Modeling of Electrochemical Impedance Data of a Magnesium-Rich Primer

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The application of Mg-rich primers (MRPs) for the protection of aluminum structures represents an attractive alternative to the environmentally unfriendly Cr-rich primers that are presently used. The protective modes of MRPs are similar to those of Zn-rich primers (ZRPs) on steel and include cathodic protection driven by the more active Mg particles compared to the Al substrate and a barrier-type protection due to the insulation of the substrate from the environment. Interpretation of EIS data has been accomplished using a transmission-line model that accounted for the contact impedance between the zinc particles, the impedance associated with the zinc dissolution, and the percolation resistance of the coating.

Experiments were conducted to gather EIS data associated with the evolution of the electrochemical behavior of MRPs on a gold substrate exposed to immersion in dilute Harrison’s solution. The objective of this work was to determine the applicability of the transmission-line model for characterizing EIS data of MRPs. The EIS data obtained in the 1 mHz to 10 kHz frequency range were shown to be consistent with Kramers–Kronig relationships using the measurement model technique that was developed by Orazem and co-workers. The transmission-line model was shown to be applicable to a 1 mHz to 10 kHz frequency range for the MRP investigated. The evolutions of the contact impedance, dissolution impedance, and percolation resistance demonstrate the use of the transmission-line model for analyzing the protection afforded by the MRP and demonstrate the similarity between the protective modes of MRPs and ZRPs.

Experimental

Method.—The MRP primer was applied onto a gold substrate that consisted of sputtered gold on a silica disk. The MRP coating consisted of a 10 μm average-sized Mg particulate in a two-component epoxy of Epox resin 828 and Enamine 3164 that was supplied by Resolution Performance Products, Houston, TX. The Mg particulate was supplied by Ecka-granules of America, Louisville, KY, and was covered by a thin layer of MgO that limited its reactivity. The dispersion of the Mg particles was aided by an anti-settling agent. The coating was formulated at 45% pigment volume concentration that was approximately equal to the critical pigment volume concentration. The primer was applied using a compressed air spray gun to a thickness of approximately 50 μm. A drying period in excess of 3 days was used.

The experimental apparatus included a Perspex cylinder cell that exposed a 7.07 cm2 area of the primer. The cell was clamped to the 0.1 wt % NaCl. The protective modes of MRPs are similar to those that have been associated with Zn-rich primers (ZRPs). The cathodic and barrier-type protection provided by ZRPs for steel substrates have been extensively investigated by electrochemical methods. Early interpretation of EIS data was accomplished using Randles-type circuits, but recently the transmission-line model has been shown to be applicable to ZRPs. This model includes parameters that were attributed to the contact impedance between the zinc particles, the impedance associated with the zinc dissolution, and the percolation resistance of the coating. An extended transmission-line model has also been presented that accounted for the oxygen reduction on the zinc particles at the outermost part of the coating.

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Available commercial, nonchromate inhibitor pigments have been shown to be much less effective in corrosion protection as compared to the industrial standard of SrCrO4. A nonchromate pigment has been reported to perform as effectively as SrCrO4 on Alodine. Alodine does expose the surface to environmental conditions and represents a Cr-free system.

The cathodic and barrier-type protection due to the insulation of the substrate from the environment has been reported to perform as effectively as SrCrO4 on Alodine. Alodine does expose the surface to environmental conditions and represents a Cr-free system.

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Results.— The evolution of the open-circuit potential (OCP) is shown in Fig. 1 with the value and all potential values in the text referenced to the saturated calomel reference. The OCP value for the Mg particulate was reported as −1.6 V,1 while the measured OCP value for the gold/silica substrate used was 0.05 V. The OCP value decreased from 0.55 to −0.5 V within the first 15 min of immersion and remained at that value for the following 15 min. The OCP value increased from −0.5 to −0.22 V over the first day and from −0.22 to 0.05 V from day 1 to day 7. The initial decrease in OCP value during the first 15 min represented a period where the mixed potential between the Mg particles and the gold substrate developed. The mixed potential OCP value of −0.5 V, between 0.05 and −1.6 V, was maintained for less than a day as the OCP value of −0.22 V on day 1 indicated that the mixed potential was moving toward that of the gold substrate. The measured values evolved to the OCP of the gold substrate, indicating the decrease in cathodic protection provided by the Mg particulate. Experiments conducted for Mg-rich primers of AA 2024-T3 substrates under immersion in DHS have shown cathodic protection for 20 days.24 The change in OCP from the mixed potential value of −0.5 to 0.05 V associated with the gold substrate took 7 days. The faster loss of the cathodic protection for the Mg-rich primer on the gold substrate was attributed to the larger potential difference between the mixed potential and the OCP value associated with Mg.

The EIS data obtained for days 1–5 and day 7 immersion times are shown in Fig. 2a. The spectra associated with days 1–4 overlapped, with high and low-frequency features observable. The spectra for days 5 and 7 indicated that the low-frequency features became more dominant with time. The EIS data for three replicated scans designated a, b, and c on day 1 are shown in Fig. 2b. The scans were taken sequentially approximately 20 min apart. The three scans overlapped; this demonstrated the reproducibility of the EIS data on a particular day.

Measurement Model Analysis

In this work the EIS data associated with an MRP were regressed to a transmission-line model, which is an equivalent circuit model representative of the impedance of a particulate network.13 The regression of EIS data associated with a coating to an equivalent circuit model is performed under the assumptions that the data are free of instrument artifacts due to nonstationary behavior, that the noise level in the data is acceptable, and that the weighting strategy is appropriate. Application of the measurement model technique can be used to qualify these assumptions by analyzing the residual error between the measurement model impedance fit and the measured impedance data. The technique has been applied to identify the contributions of systematic, bias, and stochastic errors to the residual error.19

The measurement model technique involves using a generalized Voigt model to analyze the error associated with replicated EIS data. The model is shown in Fig. 3 and consists of a series of Voigt elements comprising a parallel arrangement of a resistor $R_k$ and capacitor $C_k$, in series with a resistor $R_0$ that represents the solution.
The resistor and time constant values obtained for the regression with the scans; an example of this agreement can be seen in Fig. 4a. The maximum number of elements that could be shown in Fig. 2b. The line through the data is a fit of the model given by Eq. 2 to the data.

resistance. The characteristic time constant associated with a Voigt element is \( \tau_e = R_e C_e \), and the impedance of the model can be expressed as

\[
Z = R_0 + \sum_{k=1}^{\infty} \frac{R_k}{1 + j \omega \tau_k}
\]

[1]

The Voigt measurement model is consistent with Kramers–Kronig relations, and the application of the technique can determine the internal consistency of the measured EIS data without need for explicit integration of the Kramers–Kronig relations. The technique involves using a weighting strategy for the complex nonlinear least-squares regression that is based on the measured error structure associated with replicated EIS data.

Technique.— The measurement model technique is demonstrated here using the replicated EIS data associated with day 1 that are shown in Fig. 2b. The maximum number of elements that could be regressed to scans \( a, b, \) and \( c \) was 12. There were good agreements between the fit of the measurement model and the data associated with the scans; an example of this agreement can be seen in Fig. 4a. The resistor and time constant values obtained for the regression using modulus weighting are given in Table I. The resistance associated with the solution is also given. The parameters are arranged in order of increasing time constant with an error of \( \pm \sigma \) included with each parameter. The \( R \) and \( \tau \) parameters for a given Voigt element were similar among the scans and indicated that there was no significant difference among the scans.

The data shown in Table I were used to calculate the standard deviations of the real and imaginary parts as functions of frequency. The standard deviation that is calculated can be used to calculate the standard deviation of the residual errors from which the standard deviation of the stochastic error can be identified. This procedure is based on the assumptions that the model parameters account for systematic differences with the systematic errors associated with lack of fit, nonstationary behavior, and instrument artifacts being unchanged from one scan to another. The standard deviations of the real and imaginary parts as functions of frequency are shown in Fig. 4b. The expression

\[
\sigma_{Z_e} = \sigma_{Z} = \sqrt{\frac{|Z|^2}{R_q} + \delta}
\]

[2]

was used to model the standard deviation, where \( R_q \) is the current measuring resistor used in the experiment, and \( \alpha, \beta, \gamma, \delta \) are constants to be determined by regressing the real and imaginary parts to the expression. The values of \(-0.0040, 0.0041, 0.0005, \) and 1.68 were obtained for \( \alpha, \beta, \gamma, \) and \( \delta \), respectively, and the value of 10^\( 2 \) \( \Omega \) was used for \( R_q \).

Consistency with Kramers–Kronig relations.— The consistency of the impedance data to the Kramers–Kronig relations was performed by fitting the Voigt measurement model to the data using the error structure as the weighting strategy. The approach suggested by Orazem is to fit the model using the maximum number of Voigt elements to the imaginary part of the data. A 12-element Voigt model was fit to the imaginary part of the EIS data associated with scan \( a \) of day 1. The measurement model values and data are shown in Fig. 5, together with dashed lines that represent the 95.4% confidence interval for the model obtained by Monte Carlo simulation using the confidence interval associated with the estimated parameters. The parameters obtained from the fitting of the imaginary part were used to predict the real part. There was agreement between the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Scan a</th>
<th>Scan b</th>
<th>Scan c</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1 ) (( \Omega ) ( \text{cm}^2 ))</td>
<td>663 ± 115</td>
<td>646 ± 113</td>
<td>639 ± 127</td>
</tr>
<tr>
<td>( \tau_1 ) (( \mu \text{s} ))</td>
<td>3.4 ± 0.5</td>
<td>3.4 ± 0.5</td>
<td>3.4 ± 0.5</td>
</tr>
<tr>
<td>( R_2 ) (( \text{k}\Omega ) ( \text{cm}^2 ))</td>
<td>1.1 ± 0.2</td>
<td>1.0 ± 0.2</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>( \tau_2 ) (( \mu \text{s} ))</td>
<td>15 ± 4</td>
<td>15 ± 4</td>
<td>15 ± 4</td>
</tr>
<tr>
<td>( R_3 ) (( \text{k}\Omega ) ( \text{cm}^2 ))</td>
<td>1.6 ± 0.5</td>
<td>1.5 ± 0.5</td>
<td>1.4 ± 0.5</td>
</tr>
<tr>
<td>( \tau_3 ) (( \mu \text{s} ))</td>
<td>67 ± 29</td>
<td>64 ± 27</td>
<td>61 ± 31</td>
</tr>
<tr>
<td>( R_4 ) (( \text{k}\Omega ) ( \text{cm}^2 ))</td>
<td>3.0 ± 1.1</td>
<td>2.9 ± 1.0</td>
<td>2.8 ± 0.9</td>
</tr>
<tr>
<td>( \tau_4 ) (ms)</td>
<td>0.28 ± 0.13</td>
<td>0.26 ± 0.13</td>
<td>0.24 ± 0.13</td>
</tr>
<tr>
<td>( R_5 ) (( \text{k}\Omega ) ( \text{cm}^2 ))</td>
<td>5.8 ± 1.9</td>
<td>5.5 ± 1.8</td>
<td>5.4 ± 1.7</td>
</tr>
<tr>
<td>( \tau_5 ) (ms)</td>
<td>1.1 ± 0.5</td>
<td>1.1 ± 0.5</td>
<td>1.0 ± 0.5</td>
</tr>
<tr>
<td>( R_6 ) (( \text{k}\Omega ) ( \text{cm}^2 ))</td>
<td>12 ± 4</td>
<td>12 ± 4</td>
<td>11 ± 3</td>
</tr>
<tr>
<td>( \tau_6 ) (ms)</td>
<td>4.6 ± 2.0</td>
<td>4.3 ± 2.0</td>
<td>4.2 ± 1.8</td>
</tr>
<tr>
<td>( R_7 ) (( \text{k}\Omega ) ( \text{cm}^2 ))</td>
<td>31 ± 5</td>
<td>28 ± 5</td>
<td>28 ± 5</td>
</tr>
<tr>
<td>( \tau_7 ) (ms)</td>
<td>19 ± 6</td>
<td>17 ± 5</td>
<td>17 ± 5</td>
</tr>
<tr>
<td>( R_8 ) (( \text{k}\Omega ) ( \text{cm}^2 ))</td>
<td>61 ± 6</td>
<td>57 ± 6</td>
<td>55 ± 5</td>
</tr>
<tr>
<td>( \tau_8 ) (ms)</td>
<td>81 ± 15</td>
<td>71 ± 13</td>
<td>75 ± 14</td>
</tr>
<tr>
<td>( \tau_9 ) (s)</td>
<td>79 ± 10</td>
<td>77 ± 8</td>
<td>74 ± 9</td>
</tr>
<tr>
<td>( \tau_{10} ) (s)</td>
<td>0.52 ± 0.11</td>
<td>0.46 ± 0.08</td>
<td>0.49 ± 0.10</td>
</tr>
<tr>
<td>( \tau_{11} ) (s)</td>
<td>4.1 ± 1.0</td>
<td>3.8 ± 0.8</td>
<td>4.0 ± 0.9</td>
</tr>
<tr>
<td>( \tau_{12} ) (s)</td>
<td>1.0 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>( \tau_{13} ) (s)</td>
<td>12 ± 2</td>
<td>12 ± 2</td>
<td>12 ± 2</td>
</tr>
<tr>
<td>( \tau_{14} ) (s)</td>
<td>0.65 ± 0.08</td>
<td>0.60 ± 0.06</td>
<td>0.55 ± 0.06</td>
</tr>
<tr>
<td>( \tau_{15} ) (s)</td>
<td>67 ± 11</td>
<td>70 ± 10</td>
<td>78 ± 14</td>
</tr>
<tr>
<td>( R_{\text{rel}} ) (( \Omega ) ( \text{cm}^2 ))</td>
<td>356 ± 15</td>
<td>352 ± 14</td>
<td>351 ± 15</td>
</tr>
</tbody>
</table>
Figure 5. Results of the fit of a 12-element Voigt measurement model to the impedance data associated with the scan of day 1 shown in Fig. 2b. The error structure was used as the weighting strategy. The experimental data and model are represented by open symbols and a superimposed solid line, respectively. The dashed line represents the 95.4% confidence interval for the model obtained by Monte Carlo simulation using the calculated confidence interval for the estimated parameters. (a) Fit to the imaginary part, (b) prediction of the real part.

Figure 6. Relative residual errors for the fit of a 12-element Voigt measurement model to the impedance data associated with scan a of day 1 shown in Fig. 2b. The experimental data are represented by open symbols and the dashed lines represents the 95.4% confidence interval for the model obtained by Monte Carlo simulation using the calculated confidence interval for the estimated parameters. (a) Imaginary part and (b) real part.

Kramer–Kronig relations, they were not excluded from the spectra during further analysis as the technique has only been used to truncate data at high and low-frequency ends.

Transmission Line Model

The transmission line model has been shown to be applicable to ZRPs, a schematic diagram of the model used is shown in Fig. 7. The ZRPs were viewed as zinc particles distributed in a poorly conducting polymer matrix with a behavior as a porous electrode. This provided justification that using the model as the transmission line model is applicable to a porous electrode. The application of de Levie’s transmission-line model was used for ZRPs. However, the circuit that is shown in Fig. 7 includes a contact impedance between the particles. The inclusion of this contact impedance is attributed to Gabrielli, who applied it to analyze the EIS data associated with electroactive fluidized beds. The circuit shown in Fig. 7 includes the contact impedance $Z_m$ with

$$Z_m = \frac{R_m}{1 + (j\omega R_m C_m)^{\alpha_m}}$$

where $R_m$ and $C_m$ are resistance and capacitance components and $\alpha_m$ is included for the dispersion of the time constants associated with the contact impedance. The impedance between the particles and the electrolyte in the pores for a small segment is given by $Z_l$ with...
Figure 7. Schematic representation of the transmission-line model given by Abreu et al. The impedance of a uniform transmission line is given by

\[
Z = Z_m R_e + \frac{Z_m R_e}{Z_m + R_e} + \frac{\left(\frac{Z_m}{Z_m} + R_e\right)^2 \cosh(L\gamma) + 2Z_m R_e}{\left(\frac{Z_m}{Z_m} + R_e\right) \sinh(L\gamma)}
\]

where \(Z_m\) is the modulus of data and model as shown by the fit for the 1 mHz to 100 kHz range. There was agreement between the data and model for the 1 mHz to 10 kHz frequency range, but at frequencies greater than 10 Hz the model was not in agreement with the data. This dissimilarity for frequencies greater than 10 Hz was also observed from fits of the model to the impedance data associated with days 2 through 4. Observation of the phase angle experimental data in Fig. 8b indicated that there was an increase in phase angle from 100 Hz to 5 kHz followed by a decrease from 5 to 100 kHz. The fit of the model for the 1 mHz to 10 kHz range exhibited an increase in phase angle for frequencies greater than 100 Hz without any decrease at higher frequencies. The results of the fit of model to the data for the frequency range 1 mHz to 10 kHz is also shown Fig. 8. There was agreement between the model and data for this frequency range.

The parameters from the fit of the model to the data for the frequency ranges 1 mHz to 100 kHz and 1 mHz to 10 kHz are given in Table II. There were no significant differences between the values associated with the two frequency ranges for a given parameter. The similarity between the parameters was attributed to the transmission-line model of Eq. 5 being adequate for the 1 mHz to 10 kHz range. As seen in Fig. 8b, the model was suitable up to 10 kHz, after which the data exhibited a decrease in phase angle with frequency which was not accommodated by the model, as shown by the fit for the 1 mHz to 100 kHz range.

The experimental data associated with the frequency range 10 kHz to 100 kHz were shown to be consistent with the Kramers–Kronig relations. The influence of truncating the 10 data points at the high-frequency end was determined by fitting a measurement model to the data of scan a of day 1 for the frequency range 1 mHz to 10 kHz. A Voigt model of 11 elements maximum was fit to the data in this frequency range. The value of the resistance as a function of time constant for the Voigt models used for the 1 mHz to 100 kHz and 1 mHz to 10 kHz ranges are given in Fig. 9. There were 12 time constants associated with the 1 mHz to 100 kHz, and only 9 were common with the 11 time constants of the 1 mHz to 10 kHz range. This demonstrated that the truncated data set of 1 mHz to 10 kHz range did not contain all the information as the 1 mHz to 100 kHz data set. It was concluded that the data in the range 10 kHz to 100 kHz, which were Kramers–Kronig consistent, contained information for processes with small time constants that could not be resolved from the transmission-line model given by Eq. 5. It would be necessary to adjust the model to accommodate data in the 10 kHz to 100 kHz range.

A modification to the transmission-line model given by Abreu et al. to model the EIS data associated with a ZRP substrate. This was based on the assumption that the zinc particles...
Changes in the values of active surface area of the Mg particles as they are being consumed. The drop in contact resistance coupled with the OCP moving toward a more positive value was attributed to the products of these processes at the high-frequency end of the spectra. The model in its present form was applicable to determine the contributions of the contact and interfacial impedance, and the electrolyte resistance of an MRP on a gold substrate for the period where the potential changed from a mixed potential value to a value more associated with the gold substrate.

### Conclusions

Experimental EIS data of an MRP on an inert gold substrate were analyzed for consistency with Kramers–Kronig relations and applicability for use with a transmission-line model. The Kramers–Kronig consistency was determined with the use of the measurement model technique and its application yielded that the data in the frequency range of 1 mHz to 100 kHz were Kramers–Kronig consistent. The reproducibility of the data at the low-frequency end of 1 mHz to 10 mHz indicated that the processes with the large time constants were stable. The transmission-line model reported by Abreu et al. was shown to be applicable for the 1 mHz to 10 kHz frequency range. The data of the 10 kHz to 100 kHz range were consistent with the Kramers–Kronig relations and were not resolvable by the transmission-line model used. Additional features may need to be included in the transmission-line model that can resolve these processes at the high-frequency end of the spectra. The model in its present form was applicable to determine the contributions of the contact and interfacial impedance, and the electrolyte resistance of an MRP on a gold substrate for the period where the potential changed from a mixed potential value to a value more associated with the gold substrate.

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**Table II.** Parameters associated with the regression of the transmission-line model to the impedance of scan a of day 1 for the frequency ranges 1 mHz to 100 kHz and 1 mHz to 10 kHz.

<table>
<thead>
<tr>
<th>Frequency range</th>
<th>$R_e$ (GΩ cm)</th>
<th>$C_m$ (nF cm$^{-1}$)</th>
<th>$\alpha_m$</th>
<th>$R_i$ (kΩ cm$^{-1}$)</th>
<th>$C_i$ ($\mu$F cm)</th>
<th>$\alpha_i$</th>
<th>$R_e$ (MΩ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mHz to 100 kHz</td>
<td>0.79</td>
<td>61</td>
<td>0.67</td>
<td>6.1</td>
<td>1670</td>
<td>0.87</td>
<td>59</td>
</tr>
<tr>
<td>1 mHz to 10 kHz</td>
<td>0.92</td>
<td>22</td>
<td>0.72</td>
<td>5.1</td>
<td>2650</td>
<td>0.81</td>
<td>45</td>
</tr>
</tbody>
</table>

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**Figure 9.** Distribution of the time constants for the fits of measurement model to the impedance data of scan a of day 1. A 12-element Voigt model was used to fit the data in the frequency range of 1 mHz to 100 kHz and a 11-element Voigt model was used to fit the data in the frequency range of 1 mHz to 10 kHz. The error bars correspond to ±σ and were calculated using a linear approximation. Nine circles/ovals are used to identify the nine time constants that were similar between the fit results.

**Figure 10.** Resistance values of the contact impedance, interfacial impedance, and the electrolyte resistance parameters obtained from the fit of the transmission-line model to the daily impedance data shown in Fig. 2a as functions of the OCP.
Figure 11. Parameter values of the contact impedance, interfacial impedance, and the electrolyte resistance parameters obtained from the fit of the transmission-line model to the daily impedance data shown in Fig. 2a as functions of the OCP: (a) Capacitance parameters and (b) parameters associated with the dispersion of the contact and interfacial impedance.

References