Application of Measurement Models for Analysis of Impedance Spectra

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ABSTRACT

Measurement models have been applied to electrochemical impedance data collected at the corrosion potential for a copper disk rotating in alkaline- and acid-aerated 0.5 M chloride solutions. Several applications of measurement models for the interpretation of experimental impedance data are demonstrated. Corrosion is a nonstationary process, and nonstationary behavior associated with corrosion frequently influences impedance data. If data can be shown to be consistent with the Kramers-Kronig relations, nonstationary influences can be neglected. Measurement models provide a quantitative method for identifying the portion of an impedance spectrum that is consistent with the Kramers-Kronig relations and, therefore, can be interpreted in terms of pseudo-steady-state models. Measurement models also provide a very sensitive means of interpreting impedance spectra in terms of the effects of physical parameters, such as immersion time and disk rotation speed.

KEY WORDS: chloride, copper, impedance, Kramers-Kronig relations, measurement model

INTRODUCTION

The object of this work was to demonstrate how measurement models can be used to facilitate interpretation of electrochemical impedance data. Measurement models are applied to the impedance spectra obtained for copper in chloride solutions. Oxide and salt films form on copper in alkaline solutions,1 and the thickness of these layers is a function of immersion time. Therefore, the electrochemical character of corrosion systems for which salt films are growing may change during the time required to collect impedance data. Since models usually used to interpret the impedance spectra assume a pseudo-steady-state condition, it is important to determine whether the collection time was sufficiently short to model the system as stationary. Impedance data collected under nonstationary conditions will fail to satisfy the Kramers-Kronig relations. Measurement models were used to identify the portion of the impedance spectra that satisfies the Kramers-Kronig relations and, therefore, that can conform to the pseudo-steady-state assumption.2 Measurement models also were applied to determine whether disk rotation speed can influence the impedance response of copper in alkaline solutions where a surface film has been reported to dominate the mass transfer resistance of a rotating copper disk electrode.3

CONCEPT

Models are classified as process or measurement models.2,4 Process models are used to predict the response of a system based on hypothesized physical phenomena. Regression of process models to data allows identification of physical parameters based on
the original hypothesis. In contrast, measurement models are built by sequential regression of line shapes to the data. The line shapes of the measurement model do not necessarily correspond to specific physical processes, but the model regression can be used to identify characteristics of the data set and to facilitate selection of an appropriate process model.

Measurement models can be used to determine whether data are consistent with the Kramers-Kronig relations. Several approaches have been taken to check the consistency of impedance data. Experimental verification of consistency with the Kramers-Kronig relations can be achieved by replication; however, without an a priori estimate for the confidence limits of the experimental data, the comparison is more qualitative than quantitative. Consistency can be verified through direct integration of the Kramers-Kronig relations, but measured frequency ranges are often insufficient to allow integration over the frequency limits of zero to infinity. An apparent inconsistency with the Kramers-Kronig relations, therefore, could be also attributed to using a very narrow frequency domain. Consistency can be verified by fitting the data to electrical circuit analogues because passive circuit elements inherently satisfy the relations. The major problem with the use of electrical circuit models to determine consistency is that interpretation of a poor fit is ambiguous. A poor fit could be attributed to the use of an inadequate model as well as to inconsistency of the data with the Kramers-Kronig relations.

The regression of measurement models as a means of determining consistency with the Kramers-Kronig relations is an extension to the use of electrical circuit analogues. Because the model itself is consistent with the Kramers-Kronig relations, successful regression of the model to a given spectrum demonstrates the consistency of the data without requiring integration from zero to infinity in frequency. The success of the measurement model approach, compared to use of specific electrical circuit models, is based on the observation that a model with a sufficient number of line shapes provides a statistically adequate fit to any consistent data set. The ambiguity associated with a poor fit of more specific electrical circuit models to the data is eliminated by using measurement models. Since the model will provide an adequate representation of a consistent spectrum, failure to fit the data can be attributed to inconsistency with the Kramers-Kronig relations. Another result of the adequacy of the model is that the model can be used to identify the frequency-dependent error structure of impedance spectra. The error structure can then be used to weight the data during regression and to provide a means of deciding whether a given regression provided a good fit.

The line shape used here was based on the Voigt circuit and is given by

$$Z(\omega) = Z_0 + \sum_k \frac{\Delta_k}{(1 + j\omega \tau_k)}$$  \hspace{1cm} (1)

By using a sufficient number of Voigt elements, a statistically adequate fit is obtained for impedance data collected from stationary electrochemical systems.

**EXPERIMENTAL PROCEDURE**

Electrochemical data were obtained using a copper rotating disk electrode in aerated 0.5 M chloride solutions. The electrodes were constructed from high-purity copper rods (99.999% Cu) that were annealed under argon at 500°C for five to eight hours and then allowed to cool in the furnace. Each rod was soldered onto a stainless steel shaft and embedded in epoxy. The face of the copper disk electrode had an exposed cross-sectional area of 0.385 cm². The disks were wet-polished with increasingly finer SiC papers followed by 1 µm alumina powder to produce a mirror-like surface. The electrodes were cleaned ultrasonically in deionized water for approximately one minute before immersion. A Pine® analytical rotator was used to spin the disk in 2 L of electrolyte. The pH was regulated with a Cole-Parmer Model 5652® pH controller using NaOH and HCl solutions of 0.5 N chloride concentration. The electrolyte was aerated with air pumped from the laboratory and passed over Ascarite II to remove CO₂. A saturated calomel electrode served as a reference electrode, and a Pt foil was used as the counter electrode for all experiments. Galvanostatic and potentiodynamic experiments were performed with a Princeton Applied Research Model 273® potentiostat. Impedance experiments were conducted with a Schlumberger Solartron 1250® frequency response analyzer and a Solartron 1286® electrochemical interface. All impedance measurements were performed at the open-circuit (corrosion) potential.

**RESULTS AND DISCUSSION**

Electrochemical experiments were performed on copper in chloride environments at pH values of 1, 7, 9.5, and 11.5. Impedance data were collected at open-circuit potentials, and galvanostatic and potentiodynamic experiments were performed to support interpretation of the impedance results. The measurement model was applied to aid in the analysis and interpretation of the impedance data.

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1 Trade name.
**Electrochemical Impedance Data**

Impedance plane plots are presented in Figure 1 for six consecutive impedance scans for copper in 0.5 N chloride solutions with pH 11.5. The first scan was collected at the time of electrode immersion, and the following scans were taken over a one-hour span. The data appear to be replicate, suggesting that the oxide film or other solid diffusion barrier forms rapidly and is stable at this pH. Application of measurement models to determine replicacy quantitatively will be discussed in a following section. The large magnitude of the impedance at low frequencies indicates that the film is protective. A similar series of six consecutive impedance scans is presented in Figure 2 for copper in neutral solution (pH = 7). The observation that the polarization resistance increases with time can be explained by growth of a protective film on the surface of the electrode. In acid solutions (Figure 3), the trend in polarization resistance reverses, and the magnitude of the impedance is larger at short times than at long times. The decrease in polarization resistance may be attributed to the dissolution of a native oxide film initially present on the surface of the electrode. The behavior shown in Figures 1, 2, and 3 suggests that film formation or dissolution is important for corrosion of copper in alkaline, neutral, and acidic chloride systems. The influence of the film, seen clearly in alkaline solutions, is less apparent in acid environments.

It is well-known that surface films exist on copper in alkaline solutions. The suggestion that films influence the impedance response for copper in acid, neutral, and alkaline chloride solutions is supported by previous work and by the results of a
physicochemical model that explained the mass transfer resistance associated with a film and a convective mass transfer boundary layer. The model provided a good fit for copper at moderately anodic potentials in acid as well as alkaline environments.

**Galvanostatic and Potentiodynamic Experiments**

The time-dependent behavior seen in the impedance data was investigated by additional electrochemical experiments. The corrosion potential in Figure 4 is presented for four pH values as a function of time following immersion. Curve a was collected from copper in acid solution. Initially, the corrosion potential was $-308$ mV (SCE). The corrosion potential increased by approximately $2$ mV/min for 30 min and $0.2$ mV/min for the next 90 min. This corrosion potential behavior is consistent with the observed rate of change of the polarization resistance shown in Figure 3, i.e., the polarization resistance $R_p$ decreased rapidly for the first few impedance scans and slowly for those collected later. The corrosion potential curve in neutral solutions labeled b1 in Figure 4 starts at approximately $-275$ mV, falls and rises for approximately 30 min, and then exhibits a spike. A replicate experiment, presented as curve b2, demonstrates the reproducibility of the spike. The rate of change of the corrosion potential is consistent with Figure 2. At pH 9.5 (curve c), the corrosion potential started at $-215$ mV, increased for 20 min, and then slowly decreased. At pH 11.5 (curve d), an initial sharp decrease was followed by a constant corrosion potential. Observation of a constant corrosion potential is consistent with data of Figure 1, which showed reproducible impedance scans.

The observed changes in the corrosion potential indicate the chemical environment near or on the surface of the electrode was a function of time. The corrosion rate observed would lead to a change in composition of the bulk electrolyte over a two-hour span of less than $1$ μm. The mass transfer boundary layer associated with the rotating disk electrode also did not change. Therefore, the changes observed in the impedance response cannot be attributed to changes in electrolyte concentration near the metal over long times. All four time traces for the corrosion potential, however, are consistent with growth or decay of a surface film.

A typical potentiodynamic result for copper in the pH 9.5 chloride solution is presented in Figure 5. The passive region at low anodic potentials clearly is associated with the presence of a surface film. A breakdown potential at $100$ mV (SCE) was observed during the forward sweep. Films exist on copper in alkaline solutions at open circuit and at potentials where current oscillations are seen (>800 mV in

**Figure 4.** Corrosion potential $E_{corr}$ as a function of time for Cu in aerated 0.5M Cl⁻ solutions. For a, pH = 1.0. For replicate runs b1 and b2, pH = 7.0. For c, pH = 9.5, and for d, pH = 11.5.

**Figure 5.** Current as a function of potential for Cu in aerated 0.5M Cl⁻ solution with pH 9.5. Arrows indicate direction of potential scan.

Figure 5). Salt films have also been observed visually at anodic potentials below the plateau region for all pH values used in this work.

**Analysis of Impedance Spectra by Measurement Models**

In the procedure used to check for the consistency of the data, the measurement model was regressed to the real or the imaginary part of the experimental spectrum. The model then was used to predict the other part of the spectrum (i.e., the real part if the regression was done to the imaginary and the imaginary part if the regression was done to the real).
FIGURE 6. Regression of the measurement model to the imaginary part of the impedance obtained immediately following immersion of a copper electrode in acid chloride solutions (run 1, of Figure 3). The middle lines represent the model, and the upper and lower lines represent the predicted 95 percent confidence interval for the regression.

FIGURE 7. Residual errors for regression presented in Figure 6. The predicted 95 percent confidence interval for the model fit is given by solid lines. Dashed lines represent the estimated error structure for the data.

From the estimated variance of the model parameters, a 95 percent confidence interval was found for the model predictions using Monte-Carlo simulation.\textsuperscript{9,10} If the data lie within the 95 percent confidence interval, the system was regarded as being stationary during the course of the experiment. If a significant portion of the data fell outside the 95 percent confidence interval, the data do not satisfy the Kramers-Kronig relations, and the system was likely to have been nonstationary. To ensure that impedance values followed a Gaussian distribution, 5,000 simulations were performed at each frequency.

The regression of the measurement model is shown in Figure 6 for the impedance spectrum labeled $t_1$ in Figure 3 (pH = 1). These data were obtained immediately following immersion. The model was regressed to the imaginary part of the impedance, and the real part was predicted from the regressed model parameters. The circles represent the experimental data, the center lines represent the model fit, and the
upper and lower lines represent the 95 percent confidence interval for the model regression.\textsuperscript{2} The comparison between model and experiment is seen more clearly in Figure 7, where the open circles represent the normalized residual error between the data and the model fit. The dashed lines represent the estimated error structure for the experiment, given by

$$\varepsilon = \pm 0.01 \sqrt{Z_r^2 + Z_i^2}$$ \hspace{1cm} (2)

such that the 95 percent confidence interval for the experimental data is estimated to be

$$Z_r = Z_r^{\text{expt}} \pm \varepsilon$$ \hspace{1cm} (3)

and

$$Z_i = Z_i^{\text{expt}} \pm \varepsilon$$ \hspace{1cm} (4)

Equation (2) is a preliminary model for the error structure suggested by the specification of the frequency response analyzer for variance of the results at 90 percent confidence using a long integration mode with a signal greater than 0.02 percent of the range. The error structure for the data would be dependent on the instrumentation used and on other aspects of experimental technique. Work is currently underway to refine the model for the error structure.\textsuperscript{11} The solid lines in Figure 7 again are the 95 percent confidence interval for the model fit. At the high-frequency region of Figure 7, the data deviate considerably from the model fit and lie well outside both the confidence interval for the model and the error structure. High-frequency anomalies have been attributed to instrumental artifacts that appear to have a nonlinear character.\textsuperscript{12} It is clear that passive elements alone cannot model the high-frequency response because inconsistency with the Kramers-Kronig relations is observed through the measurement model. High-frequency anomalies are often observed, and experimental spectra are routinely truncated before model regression. The application of measurement models provides a quantitative basis for a decision that is otherwise made under qualitative reasoning.

Further application of the measurement model with trial and error truncation of data suggested that data at frequencies greater than 2,000 Hz should be discarded. The fit to the remaining data is shown in Figure 8, and the residual errors are shown in Figure 9. The regression indicates that several points at the low-frequency end are inconsistent with the Kramers-Kronig relations because they lie outside the 95 percent confidence interval. Note that the error structure given by the dashed line predicts a large uncertainty in the imaginary part of the impedance at low frequencies. The large uncertainty is seen because the errors were assumed to be directly proportional to the magnitude of the impedance. Since the imaginary part of impedance tends toward zero at low frequency and the real part tends toward a finite value, the relative error for the imaginary component is large. Data points with large, calculated variance were given less importance in the regression by weighting the data according to the frequency-dependent error structure (Equation [2]). Upon deletion of the last two points of the spectrum, the measurement model approach indicated that the remainder of the data was consistent.

**FIGURE 8.** Regression of the measurement model to the imaginary part of the impedance obtained immediately following immersion of a copper electrode in acid chloride solutions (run 1, of Figure 3). High-frequency data points influenced by instrumental artifacts were deleted for the analysis. The middle lines represent the model, and the upper and lower lines represent the predicted 95 percent confidence interval for the regression.
FIGURE 9. Residual errors for regression presented in Figure 8. The predicted 95 percent confidence interval for the model is given by solid lines. Dashed lines represent the estimated error structure for the data.

FIGURE 10. Regression of the measurement model to the imaginary part of the impedance obtained one hour after immersion of a copper electrode in acid chloride solutions (run t₀ of Figure 3). High-frequency data points influenced by instrumental artifacts were deleted for the analysis. The middle lines represent the model, and the upper and lower lines represent the predicted 95 percent confidence interval for the regression.

with the Kramers-Kronig relations. Therefore, the truncated portion of the data could be applied to a model that does not account for time-dependent behavior. Note that deleting data in this way has the disadvantage of losing information about the system. A preferred approach would be to use all the data and to interpret the impedance response by using a model that accounts for the time-dependent behavior.

The measurement model was regressed to impedance data collected after an hour of immersion at pH 1 and presented as curve t₀ of Figure 3. The high-frequency data shown to be inconsistent due to instrumental artifacts were deleted. As shown in Figures 10 and 11, the remaining data are consistent with the Kramers-Kronig relations since the data lie within the 95 percent confidence interval for the model fit. Note that the data at low frequency, which reflect an inductive process, also are consistent. The spike in the imaginary part of the residual errors occurs where the imaginary impedance crosses zero. The residual errors
for the real part at high frequency are larger than the error structure of the data but are randomly distributed around the model, suggesting that the one percent instrumentation noise on which the error structure is based was not achieved in the experiment. Analysis of Figure 3 suggests that impedance spectra collected after the copper was immersed for approximately one hour in acid chloride solution can be applied to a pseudo-steady-state model.

The measurement model also was used to identify the extent to which physical parameters influence impedance spectra. To investigate the influence of rotation speed on corrosion of copper in alkaline solutions (pH = 11.5), data were collected sequentially at rotation speeds of 1,000, 700, 500, 1,500, 2,000, and 1,000 rpm after the copper electrode had been immersed for three days at a constant rotation speed of 1,000 rpm. A dependence on rotation speed is not evident in the impedance plane plot given (Figure 12). In fact, the six data sets collected at five rotation speeds appear to be replicate. The measurement model was applied to determine whether a systematic effect of rotation speed exists. Individual data sets, examined with the measurement model, were found to be consistent with the Kramers-Kronig relations, and the residual errors for the regression fell within the predicted 95 percent confidence interval for the data given as Equation (2).

The model then was regressed to the combined data from all experimental runs. The results of the complex fit are shown in Figure 13, where the circles represent the data and the lines are the model. The normalized residual errors for the regression are shown in Figure 14, where solid lines represent the 95 percent confidence interval (twice the standard deviation) of the combined data sets. The observation that the residual errors fell within the confidence interval of the data indicates that the fit is good. The residual errors, however, lie outside of the estimated model for error structure at all frequencies, suggesting that the runs are not replicate and that rotation speed does influence the impedance response of copper in alkaline chloride solutions. This interpretation is
supported by the observation that the six data sets can be individually distinguished. The sequence of data set lines does not, however, correlate directly with rotation speed. The influence of rotation speed in these experiments cannot be attributed to a simple effect of convective diffusion. It is possible that the film thickness or some other physical film property depends on rotation speed in solutions of pH 11.5.

Since these runs were taken over a period of approximately one hour, a time dependence for the impedance response could provide another explanation for nonreplicacy. To test this hypothesis, consecutive runs taken over a period of approximately one hour were performed at a constant rotation speed of 1,000 rpm (Figure 15). As in the previous test, the data were collected after the copper electrode had been immersed for three days at a constant rotation speed of 1,000 rpm. As shown in Figure 16, the measurement model provided a good fit to the data. The residual errors presented in Figure 17 (with a
constant rotation speed) are much smaller than those presented in Figure 14 (with varying rotation speed), and the sequence of lines is consistent with a modest increase in both real and imaginary impedance with increasing immersion time. The time dependence apparent in Figure 17 cannot account for the larger residual errors seen in Figure 14; therefore, the impedance response does depend on rotation speed.

The influence of rotation speed may be seen more clearly by plotting the residual errors for the regression as a function of temporal sequence (Figure 18 for varied rotation speed and Figure 19 for constant rotation speed). The residual errors in both figures are functions of time (within a 99.99 percent significance level by the two-sided t-test\(^2\)), but the dependence is weaker in the case where the rotation speed was constant. The residual errors for both the real and imaginary components decreased with time when rotation speed was varied, but the opposite trend was observed for a constant rotation speed.

These results suggest rotation speed influences the impedance response of the copper electrode in alkaline chloride solutions by changing the character of a surface film. These results also suggest a different experimental design is needed to discriminate clearly between the effects of convective diffusion and the influence of the film. The dependence on the history of the experiment apparent in the different response seen at 1,000 rpm before (×) and after (Δ) the rotation speed excursions (Figures 14 and 18) suggests the influence of rotation speed can be best ascertained by holding the electrode at the specified rotation rate for a much longer period of time. By identifying the factors that influence the impedance response, the measurement model analysis can be used to guide experimental design and to facilitate development of physicochemical process models for copper in alkaline chloride solutions. Such models are currently being developed in this group.\(^7\)

**CONCLUSION**

This work illustrates the manner in which measurement models can provide a useful intermediate step for the analysis of impedance data. The models were used to check data for consistency with the Kramers-Kronig relations, allowing identification of portion of the spectra that were not...
influenced by instrumental artifacts (observed at high frequencies) or nonstationary phenomena (observed at low frequencies). This analysis was used to select a portion of the impedance spectrum that can be fit by a pseudo-steady-state model. Measurement models also were used to provide a sensitive interpretation of the effects of physical parameters, such as disk rotation speed, on experimental impedance data. The intermediate analysis can be used to guide design of more directed experiments and to suggest the physical phenomena that should be incorporated into a physicochemical model for the impedance response of copper in chloride solutions.

ACKNOWLEDGMENTS

The portion of this work performed at the University of Florida (PAN, OCM, and MEO) was supported by the Office of Naval Research under grant no. N00014-89-J-1619 (A.J. Sedriks) and by Gates Energy Products, Gainesville, FL. The work performed at the University of South Florida (LHGR) was
FIGURE 19. Residual error for the regression shown in Figure 16 plotted as a function of experiment sequence. The solid line is the mean residual error for all samples. The individual runs were conducted at a rotation speed of 1,000 rpm in the following order: *, +, a, □, °, and Δ.

supported by the National Science Foundation under grants no. RII-8507956 and INT-8602578.

REFERENCES


LIST OF SYMBOLS

\[ E_{corr} = \text{corrosion potential, V} \]
\[ R_p = \text{polarization resistance, } \Omega \]
\[ Z_0 = \text{solution resistance, } \Omega \]
\[ Z_j = \text{imaginary component of impedance, } \Omega \]
\[ Z_r = \text{real component of impedance, } \Omega \]
\[ Z(\omega) = \text{complex impedance, } \Omega \]
\[ \Delta_k = \text{resistance of Voigt element, } \Omega \]
\[ \omega = \text{frequency, } s^{-1} \]
\[ \tau_k = \text{time constant of Voigt element, s} \]