT} \right)$$

yields:

$$i = i_0 \left( \alpha_a + \alpha_c \frac{F \eta_s}{RT} + \frac{(\alpha_a^2 - \alpha_c^2)}{2} \left( \frac{F \eta_s}{RT} \right)^2 \right.$$

$$+ \frac{(\alpha_a - \alpha_c)^3}{6} \left( \frac{F \eta_s}{RT} \right)^3 + O(\eta_s^4) \right)$$

where $i_0$ is the exchange current density; $\alpha_a$ and $\alpha_c$ are the apparent transfer coefficients for the anodic and cathodic reactions, respectively; $\eta_s$ is the surface overpotential; $F$ is Faraday's constant; $R$ is the gas constant; $T$ is absolute temperature; and the remaining terms are of the order of $\eta_s^2$ or smaller. For typical parameter values for a symmetric reaction ($\alpha_a = \alpha_c = 0.5$) and for $T = 298$ K, the second term is equal to zero, and the third term is equal to 1% of the first (linear) term for potentials of $\sim 13$ mV. Potential perturbations of 5 mV to 20 mV are used often.
The need for a small-amplitude potential perturbation is even greater for typical corrosion studies using impedance measurements conducted at the corrosion potential. If hydrogen evolution can be neglected close to the corrosion potential, oxidation of the metal is balanced by the mass transfer-limited reduction of oxygen. Thus, total current density is:

$$i_n = i_{oM} \exp \left[ \frac{\alpha_M F}{RT} \left( V - V_M \right) \right] - i_{o2}$$

(3)

where $\alpha_M$ is the apparent transfer coefficient for oxidation of the metal, $i_{oM}$ is the exchange current density for the oxidation of the metal, $V_M$ is the equilibrium potential for the oxidation reaction, $V$ is the applied potential, and $i_{o2}$ is the mass transfer-limited current density associated with reduction of oxygen ($O_2$). At the corrosion potential $V = V_{corr}$, the net current $i_n$ is equal to zero, and:

$$V_{corr} = V_M + \frac{RT}{\alpha_M F} \ln \left( \frac{i_{o2}}{i_{oM}} \right)$$

(4)

An increase in the mass transfer-limited current for oxygen reduction will shift the corrosion potential to more positive values and, thereby, increase the rate of corrosion. Equation (3) can be rewritten in terms of the corrosion potential as:

$$i_n = i_{o2} \left\{ \exp \left[ \frac{\alpha_M F}{RT} \left( V - V_{corr} \right) \right] - 1 \right\}$$

(5)

At low current densities, linearization of the exponential term about the corrosion potential yields:

$$i_n = i_{o2} \left\{ \frac{\alpha_M F}{RT} \left( V - V_{corr} \right) + \frac{1}{2} \frac{\alpha_M F}{RT} \left( V - V_{corr} \right)^2 \right\} + \ldots$$

(6)

In contrast to the expansion for the Butler-Volmer reaction, the second term contributes to the expansion and is equal to 1% of the first (linear) term for potentials of 0.5 mV if $\alpha_M = 1.0$, corresponding to a Tafel slope of ~60 mV/decade.

**MOTIVATION**

The goal of the present work was to devise a method to use impedance spectroscopy to monitor the temporal evolution of a corroding system held at the corrosion potential. While the primary goal of the measurement was to assess the time-dependent electrochemical and physical properties of the system, a second critical concern was that the measurement technique should not interfere with the natural temporal evolution of the system. The conventional approach for measuring the impedance response uses potentiostatic regulation, in which the potential is set to the value of the corrosion potential at the beginning of the measurement, and the potential is perturbed by a value sufficiently small to ensure linearity.

Potentiostatic regulation is satisfactory for measuring the impedance at the corrosion potential if the corrosion potential does not change during the course of the measurement. Under conditions where the corrosion potential changes with time, the potentiostatically controlled impedance scan alters the behavior of the system under study by forcing the potential to be constant during the period of the measurement. A schematic representation of the influence of potentiostatically controlled impedance spectroscopy on a system with a changing corrosion potential is given in Figure 1. The potential decay represented in Figure 1 could be the result of growth of surface films associated with corrosion products or calcareous deposits. The potentiostatically modulated impedance measurement in this case is invasive because the decay in potential is arrested during the measurement. As illustrated in Figure 2, one consequence of applying a fixed potential for a system in which the corrosion potential otherwise would be
changing is that the direct current (DC) component of the current becomes nonzero. For corrosion measurements, the resulting anodic or cathodic current can disrupt the growth of surface films and lead to current overloads.

Galvanostatic modulation of impedance experiments eliminates application of a potential that is anodic or cathodic to the true open-circuit potential. Under galvanostatic control, the desired zero-current baseline condition is maintained throughout the impedance measurement, even when the corrosion potential drifts during the course of the measurement of a impedance spectrum. One difficulty with galvanostatic measurements is that the extent to which a true zero current is applied by the galvanostat depends upon the value of the current measuring resistor used. The error associated with imprecision in the applied current can be reduced by selecting a current measuring resistor appropriate for the smallest current range available. The more significant difficulty with galvanostatic measurements is that, with a fixed amplitude for the current perturbation, such measurements can result in severe swings in potential, especially at low frequencies where the impedance is large. The amplitude of the potential variation \( \Delta V \) associated with a perturbation amplitude of current \( \Delta I \) is given by:

\[
\Delta V = \Delta I |Z(\omega)|
\]

where \( |Z(\omega)| \) is the magnitude of the impedance at frequency \( \omega \). A current perturbation as small as 10 \( \mu \)A can result in potential swings of 1 V for systems with a polarization resistance of 10^9 \( \Omega \), a value typical of many membranes and some slowly corroding systems with well-developed, dense films.

The potential swing associated with galvanostatically modulated impedance measurements with a fixed perturbation amplitude can be significant, even for systems with a small polarization impedance. The potential perturbations resulting from three fixed-amplitude current perturbations on an electrical circuit consisting of a 10-\( \Omega \) leading resistor in series with a parallel resistor (90 \( \Omega \))-capacitor (88 \( \mu \)F) combination are shown in Figure 3. The impedance for this system changed only one order of magnitude over the entire frequency range. The 1-mA perturbation amplitude (triangles) was sufficiently large to ensure an acceptable signal-to-noise ratio at high frequency (10 mV) but yielded a potential swing of 100 mV at low frequency. For most electrochemical systems governed by kinetics, a 100-mV potential perturbation lies well above the threshold defining linearity. Conversely, if care is taken to choose a current perturbation that will ensure that the low-frequency potential perturbation is within the limits of linearity, the high-frequency potential response can fall below the resolution limits of the potentiostat, as demonstrated by the results obtained with a 0.01-mA current perturbation.

The need to adjust the amplitude of the current perturbation has been addressed in some frequency response analyzers by incorporation of an amplitude compression feature. Amplitude compression provides a linear prediction of the current perturbation amplitude. While amplitude compression does not incorporate automated selection of current measur-
ing resistors, it provides current perturbation amplitudes in agreement with the preliminary algorithm developed by Wojcik, et al., in which galvanostatic regulation is conducted with an amplitude of current perturbation that is adjusted at each frequency to yield a desired variation in potential.\(^6\) The algorithm of Wojcik, et al., can be applied for any frequency response analyzer because it does not rely on special nonstandard features of the instrument.\(^6\) The prediction approach also allows selection of an optimal current measuring resistor. This approach retains the advantage of galvanostatic modulation in that the experiment does not disturb the transients that otherwise would exist in the system while ensuring the maximum signal-to-noise ratio for perturbations that stay within the linear regime.

The objective of the present work was to present recent improvements to the variable-amplitude galvanostatic modulation (VAG) algorithm and to demonstrate its utility for monitoring transient corrosion processes.

**VAG MODULATION**

The VAG algorithm consists of a method to select an appropriate amplitude for the current perturbation and for the current measuring resistor. The algorithm was implemented using a general graphical interfacing software on a personal computer (PC).

**Prediction of the Amplitude of the Current Perturbation**

Measurements at previous frequencies were used to estimate the value of the impedance at the target frequency. The current perturbation to be used was given by:

\[
\Delta I(\omega) = \frac{\Delta V_{\text{target}}}{|Z(\omega)|_{\text{estimated}}} \quad (8)
\]

where \(\Delta I(\omega)\) is the current perturbation at a given frequency, \(\Delta V_{\text{target}}\) is the desired potential perturbation at the surface of the electrode, and \(|Z(\omega)|_{\text{estimated}}\) is the magnitude of the impedance taken from the preceding measurement. In this approach, the magnitude of the impedance at the frequency to be measured was predicted from values obtained at previously measured frequencies. This prediction, therefore, was obtained without additional probing of the system. A sequential collection of data in logarithmic increments of decreasing frequency was assumed.

In previous work, a one-point prediction algorithm was used:\(^6\)

\[
Z(\omega_k) = Z(\omega_{k-1}) + O \left[ \log \left( \frac{\omega_k}{\omega_{k-1}} \right) \right] \quad (9)
\]

where the impedance at frequency \(\omega_k\) was assumed to be equal to the impedance obtained at the previous frequency \(\omega_{k-1}\). The error in Equation (9), as given by:

\[
O \left[ \log \left( \frac{\omega_k}{\omega_{k-1}} \right) \right] \quad (10)
\]

is of the order of the inverse number of points per decade. The error in Equation (9) is the same as would be obtained by using the amplitude compression algorithm available on a few frequency response analyzers.\(^4,5\)

In the present work, Equation (9) was replaced by:

\[
Z(\omega_k) = 3Z(\omega_{k-1}) - 3Z(\omega_{k-2}) + Z(\omega_{k-3}) + O \left[ \log \left( \frac{\omega_k}{\omega_{k-1}} \right) \right]^2 \quad (11)
\]

The error in Equation (11) is of the order of the square of the inverse number of points per decade. For 10 points per decade, an order of magnitude improvement is expected when Equation (11) is used as compared to Equation (9).

At the first measured frequency, the initial guess for the impedance was used. The estimated solution resistance provided a good initial guess for impedance scans made from high frequency to low. At the second measured frequency, Equation (9) was used. At the third measured frequency, the estimated impedance was obtained from a two-point formula:

\[
Z(\omega_k) = 2Z(\omega_{k-1}) - Z(\omega_{k-2}) + O \left[ \log \left( \frac{\omega_k}{\omega_{k-1}} \right) \right]^2 \quad (12)
\]

which has an accuracy of the order of the square of the inverse number of points per decade. The three-point algorithm given as Equation (11) provided a refinement to the two-point algorithm (Equation [12]) by including an estimate for the second derivative of impedance with the log of frequency.

A comparison of the one-point and three-point algorithms is presented in Figure 4 for the test cell used to generate Figure 3. The largest errors in the prediction algorithm appeared at frequencies where the impedance was a strong function of frequency. For a 10-mV target perturbation, the one-point technique, displayed by triangles, resulted in a maximum perturbation of 11.7 mV. The maximum error in the three-point variable-amplitude prediction was 0.2 mV for the one-point method as compared to 1.7 mV for the three-point algorithm. The largest error for the three-point algorithm was at the first measured frequency where an initial guess was used to predict the appropriate current perturbation.
Prediction of the Value for the Current Measuring Resistor

The value of the current perturbation obtained from Equation (8) also was used to guide automated selection of the current measuring resistor. Automated selection of current measuring resistors is not new, but its implementation is an essential feature of the algorithm. Several changes of the current measuring resistor often were needed when the current perturbation varied over several orders of magnitude during a scan.

The current measuring resistors available for the potentiostat used in this work are presented in Table 1, along with the nominal current ranges for each selection. The nominal current range was 15% to 190% of the posted current with the exception of the 1-Ω resistor, which had an upper limit of 200% of the posted current. Selection of the proper current measuring resistor was crucial to ensure reliable data collection. Selection of too large a current measuring resistor resulted in a current overload in the potentiostat, and too small a current measuring resistor resulted in a poor signal-to-noise ratio. An overlap in the current ranges is evident in Table 1. Measurements conducted toward the full-scale-limit side of the current range tended to be more sensitive than those taken at the lower limits of the allowable range (e.g., a current value of 12 mA was measured more accurately using the 10-Ω rather than the 100-Ω current measuring resistor).

However, there were situations where the current from an electrochemical experiment was augmented by an additional current resulting from noise, external perturbation, or change in the system under study. When the selection of the optimum current measuring resistor was based solely on the perturbation being applied, the additional currents, in many instances, caused a current overload. With the current measuring resistor selection algorithm described below, a more conservative approach could be taken in situations where overloads are common.

The algorithm for selecting the proper current measuring resistor was based on calculation of:

$$\log \frac{I_{\text{predict}}}{I_{\text{min}}} = x y$$  \hspace{1cm} (13)

where x and y are the characteristic and mantissa of the logarithm, respectively; $I_{\text{predict}}$ is the predicted value for the current; and $I_{\text{min}}$ is the nominal minimum measurable current for the instrument, given in Table 1 to be 100 nA. A switch-over factor ($y_s$) was defined as having a value between 1.5 and 1.9. If $y_s = y$, the current measuring resistor index ($k_r$, Table 1) was obtained from $k_r = 7 - x$. If $y_s > y$, $k_r = 6 - x$. This algorithm does not depend upon past history, and increases or decreases in current measuring

![Comparison between the one-point and three-point prediction methods for the VAG algorithm with a 10-mV target potential perturbation.](image)

**TABLE 1**

| Current Measuring Resistor Ranges for the Potentiostat/Galvanostat Used
<table>
<thead>
<tr>
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<th></th>
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<tbody>
<tr>
<td>Current Nominal Resistor Index ($k_r$)</td>
<td>Measuring Resistor Value</td>
<td>Nominal Current Value</td>
<td>Nominal Current Range</td>
</tr>
<tr>
<td>0</td>
<td>1 Ω</td>
<td>1 A</td>
<td>150 mA – 2 A</td>
</tr>
<tr>
<td>1</td>
<td>10 Ω</td>
<td>100 mA</td>
<td>15 mA – 190 mA</td>
</tr>
<tr>
<td>2</td>
<td>100 Ω</td>
<td>10 mA</td>
<td>1.5 mA – 19 mA</td>
</tr>
<tr>
<td>3</td>
<td>1,000 Ω</td>
<td>1 nA</td>
<td>150 μA – 1.9 mA</td>
</tr>
<tr>
<td>4</td>
<td>10,000 Ω</td>
<td>100 μA</td>
<td>15 μA – 190 μA</td>
</tr>
<tr>
<td>5</td>
<td>100,000 Ω</td>
<td>1 μA</td>
<td>1.5 μA – 19 μA</td>
</tr>
<tr>
<td>6</td>
<td>1 MΩ</td>
<td>100 nA</td>
<td>15 nA – 1.9 μA</td>
</tr>
<tr>
<td>7</td>
<td>100 MΩ</td>
<td>100 nA</td>
<td>15 nA – 190 nA</td>
</tr>
</tbody>
</table>

resistor values are possible based upon the predicted current value.

The method for calculating a value for $I_{\text{predict}}$ depended upon the mode of regulation used. For galvanostatic regulation, $I_{\text{predict}}$ was calculated by:

$$I_{\text{predict}} = \frac{V_{\text{target}}}{Z_{\text{predicted}}} + I_{\text{bias}}$$  \hspace{1cm} (14)

and under potentiostatic regulation by:

$$I_{\text{predict}} = \frac{V_{\text{perturb}}}{Z_{\text{predicted}}} + I_{\text{pol}}$$  \hspace{1cm} (15)

where $V_{\text{target}}$ is the desired potential perturbation at the electrode surface, $Z_{\text{predicted}}$ is the value predicted for
the impedance by the prediction algorithm, $i_{bias}$ is a current bias applied by the potentiostat, and $i_{pot}$ is any DC present after a potential bias is set.

APPLICATION TO CORROSION MEASUREMENTS

The copper/synthetic seawater system chosen to illustrate the benefits of the VAG algorithm is affected strongly by the formation of salt and oxide films. The corrosion potential of a freshly polished copper electrode submerged in electrolyte changes rapidly at first as a result of the removal and formation of surface films, then reaches a pseudo steady-state condition after several days.

Details of the experimental design have been presented previously, and a schematic of the impinging jet cell is shown in Figure 5. An annealed copper cylinder (0.3175-cm [0.125 in.] radius) was embedded in an inert epoxy resin puck designed to expose the disk-shaped face with an area of 0.317 cm² (0.049 in.²) to flow from the submerged impinging jet. The cell configuration was designed to ensure that the flow near the working electrode was in the stagnation regime. The cell design provided uniform accessibility of the electrode to mass transfer. The experimental system was controlled and data was collected by a PC. The program used to run the experiments was constructed using a commercially available graphical interfacing software. A potentiostat/galvanostat and an impedance/gain-phase analyzer were connected to the PC via a general purpose interface bus (GPIB) connection. Impedance measurements were collected frequency-by-frequency from high frequency to low. The long-integration feature of the frequency response analyzer was used, which terminated measurement at a given frequency when a 1% closure error was achieved on the measured channel.

Comparison of Modulation Techniques

The change in the corrosion potential as a function of time, as evident in Figure 6 for the copper synthetic seawater system, created problems using the impedance spectroscopy under potentiostatic modulation. The data presented were obtained after 12 h of immersion in order to bypass initial transients. Impedance spectra collected under potentiostatic and VAG modulation are presented in Figure 7. The reproducibility of the three sequential VAG scans showed that, during the 30-min period required to collect the three scans, the system impedance did not change. The subsequent three potentiostatic scans demonstrated significant differences, caused by imposition of a small anodic bias as the system changed with time (Figure 2). The data collected under potentiostatic modulation were shown by the measurement model technique to be inconsistent with the Kramers-Kronig relations at low frequencies, whereas the low-frequency data collected under VAG modulation were consistent with the Kramers-Kronig relations. The low-frequency
inconsistency with the Kramers-Kronig relations of the data obtained under potentiostatic modulation supported the conclusion that potentiostatically modulated impedance experiments changed the behavior of the copper electrode.

The VAG modulation technique was compared to use of constant-amplitude galvanostatic modulation. The large range of impedance values seen for this system as a function of frequency made it impossible to collect consistent data using the conventional constant-amplitude galvanostatic techniques. The problem was that, to retain an acceptable signal-to-noise ratio at high frequencies, the perturbation had to be sufficiently large to cause a nonlinear response at low frequencies. The problem is demonstrated in Figure 8, where spectra collected with the conventional galvanostatic, conventional potentiostatic, and VAG modulation are presented. A fixed current amplitude of 0.01 mA yielded errors at high frequency which, surprisingly, had the appearance of a bias error rather than that of a stochastic noise. Comparison of the galvanostatic results to those obtained under VAG modulation (Figures 9 and 10 for real and imaginary components, respectively) revealed that the spectrum obtained under galvanostatic modulation with 0.01-mA amplitude was in good agreement with VAG results at low frequency but showed large discrepancies at high frequency. The high-frequency errors were reduced (but not eliminated) by increasing the current perturbation amplitude to a value of 0.1 mA. Violation of linearity constraints were evident at low frequency.

Consistent with the results presented in Figure 7, the data presented in Figures 8 through 10 revealed that results obtained under conventional potentiostatic modulation (triangles) were not as reproducible as those obtained under the VAG method (squares). Slight drifts in the corrosion potential created DC conditions that perturbed the system and caused errors in the impedance results.

**Application as a Monitor for Corrosion Systems**

The manner in which VAG impedance spectroscopy can be used to monitor the reactivity of a corrosion system as a function of time was considered. The corrosion potential is presented in Figure 11 for a copper disk subjected to a submerged impinging jet of aerated synthetic seawater. The transient presented in Figure 6 represented the first 24 h of the 480-h duration experiment in Figure 11. The initial jet velocity was 1 m/s, and the jet velocity was changed from 1 m/s to 2 m/s after 290 h, from 2 m/s to 4 m/s after 340 h, and from 4 m/s to 6.2 m/s after 364 h. The velocities and corresponding time intervals are indicated in Figure 11. The objective was to explore the reactivity of the copper coupon as a function of time and as a function of jet velocity. The VAG method was used to monitor the corrosion system at the open-circuit condition at regular intervals. Typical results are presented in Figure 12 for the time frame in which changes in jet velocity were made. Small differences in features were evident in the impedance plane format.

Results demonstrated that the VAG impedance technique satisfied the requirement that the impedance method not distort the transients associated with a freely corroding system. To be useful as a monitor of corrosion processes, the data obtained
The impedance technique allowed measurements that did not distort the transients associated with a freely corroding system, and the measurement model allowed identification of the portion of the measurement that could be used to extract physical properties.

In addition to its use to assess consistency with the Kramers-Kronig relations, the measurement model approach was used to quantify differences in surface reactivity. Interpretation of the spectra presented here followed:

- Identification of the frequency-dependent stochastic component of the error structure following the method presented by Agarwal, et al. This information was used to weight subsequent regressions.
- Identification of the portion of the spectrum that was consistent with the Kramers-Kronig relations following the method presented by Agarwal, et al. The error structure found in the previous step was used to weight the regression. High-frequency data were corrupted by instrumental artifacts. The low-frequency data typically were consistent with the Kramers-Kronig relations except for data collected early in the experiment where the system was changing rapidly. Nevertheless, a significant portion of even the first impedance measurements was consistent with the Kramers-Kronig relations, and acceptable values of polarization impedance were obtained.
- Regression of the measurement model to the part of the spectrum found to be consistent with the Kramers-Kronig relations. The regressed parameter values were used to extrapolate the zero-frequency limit and Monte Carlo simulations were performed using the standard deviations of the regressed parameters to estimate the confidence interval for the extrapolation. The polarization impedance

**FIGURE 9.** Real component of impedance for data in Figure 8.

**FIGURE 10.** Imaginary component of impedance for data in Figure 8.

**FIGURE 11.** Corrosion potential measured as a function of time for a copper disk copper disk subjected to an impinging jet of synthetic seawater with jet velocity as indicated. Data presented in Figure 6 represent the short-time behavior of the data presented here.

also should allow ready interpretation in terms of physical properties. If the time constant for the transient process is of the same order as the time required for the impedance scan, the nonstationarity of a system will introduce bias errors in the impedance measurement and will cause the data to be inconsistent with the Kramers-Kronig relations. The use of the measurement model concept to assess the error structure of the impedance scans allowed identification of the portion of the measurement that was unaffected by bias errors. Thus, the VAG impedance

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was obtained by subtracting the regressed solution resistance from the extrapolated zero-frequency value.

Results are presented in Figure 13 for the polarization impedance as a function of time for the impedance data shown in Figure 12. The polarization impedance increased from an initial value of roughly 1,600 $\Omega$-cm$^2$ to 10,000 $\Omega$-cm$^2$. Results showed that, for this experiment, there was no dramatic change in the surface reactivity associated with changes in jet velocity. Other examples of the use of VAG modulated impedance spectroscopy for monitoring reactivity changes have been presented elsewhere.$^9,10$

The utility of the VAG method was emphasized by its use for monitoring the short-term behavior shown in Figure 6. As shown, the trends in corrosion potential were unaffected by the impedance scans. The impedance scans given in Figure 14 showed that the surface reactivity changed dramatically over the course of 24 h. The resulting polarization impedance values are given in Figure 15. The impedance decreased initially as a result of removal of the native oxide layer and then increased as the films associated with the corrosion products formed and grew. The role of the measurement model for evaluating consistency with the Kramers-Kronig relations was evident in that the apparent low-frequency asymptote of the scan obtained at 0.2 h (Figure 14) was 1,800 $\Omega$-cm$^2$; whereas, the corresponding polarization impedance shown in Figure 15 obtained by the analysis outlined above was 1,500 $\Omega$-cm$^2$. The low-frequency data were corrupted by nonstationary behavior, but a polarization impedance still could be obtained from the portion of the data that satisfied the Kramers-Kronig relations.

CONCLUSIONS

- Impedance spectroscopy can be used to follow the temporal evaluation of surface properties at the corrosion potential, but the perturbation must be small and the modulation must not distort transients associated with the freely corroding system.
- Galvanostatic regulation is ideal for the use of impedance spectroscopy to observe periodically the
condition of a metal held at the corrosion potential because the required zero-current condition is maintained even when the corrosion potential is a strong function of time.

- While galvanostatic measurements with a fixed amplitude for the current perturbation can result in severe swings in potential, the algorithm described provides a good means for adjusting the modulation amplitude for current to prevent large perturbations to the system.

- Measurement of an impedance spectrum with this technique does not distort the natural evolution of a system, even under conditions where rapid evolution of surface properties distorts the resulting impedance scan. Use of the measurement model concept to assess the error structure of the impedance scans allows use of the uncorrupted portion of the measurement to evaluate physical properties.

ACKNOWLEDGMENTS

This work was supported by the U.S. Office of Naval Research under grant nos. N00014-93-1-0056 and N00014-93-1-1113 (A.J. Sedriks, program monitor).

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