samples, to Thomas J. Pisklak for cross-sectioning of the membranes, to Jim Smith and co-workers for assistance in the analysis of water uptake of the membranes, to Larry Smith and Bob Aikman for supplying the membranes, and to Charlie Martin for helpful discussions.

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REFERENCES

Measurement Models for Electrochemical Impedance Spectroscopy

I. Demonstration of Applicability

Pankaj Agarwal* and Mark E. Orazem**

Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611

Luis H. Garcia-Rubio

Department of Chemical Engineering, University of South Florida, Tampa, Florida 33620

ABSTRACT

Use of measurement models is suggested as an intermediate step in the analysis of impedance data. In a manner analogous to the routine use of measurement models in the deconvolution of optical spectra, the measurement model could be used to guide development of physicoelectrochemical models by determining whether a data set is consistent with the Kramers-Kronig relations, by suggesting a form for the error structure of the data, and by providing an indication of the number and type of physical processes that can be resolved from the data. In this paper, a general measurement model is shown to apply for a wide variety of typical electrochemical impedance spectra. The application of the measurement models as a data filter will be addressed in subsequent papers.

Impedance spectroscopy has become a powerful tool for investigating the properties of electronic materials and electrochemical systems (1, 2). The response of a system to a sinusoidal perturbation can be used to calculate the impedance as a function of the frequency of the perturbation. Interpretation of electrochemical impedance spectra requires selection of an appropriate model which is regressed to the data. The most commonly used model is an electrical circuit analogue consisting of resistors, capacitors, inductors, and specialized distributed elements. Development of detailed physicoelectrochemical models is becoming more common but is still less often pursued. Selection of an appropriate model can be time consuming, particularly if a detailed physicoelectrochemical model is desired. Some of the questions that must be addressed in developing an appropriate model are:

1. Was the experimental system stationary? One distinction between electrochemical and electrical systems is that electrochemical processes are typically dynamic, i.e., the rate of electrochemical reactions can change in response to dissolution of the electrode, deposition of salt or oxide films, and adsorption or absorption of reacting species. If the system changed significantly during the time in which data were collected, this nonstationary behavior should be incorporated into the model.

2. How many physical processes can be resolved from the data? Electrochemical systems rarely display well-resolved peaks in the impedance spectra. Since the ultimate goal of interpreting impedance spectra is to gain insight into the physical processes that control the system, the model developed must incorporate time constants for the relevant physical processes. Another way to phrase this question is to ask whether the lack of complete agreement between the data and the model should be attributed to experimental error, to nonstationary processes, or to use of an inadequate or incomplete model.

Determination of stationary behavior.—A system can be determined to be stationary through careful experimentation, through successful regression of the data to electrical-circuit analogues, or through direct integration of the Kramers-Kronig relations. Stationary behavior can be identified experimentally by replication of the impedance spectrum. If the experimental frequency range is sufficiently broad the extrapolation of the impedance spe-
trum to zero frequency can be compared to the corresponding values obtained from separate steady-state experiments. The Kramers-Kronig relations, e.g.,

\[
Z_z(\omega) = -\left(\frac{2\omega}{\pi}\right) \int_0^\infty \frac{Z(x) - Z_z(\omega)}{x^2 - \omega^2} \, dx \tag{1}
\]

and

\[
Z_z(\omega) = Z_z(\omega) + \frac{2}{\pi} \int_0^\infty \frac{xZ(x) - i\omega Z_z(\omega)}{x^2 - \omega^2} \, dx \tag{2}
\]

provide a relationship between the real and imaginary components of impedance \(Z_z(\omega)\) and \(Z_z(\omega)\) respectively) that hold under the assumptions of stability, causality, and linearity (3-6). Lack of consistency with the Kramers-Kronig relations in electrochemical systems can often be attributed to failure of the stability criterion. Since electrical circuit models satisfy the Kramers-Kronig relations, a system can be judged to be stationary if a satisfactory fit to a circuit model is obtained. If a satisfactory fit is not obtained, the question remains as to whether the lack of fit is caused by use of an insufficient model or by nonstationary behavior. Direct application of the Kramers-Kronig relations eliminates the need to select a model. Use of the relations, however, requires integration from 0 to \(\infty\) in frequency, and most electrochemical impedance data do not adequately approximate the required frequency domain. Several approaches have been taken for extrapolating data into the unmeasured frequency domain (7-16). Additional problems are caused by imprecision in the integration associated with a poor signal to noise ratio at the extremes of the frequency domain. As a result of these issues, direct application of the Kramers-Kronig relations in experimental electrochemistry is not commonplace.

If a system is not stationary, the model for the impedance response could be developed to account for the time-dependent behavior. The current practice, however, is to revise the experimental conditions to reduce the time required for the experiment and thereby allow the system to be represented by a pseudo-steady state model.

**Selection of an appropriate model.**—Lack of complete agreement between the data and a model could be attributed to the error structure (or noise) of the experimental data, to nonstationary processes, or to the use of an inadequate or incomplete model. Whether based on electrical circuit analogues or on solution of conservation equations, models for impedance spectra are sufficiently constrained that they cannot provide a framework for determining the noise in the data. Several approaches have been taken to resolve this issue. Artificial-intelligence methods have been suggested to identify optimal electrical circuit analogues for regression to data (17-19). A model is built sequentially until all features of the data are represented. Interpretation of the resulting regressed circuit components in terms of physical processes may be difficult because several electrical-circuit models could be used to model a given impedance spectrum. On another extreme, exclusive use of a limited group of circuit models has been proposed for screening of “industrial” corrosion data (20). This approach resolves the issue by accepting the best of a limited number of regressions, and therefore information on relevant physical processes may be lost. Usually, trial and error selection of circuit models is made until the fit is deemed to be acceptable.

**Measurement Models**

Models can be classified as being one of two types. Process models are used to predict the response of a system from physical phenomena that are hypothesized to be important. Regression of process models to data allows identification of physical parameters based upon the original hypothesis. In contrast, measurement models are built by sequential regression of line shapes to the data. The model can be used to identify characteristics of the data set that could facilitate selection of an appropriate process model.

The measurement model selected for this work was the Voight model, i.e.,

\[
Z(\omega) = Z_0 + \sum \frac{\Delta_k}{\pi (1 + j\omega \tau_k)} \tag{3}
\]

An electrical circuit corresponding to the Voight model is presented in Fig. 1. Use of the Voight model was motivated by the routine use of measurement models in the deconvolution of optical spectra (21). To be useful, the measurement model must contain line shapes that correspond to physical processes. Since stationary optical (and impedance) spectra satisfy the Kramers-Kronig relations, the model must also be consistent with the Kramers-Kronig relations. The impedance response of a single Voight element is usually attributed to the electrical response of a linearized electrochemical reaction (1, 2). The term \(Z_0\) corresponds to the ohmic resistance, the time constant \(\tau_k\) for element \(k\) is equivalent to \(R_k C_k\) in the Voight model, and \(\Delta_k\) is equivalent to \(R_k\). Equation [3] is consistent with the Kramers-Kronig relations.

The tenets underlying the use of measurement models for impedance spectroscopy are:

1. By including a sufficient number of terms, a general measurement model based on Eq. [3] can fit impedance data for typical stationary electrochemical systems. The object of this paper is to demonstrate that this postulate holds for electrochemical systems that exhibit the influence of mass transfer (through Warburg elements), pseudo-capacitive behavior, frequency dispersion (through constant-phase elements), and kinetic control.

2. Because the measurement model does fit stationary impedance data, an inability to predict the imaginary part of the impedance spectrum with parameters obtained by fitting the real part of the spectrum (or, conversely, to predict the real part of the impedance spectrum with parameters obtained by fitting the imaginary part of the spectrum) can be attributed to failure of the data to conform to the assumptions of the Kramers-Kronig relations rather than to failure of the model. Thus, as discussed in Ref. (22) and (23), the measurement model could be used to assess the consistency of impedance data with the Kramers-Kronig relations without integration.

3. Another result of the adequacy of the measurement 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” (22, 23). It may be possible to use an expanded form of the measurement model to provide an indication of the number and types of physical processes that can be resolved from the data. The measurement model could include mass-transfer effects by adding to Eq. [3] a line shape corresponding to the Warburg element. This approach is discussed in Ref. (24). The model is adjusted until a statistically good fit is obtained with the smallest number of elements.

The use of measurement models is superior to the use of polynomial fitting because fewer parameters are needed to model complex behavior, and because the measurement model satisfies the Kramers-Kronig relations implicitly. Experimental data can, therefore, be checked for consistency with the Kramers-Kronig relations without actually integrating the equations over frequency. The use of measurement models does not require extrapolation of the experimental data set; therefore, inaccuracies associated
Circuit 2:

Circuit 3:

Circuit 4:

Circuit 5:

**Fig. 2.** Electrical circuit analogues for: 1, hydrogen evolution on LaNi₅ (16); 2, corrosion of carbon steel in 3 w/o NaCl solution near the corrosion potential (28); 3, corrosion of iron in 0.5M H₂SO₄ at the corrosion potential (29); 4, corrosion of a model pit electrode in 0.5M NaCl (30); and 5, corrosion of a painted metal (31).

with an incomplete frequency spectrum are resolved. For the application to a preliminary screening of the data, the use of measurement models is superior to the use of more specific electrical-circuit analogues because one can determine whether the residual errors are due to an inadequate model, to failure of data to conform to the Kramers-Kronig assumptions, or to experimental noise.

**Approach for Demonstration of Applicability**

The usefulness of the measurement model depends on the extent to which the line shape for each element corresponds to that generated by physical phenomena. For example, the utility of measurement models in the field of optics is due to the accuracy of the Lorentzian, Drude, and Debye models of optical excitation (25-27). The claims made here for the measurement models require that the line shape used be adequate to represent typical impedance data. While this approach has been applied directly to experimental data (23, 24), the intent here is to demonstrate applicability to published data for some rather complex systems. The authors cited have used electrical-circuit analogues to model their results, and, in this work, the measurement models were applied to synthetic data obtained from the authors' models. The models were selected for this work because they encompass phenomena typically seen in electrochemical impedance spectra (i.e., diffusion, pseudocapacitive behavior, and frequency dispersion). The circuit analogues are presented in Fig. 2, and the associated parameter values are presented in Table I.

The "synthetic data" to which the measurement model was applied were calculated in double precision from the models presented in Fig. 2 and Table I. The data were, therefore, inherently consistent with the Kramers-Kronig relations, and the only "noise" in the data was caused by round-off error in the calculation. Use of synthetic data provides a good test of the measurement model because the errors associated with experimental noise and non-stationary behavior are avoided. A poor fit of the measurement model to synthetic data can, therefore, be attributed only to inadequacies of the model. Two nonlinear regression packages [LOMF by J. R. Macdonald (32) and a proprietary program written by L. Garcia-Rubio (33)] were used to fit the measurement model to the synthetic data, and the fits obtained were identical. The data were normalized such that each point had equal weight in the regression. This normalization was used to avoid excessive

---

**Table I. Values for circuit parameters.**

<table>
<thead>
<tr>
<th>Circuit</th>
<th>1 (a and b)</th>
<th>2 (28)</th>
<th>3 (29)</th>
<th>4 (30)</th>
<th>5 (31)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_l$, Ω</td>
<td>23.22</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>1000</td>
</tr>
<tr>
<td>$R_s$, Ω</td>
<td>418.3</td>
<td>150</td>
<td>100</td>
<td>15</td>
<td>$2 \times 10^3$</td>
</tr>
<tr>
<td>$C_1$, μF</td>
<td>18.82</td>
<td>1000</td>
<td>25</td>
<td>128</td>
<td>$1 \times 10^2$</td>
</tr>
<tr>
<td>$R_3$, Ω</td>
<td>695.2</td>
<td>200</td>
<td>—</td>
<td>—</td>
<td>$4 \times 10^3$</td>
</tr>
<tr>
<td>$C_2$, μF</td>
<td>92.58</td>
<td>—</td>
<td>50</td>
<td>—</td>
<td>$1 \times 10^2$</td>
</tr>
<tr>
<td>$R_2$, Ω</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$L$, H</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$R_w$, Ω</td>
<td>848.4</td>
<td>500</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$\tau_0$, s</td>
<td>0.7055</td>
<td>5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$\tau_{cpw}$, s</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1135</td>
<td>—</td>
</tr>
<tr>
<td>$\tau'$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>$\beta$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.79</td>
<td>—</td>
</tr>
</tbody>
</table>

---

**Fig. 3.** Regression of a measurement model with one Voight element to synthetic data ( ) obtained from Circuit 1 (hydrogen evolution on LaNi₅ (16)). Solid lines in all figures are the results of the model fit. The residual sum of squares for the fit was 37.15.
Fig. 4. Regression of a measurement model with two Voight elements to synthetic data (○) obtained from Circuit 1 [hydrogen evolution on LaNi₅ (16)]. The residual sum of squares for the fit was 0.5588. Solid lines in all figures are the results of the model fit. The lines presented in the lower two figures are the model fit and its deconvolution into the contribution of each Voight element.

weighting on the low-frequency data which typically have much larger values for the impedance.

Results and Discussion

The sequential manner in which a measurement model is constructed is demonstrated in the first subsection. The application of the measurement model is further demonstrated for systems influenced by diffusional processes and inductive behavior. The applicability of the measurement model is also demonstrated for a system that was modeled by a constant-phase element and for a high-impedance system. The interpretation of parameter values is discussed in the final subsection.

Sequential construction of a model: Circuit 1.—In accordance with Eq. [3] a measurement model is constructed by sequentially adding k Voight elements with parameters \( \Delta_k \) and \( \tau_k \) until the fit is no longer improved by the addition of yet another element. This procedure is illustrated for synthetic data obtained from the electrical-circuit model proposed for evolution of hydrogen on a LaNi₅ ingot electrode (16). A diffusional resistance was observed in this system as a result of the incorporation of hydrogen into the metal. The electrical-circuit model presented as Circuit 1 in Fig. 2 accounted for mass transfer of hydrogen with a Warburg element, and three time constants are evident in the circuit analogue. The complex Warburg impedance, given by

\[
Z_W = R_W \frac{\tanh (\sqrt{\tau_W} \omega)}{(\sqrt{\tau_W} \omega)}
\]

can be derived from the solution of \( \nabla^2 \psi = 0 \) for a film of thickness \( \delta \) (1, 2). The time constant can be expressed in terms of diffusivity and film thickness as \( \tau_W = \delta^2 / D \). The Warburg element is sometimes called a distributed element because it can be modeled by a distribution of relaxation time (1).

The manner in which the measurement model behaves upon successive incorporation of line shapes is demonstrated in Fig. 3 through 7. The difference between the simulated data and a measurement model incorporating one Voight element is presented in Fig. 3. The residual sum of squares was improved to 0.5588 by addition of a second line shape as seen in Fig. 4. Inclusion of a third line
shape, shown in Fig. 5, resulted in a three-order of magnitude decrease in the residual sum of squares. The improvement of the fit achieved by addition of a fourth element (Fig. 6) is not readily seen in a comparison of Fig. 5 and 6. The inclusion of a fourth element was, however, considered to be statistically significant because the residual sum of squares was improved by an additional three-orders of magnitude. A significant improvement in the fit was also observed for five Voight elements (Fig. 7), and the resultant residual sum of squares was $4.915 \times 10^{-18}$.

Fig. 6. Regression of a measurement model with four Voight elements to synthetic data (○) obtained from Circuit 1 [hydrogen evolution on LaNi$_5$ (16)]. The residual sum of squares for the fit was $1.772 \times 10^{-7}$. Solid lines in all figures are the results of the model fit. The lines presented in the lower two figures are the model fit and its deconvolution into the contribution of each Voight element.

Fig. 7. Regression of a measurement model with five Voight elements to synthetic data (○) obtained from Circuit 1 [hydrogen evolution on LaNi$_5$ (16)]. The residual sum of squares for the fit was $4.915 \times 10^{-18}$. Solid lines in all figures are the results of the model fit. The lines presented in the lower two figures are the model fit and its deconvolution into the contribution of each Voight element.

The residual sum of squares obtained by fitting the measurement model to the synthetic data is presented as a function of the number of Voight elements in Fig. 8. Figure 8 can be used to show that a maximum of five Voight elements can be resolved from the synthetic data because the sixth Voight element did not improve the quality of the fit. Figure 8 also shows that, while visual inspection of Fig. 5 suggests that the fit obtained with three elements was acceptable (resulting in residual errors less than 0.1%), addition of the fourth and fifth element provided significant improvement in the residual error. The residual error obtained by regressing the five-time-constant Voight
Fig. 8. Normalized sum of squares for the regression of a measurement model to synthetic data obtained from Circuit 1 [hydrogen evolution on LaNi₅ (16)] as a function of the number of Voight time constants employed in the model: (O) regression to synthetic data; (x) regression to synthetic data with random noise added; and (dashed line) normalized noise level. The residual errors were randomly distributed with respect to frequency. The parameter values obtained through regression of the measurement model to the LaNi₅ system are presented in Table II. The parameter values obtained for the first three elements changed slightly (about 5%) to compensate for the noise and the lack of the fourth and fifth elements. As expected, only a rough equivalency is seen between the fit parameters and the parameters of the original circuit. For example, the largest time constant obtained in the fit (Table II) was 0.387 s; whereas, the largest time constant in the original circuit (Table I) had a value of 0.7055 s. Good agreement was seen between the ohmic resistance of the original circuit Rₜ and the high-frequency limit of the measurement model Z₀.

Table II. The results of the regression of the Voight measurement model (Fig. 1) to the circuits shown in Fig. 2.

<table>
<thead>
<tr>
<th>Circuit</th>
<th>1a (Warburg)</th>
<th>1b (Warburg)</th>
<th>2 (Warburg)</th>
<th>3 (Inductor)</th>
<th>4 (CPE)</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z₀, Ω</td>
<td>23.22</td>
<td>23.77</td>
<td>0</td>
<td>0</td>
<td>0.50036</td>
<td>1000</td>
</tr>
<tr>
<td>A₀, Ω</td>
<td>266.48</td>
<td>239.7</td>
<td>10.69</td>
<td>58.605</td>
<td>274.35</td>
<td>436,900</td>
</tr>
<tr>
<td>ν₁, s</td>
<td>0.006404</td>
<td>0.005569</td>
<td>0.7954</td>
<td>0.002932</td>
<td>3.339</td>
<td>0.00442</td>
</tr>
<tr>
<td>A₁, Ω</td>
<td>1.159</td>
<td>1.201</td>
<td>29.14</td>
<td>-102.65</td>
<td>13.1</td>
<td>165,100</td>
</tr>
<tr>
<td>h₁, s</td>
<td>0.386</td>
<td>0.3970</td>
<td>4.101</td>
<td>0.0975</td>
<td>0.001823</td>
<td>0.0001811</td>
</tr>
<tr>
<td>Z₁, Ω</td>
<td>494.0</td>
<td>528.8</td>
<td>22.83</td>
<td>343.35</td>
<td>3.332</td>
<td></td>
</tr>
<tr>
<td>Z₂, Ω</td>
<td>0.0760</td>
<td>0.0731</td>
<td>0.1131</td>
<td>0.01709</td>
<td>0.91164</td>
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<td>A₂, Ω</td>
<td>22.61</td>
<td>25.12</td>
<td>51.50</td>
<td>3.053</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₂, s</td>
<td>0.02723</td>
<td>0.07162</td>
<td>0.97162</td>
<td>49.91</td>
<td>0.09767</td>
<td></td>
</tr>
<tr>
<td>A₃, Ω</td>
<td>9.128</td>
<td>8.094</td>
<td>0.2877</td>
<td>57.67</td>
<td>0.8158</td>
<td></td>
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<tr>
<td>h₃, s</td>
<td>0.00824</td>
<td>0.005693</td>
<td>0.8880</td>
<td>605.75</td>
<td>6.62</td>
<td></td>
</tr>
<tr>
<td>Z₄, Ω</td>
<td>0.0760</td>
<td></td>
<td>0.01248</td>
<td>12.15</td>
<td>28.01</td>
<td></td>
</tr>
<tr>
<td>A₄, Ω</td>
<td></td>
<td></td>
<td>0.00603</td>
<td>605.75</td>
<td>492.9</td>
<td></td>
</tr>
<tr>
<td>ν₄, s</td>
<td></td>
<td></td>
<td>0.0003352</td>
<td>12.15</td>
<td>28.01</td>
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<tr>
<td>A₅, Ω</td>
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<td></td>
<td>0.0004966</td>
<td>605.75</td>
<td>492.9</td>
<td></td>
</tr>
</tbody>
</table>
Application to diffusion systems: Circuit 2.—In general, the number of Voight elements needed to model a system which is affected by diffusion exceeds the number of time constants implicit in a model that incorporates a Warburg element. While the contribution of the additional Voight elements can, as shown above, be insignificant in comparison to experimental noise, the discrepancy remains because a single Voight element simply cannot account for the frequency dependence associated with mass transfer. If a measurement model is to be used to identify the correct number of time constants for a given system, additional model elements must be incorporated in much the same way as multiple models (Lorentzian, Drude, or Debye) can be used to develop measurement models for optical dispersion. The number of model elements used is, of course, irrelevant if the measurement model is to be used simply to check the consistency of data to the Kramers-Kronig assumptions.

The application of the Voight measurement model is presented in Fig. 12 for the corrosion of carbon steel in 3 weight percent (w/o) NaCl solution near the corrosion potential (28). The corresponding electrical-circuit model (presented as Circuit 2 in Fig. 2) included a Warburg diffusion element to account for the mass-transfer resistance of the solution. Eight Voight elements were needed, even though only three time constants are present in Circuit 2. The results of this regression do show that the measurement model can provide an adequate representation of experimental impedance data that can be modeled in terms of a Warburg impedance. Similar agreement was obtained for direct analysis of experimental data for systems influenced by mass transfer (23, 24).

Application to inductive systems: Circuit 3.—The appearance of a positive imaginary component of the impedance has been attributed at high frequencies to the stray capacity of the current-measuring resistor and at low frequencies to adsorption phenomena at the electrode surface (1). Transport-based models for this behavior are rare, and most electrical-circuit models account for this behavior by incorporating either an inductor or a capacitor with a nega...
Fig. 12. Regression of a measurement model with four Voight elements to synthetic data (O) obtained from Circuit 2 (corrosion of carbon steel in 3 w/o NaCl solution near the corrosion potential [28]). The residual sum of squares for the fit was 3.763 × 10⁻⁴. Solid lines in all figures are the results of the model fit. The lines presented in the lower two figures are the model fit and its deconvolution into the contribution of each Voight element.

Fig. 13. Regression of a measurement model with three Voight elements to synthetic data (O) obtained from Circuit 3 (corrosion of iron in 0.5M H₂SO₄ at the corrosion potential [29]). The residual sum of squares for the fit was 3.221 × 10⁻¹⁴. Solid lines in all figures are the results of the model fit. The lines presented in the lower two figures are the model fit and its deconvolution into the contribution of each Voight element.

The application of the measurement model to pseudo-capacitive data reported by Lorenz and Mansfeld [29] for corrosion of iron in 0.5M H₂SO₄. Their model, shown as Circuit 3 in Fig. 2, incorporated an inductor to fit the pseudo-capacitive response at low frequencies. The Voight model can account for inductive behavior if the magnitude (Δω) is allowed to have a negative sign. The regression to Circuit 3 is given in Fig. 13. The measurement model indicates that three time constants can be resolved from the synthetic data, and this result is fully consistent with the circuit. Complete agreement was obtained because the circuit is composed of only passive elements (one inductor, three resistors, and two capacitors). The residual sum of squares for this fit was found to be 3.221 × 10⁻¹⁴. The measurement model provides a good fit to data exhibiting an inductive response.

Application to constant phase elements: Circuit 4.—The broadening or depression of a semicircle in the impedance plane plot can be attributed to a variety of physical phenomena. For example, models have been developed that
The measurement model provided a one-to-one identification of the time constants for a class of processes that are described in terms of passive elements. Thus, the measurement model may allow correct identification of the number of physical processes that can be discerned from the impedance response of systems that are unaffected by mass transfer or by the frequency dispersion associated with nonuniform current/potential distributions. Solid-state systems may, for example, be suited for this type of analysis. The measurement model cannot, however, be generally used for identification of the largest number of time constants discernible in a given spectrum because several Voight elements were needed to model a distributed element. A further extension of the measurement model approach is required. It may be possible, for example, to use a measurement model to identify the number and type of physical processes discernible in a given spectrum that is influenced by mass transfer, if
model elements are included that account for diffusion phenomena. An element based, for example, on a Warburg (diffusional) impedance could represent diffusional processes with a single time constant. A measurement model for optical dispersion by summing elements representing different physical processes in a manner analogous to building a measurement model for optical dispersion by summing Lorentzian, Drude, and Debye elements (24).

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Time-Averaged Current Distribution for a Rotating-Disk Electrode under Periodic Current Reversal Conditions

K.-M. Jeong, C.-K. Lee, and H.-J. Sohn
Department of Mineral and Petroleum Engineering, Seoul National University, Seoul, Korea 151-742

ABSTRACT

The time-averaged current distribution over the surface of a rotating-disk electrode is calculated under conditions of periodic current reversal by simultaneously solving the transient-convective-diffusion equation and Laplace’s equation. The calculated results compare well with experiments performed using the copper/copper sulfate system. The grid search technique is used to determine the optimum plating conditions in terms of uniform thickness of electrodeposits by varying the duty factor and the ratio of anodic to cathodic current density.

Pulsed current (PC) technology has long been used in electroplating industries due to the improvements in the quality of electrodeposits, and its characteristics are well described in the monograph by Puippe and Leaman (1). But the current distribution over the electrode surface in pulse plating is generally less uniform than that in dc plating. Recently, Wan and Cheh (2) developed a mathematical model of the pulse plating of copper for the case below the limiting current density condition and calculated the secondary current distribution on a rotating-disk electrode. Also Chin et al. (3), computed the secondary current distribution on a planar electrode neglecting the mass-transfer effect. They showed that the nonuniform ohmic potential drop in the solution outside the diffusion layer contributed to the nonuniform current distribution.

In order to minimize the nonuniformity of thickness distribution, organic additives as well as periodic current reversal (PCR) technique has been practiced in plating industries largely based on empiricism. The organic additives which act as levelers or brighteners generally tend to increase the polarization resistance, leading to an increase in throwing power (4). Popov et al. (5) showed that the macrothrowing power was considerably better with a PCR than with a PC. Also Granato and Sobral (6) found that dendritic growth of gold was not observed even at high current density in electrorefining with PCR technique.

Fedkiw and Brouns (7) developed a mathematical model of PCR plating on a planar electrode with an assumption of steady state. Recently, Pesco and Cheh (8, 9) presented a simulation of plated through-holes, and compared the current distribution between dc, PC, and PCR. They indicated that plating with PCR appeared to be a promising technique to obtain more uniform metal-thickness distribution at low current densities. In addition, it was demonstrated that the PCR technique can decrease the energy consumption due to the low anodic overpotential at the lead electrode in the electrowinning of zinc in acidic media (11) and increase the current efficiency of zinc electrowinning.

Theoretical

A mathematical model used in this study is similar to that developed earlier by Wan and Cheh (2) except for the boundary condition for the anodic pulse current. Popov and Maksimović (14) applied the same type of model for PCR plating without convective diffusion. The transient material-balance equation together with Laplace’s equation for the modeling of PCR plating will be described briefly.

Concentration profile in diffusion layer.—Electrodeposition with PCR technique on the rotating-disk electrode can be described in terms of the time-dependent material-balance equation, which can be expressed as

$$\frac{\partial C}{\partial t} + v_r \frac{\partial C}{\partial r} + v_z \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial z^2}$$

with the boundary conditions

$$C = C_b, \quad 0 \leq r, \quad 0 \leq z \quad \text{at} \quad t = 0$$

$$C = C_b, \quad r^2 + z^2 \to \infty \quad \text{at} \quad t > 0$$

$$-D \frac{\partial C}{\partial z} \bigg|_{z=0} = \frac{i}{nF}, \quad \text{for} \quad 0 < r < r_0 \quad \text{at} \quad t > 0$$

$$\frac{\partial C}{\partial z} = 0, \quad r = 0, \quad \text{for all} \quad z \quad \text{at} \quad t > 0$$

where $C$ is the concentration of species electrodeposited, $C_b$ is the concentration of the same species in the bulk solution, $D$ is the diffusivity, $F$ is the Faraday constant, $n$ is the number of electrons involved in the electrode reaction, $t$ is time, $v_r$ and $v_z$ are the fluid velocity in axial and radial directions, respectively, $z$ is the distance from the disk in axial direction, and $r$ is the radial direction coordinate.

The local current density, $i$, in Eq. (4) is the periodic function of time as (9, 14)

$$i = \begin{cases} i_r & \text{for} \quad 0 \leq t < t_1, \ t_2 < t < t_3, \ldots \ \\ -i_b & \text{for} \quad t_1 \leq t < t_2, \ t_3 \leq t < t_4, \ldots \end{cases}$$

where $i_r$ is the local cathodic current density and $i_b$ is the local anodic current density, respectively. Figure 1 shows the shape of periodic current reversal. The applied cathodic current density $i_b$ and the anodic current density, $i_r$, are related to the local current density

$$i_b = \frac{Z}{2} \int i_r \ r \ dr \ \text{for} \quad 0 \leq t < t_1, \ t_2 \leq t < t_3 \ldots$$

References:


2. L. H. Garcia-Rubio, Report in Progress, Center for Materials Development, University of South Florida, Tampa, FL 33620.