Applications of Impedance Spectroscopy to Corrosion Research

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A method is presented for interpretation of impedance spectra which employs measurement models for assessing the error structure of the measurement. The information obtained through use of the measurement model guides refinement of the experimental procedure and suggests phenomena to be included in the process model. The ultimate goal of the experimental observation is interpretation of impedance spectra in terms of physically meaningful parameters; therefore, the measurement model is used as a statistical tool to support development and regression of process models to experimental data.

Electrochemical impedance spectroscopy can provide a powerful tool for identification of phenomena governing electrochemical systems. The development and application of mathematical models for the interpretation of electrochemical impedance data requires quantitative assessment of the fundamental characteristics of the measurement as well as quantitative identification and evaluation of the physics and chemistry of the system under study. An important factor, often ignored or understated in electrochemical impedance spectroscopy, is the nature of the error structure associated with the measurements. The importance of the error structure is neglected in spite of the fact that electrochemical impedance measurements are recognized as being, in general, heteroskedastic and time varying. Identification and quantification of the measurement error structure is essential for filtering data, designing experiments, and assessing the validity of regression assumptions and the confidence intervals of the resulting parameters.

A method for interpretation of impedance spectra has been developed which employs measurement models for assessing the error structure of the measurement.[1-3] The information obtained through use of the measurement model guides refinement of the experimental procedure and suggests phenomena to be included in the process model. The synergistic implementation of experiment, measurement model and process model has been applied to a variety of electrochemical systems, including corrosion of copper, electrochemistry of metal hydrides (for battery applications), characterization of iontophoresis for transdermal delivery of therapeutic drugs, and identification of deep-level states in semiconductors (GaAs, ZnO, ZnS, and multilayer structures). The measurement model has been developed as a statistical tool to support development and regression of process models to experimental data.

Definition of Terms
In this work, two types of models are used to facilitate interpretation of experimental results.

Process Model
A process model is a deterministic model built upon hypothesized physical and chemical phenomena. Such models can be built upon prior information. For example, the principles governing electronic transitions within semiconductors are well known and can provide a working hypothesis to develop a

model for the impedance response of a solid-state semiconducting system.[4,5] A similar level of prior understanding is available for certain aspects (e.g., mass transfer) of electrochemical systems. Typically, the major uncertainty in electrochemical systems pertains to phenomena occurring at the electrode surface.

Experiment

The inability of impedance spectroscopy to serve as a stand-alone method for identification of a correct model has been addressed experimentally by including additional analysis techniques or by incorporating multiple or more directed forcing functions. For the study of corrosion, mass loss measurements, in-situ or ex-situ microscopic visualization of coupon surfaces, and chemistry-sensitive spectroscopic techniques are often used to support model identification. Model identification can be further supported by regressing models to a set of impedance spectra obtained at different temperatures or potentials. The dependence of the model parameters on temperature or potential can be incorporated into the model, or systematic variations of regressed parameters can be noted as a function of temperature or potential.[6,7] Another approach has been to replace potential as the forcing function for the impedance experiment.[8] The impedance response has been obtained by measuring the current response to modulated light intensity,[9] disk rotation speed,[10] magnetic fields,[11] and electrode temperature.[12] Quartz microbalances have been used to monitor the electrode mass in response to a modulated forcing parameter.[13,14] Insight into the experimental system is gained because the impedance response to a voltage perturbation is separated into its component transfer functions.

Measurement Model

The non-stationary character of electrochemical measurements has limited the ability to obtain a direct assessment of the stochastic error structure, and the finite frequency range associated with most experiments has limited the direct application of the Kramers Kronig relations for assessing the degree to which non-stationary phenomena have influenced the results. In this paper, the progress made in the use of measurement models for identification of the error structure of electrochemical impedance data is presented. Error structures, identified for other types of spectroscopic techniques, are used as starting points in the development of suitable models for the interpretation of electrochemical impedance which take into consideration the nature of the experimental error. Comparison of these measurement models with experimental observations suggest avenues for the generalization of models for the error structure. The status of a generalized model for the error structure is also presented and discussed.

Classification of Measurement Errors

The residual errors ($\varepsilon_{residual}$) that arise when a model is regressed to experimental data can be described as being either systematic or stochastic. Thus (see, e.g., reference 15);

$$Z_{exp} = Z_{mod} + \varepsilon_{residual}$$

$$\varepsilon_{residual} = \varepsilon_{systematic} + \varepsilon_{stochastic}$$

(1)

The systematic errors can arise from the lack of fit of the model to the data (ε_{lof}) or from a bias (ε_{bias}) in the experiment.

$$\varepsilon_{systematic} = \varepsilon_{lof} + \varepsilon_{bias}$$

(2)

Presence of stochastic errors $\varepsilon_{stochastic}$ in any experimental data is inevitable. In electrochemical impedance spectroscopy, nonstationary behavior (ε_{ns}) and instrumental artifacts (ε_{ins}) are often contributors to the systematic errors ε_{bias}.

$$\varepsilon_{bias} = \varepsilon_{ns} + \varepsilon_{ins} \qquad (3)$$

The nonstationary contribution to the bias is usually most easily observed at low frequencies. Instrumental artifacts may be seen at high frequency resulting from equipment limitations. Most electrochemical systems are inherently non-stationary due to the change in the electrode surface during the course of an experiment. In contrast, solid state systems, as a first approximation, may be assumed to stationary. Impedance data can be corrupted by instrumental artifacts for both electrochemical and solid state systems.

Application of Measurement Models to Impedance Spectroscopy

Identification of the error structure for most radiation-based spectroscopic measurements such as light scattering can be accomplished by calculating the standard deviation of replicate measurements. This approach is successful because the measurements are made in a very short timescale, and, therefore, stochastic noise can be assumed to be the only cause of scattering between independent measurements at a given frequency. In contrast, the stochastic contribution to the error structure of electrochemical impedance spectroscopy measurements cannot be obtained from the standard deviation of replicated measurements because the inherently nonstationary character of electrochemical systems introduces a non-negligible bias contribution to the error.

To get past this hurdle, we have introduced the measurement model as a tool for assessment of measurement characteristics. The first step in this development was to demonstrate that a model composed of a superposition of lineshapes was sufficient to model electrochemical impedance data. At first glance, it is not at all obvious that such an approach should work. It is well known, for example, that the impedance spectrum associated with an electrochemical reaction limited by the rate of diffusion through a stagnant layer (the Warburg impedance) can be approximated by an infinite number of RC circuits in series (the Voigt model). In theory, then, a measurement model based on the Voigt circuit should require an infinite number of parameters to describe adequately the impedance response of any electrochemical system influenced by mass transfer. In practice, an infinite number of Voigt parameters cannot be obtained from experimental data because stochastic errors (or noise) in the measurement limit the information content of the data. An infinite number of Voigt parameters cannot be obtained even from synthetic data because round-off errors limit the information content of the calculation.[1] The residual errors associated with fitting a Voigt model to experimental impedance data which are influenced by mass transfer can, with appropriate weighting, be made to be of the order of the stochastic noise in the measurement. A Voigt circuit, or any equivalent circuit, can yield an appropriate measurement model for electrochemical impedance spectra.

Determination of Stochastic Errors

The second stage in this development was to identify a method for measuring the error structure of impedance data. The approach taken was to identify the measurement characteristics experimentally rather than to assess the noise level from the published specifications of the component instrumentation.

For non-stationary systems ε_{ns} is not equal to zero. In fact, since the system changes with time, ε_{ns} changes from one experiment to another if a set of replicate (or consecutive) experiments are performed. Hence, the standard deviation of replicate measurements yields an inaccurate estimate for σ, because ε_{ns} will also contribute to the calculation of the standard deviation. For example, the

results of six consecutive (pseudo-replicate) experiments for copper in alkaline solution are shown in Figure 1. Each spectrum shown in the figure was found to be stationary but a careful analysis of the data using the measurement model approach showed that the data were not replicate.[16] A measurement model, with eight Voigt elements was regressed to the combined data set. The normalized residual errors obtained from the regression are shown in Figures 2a and 2b. Examination of the real and imaginary part of the residual errors shows that the system changed from one experiment to the other and the residuals for the six experiments can be distinguished from one another. The plot of the imaginary versus the real residuals is shown in Figure 2c. The plot suggests that the residuals are strongly correlated. Examination of real (circles) and imaginary (triangles) σ shown in Figure 2d as a function of frequency suggests that they are not equal. This observation is counter to the result obtained for stationary data, which is plotted as a solid line in Figure 2d.[1]

Filtering Algorithm

An algorithm designed to filter out ε_{ns} from non-stationary data to obtain $\varepsilon_{stochastic}$ is proposed in this section. Instead of regressing a measurement model to the combined data set, each data shown in Figure 1 was regressed separately. The parameters for the measurement model for the each data set differ because the system changed from one experiment to the other. Hence, by regressing the measurement model to individual data sets separately, the effects of the change of the experimental conditions from one experiment to another are incorporated into the measurement model parameters. The normalized real and imaginary residual errors for six regressions are shown in Figure 3a and 3b. The results show that the six data sets can no longer be distinguished. The plot of the imaginary versus real residual errors, shown in Figure 3c, suggests that the residuals are not correlated. The real and imaginary standard deviations of the residual errors are shown as a function of frequency in Figure 3d. The real (circles) and imaginary (triangles) values for σ cannot be distinguished. The results of the filtering algorithm show good agreement with the model obtained for the standard deviation of the stochastic error for a solid-state system (see the solid line in Figure 3d) which can be assumed to be relatively stationary.

Model for the Error Structure

Following the experimental observation that

$$\sigma_r = \sigma_j = \sigma \tag{4}$$

a semi-empirical model for the error structure was obtained:

$$\sigma_j = \sigma_r = \sigma = \alpha \left| Z_r \right| + \beta \left| Z_j \right| + \gamma \frac{|Z|^2}{R_m} \tag{5}$$

where α, β, and γ are adjustable parameters and R_m is the value for the current measuring resistor. The parameters α, β, and γ should, in principle, be dependent on the instruments used and on the experimental parameters employed. For example, the parameters obtained under potentiostatic control using a Solartron 1250 frequency response analyzer and a PAR 273 potentiostat are different than those obtained using the same frequency response analyzer coupled with a Solartron 1286 potentiostat. Different parameters were obtained using galvanostatic control with a fixed current amplitude. The validity of the model for the error structure is supported by the fact that a three parameter model provides a good agreement for solid state systems as well as for corrosion systems, for data collected under a wide variety of experimental conditions and for errors ranging from mΩ to MΩ.
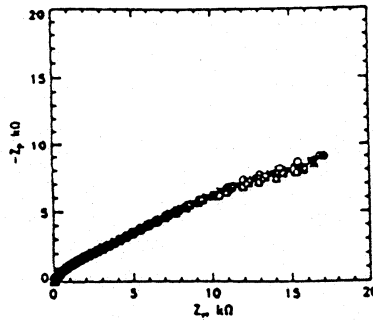
Figure 1. Pseudo replicate impedance scans obtained for a copper rotating disk in an electrolyte containing 1M Cl⁻ and with pH adjusted to 10 with NaOH. The data were collected over a period of 1 hour after 72 hours of immersion.
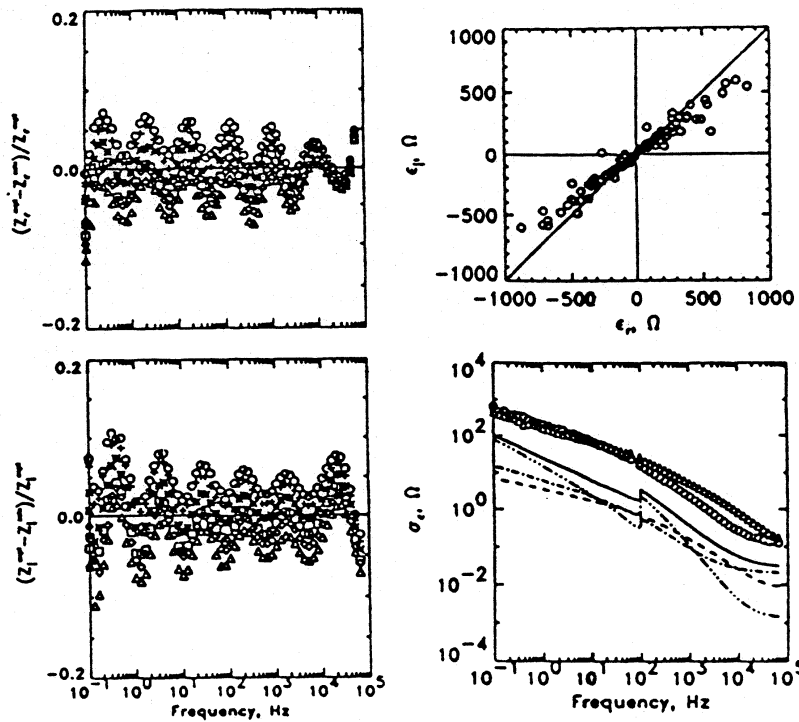

Figure 2. Results of regressions using a Voigt circuit as a measurement model. Here, a single circuit containing 7 elements was regressed to all data sets. a) and b), residual errors as a function of frequency; c) Correlation plot for the real and imaginary components of the residual errors; d) The standard deviation of the residual errors (circles are the real component, triangles are the imaginary component, and the solid line is the model of the error structure obtained from a stationary solid-state system.
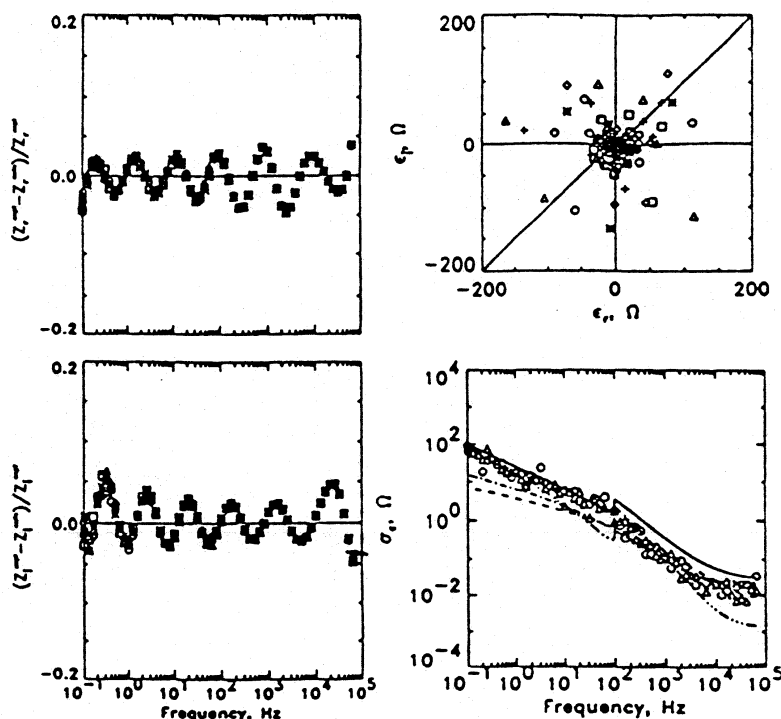
Figure 3. Results of regressions using a Voigt circuit as a measurement model. Here, a circuit containing 7 elements was regressed to each data set individually. a) and b), residual errors as a function of frequency; c) Correlation plot for the real and imaginary components of the residual errors; d) The standard deviation of the residual errors (circles are the real component, triangles are the imaginary component, and the solid line is the model of the error structure obtained from a stationary solid-state system.

Applications of the Error Structure

A priori knowledge of error structure for impedance experiments aids in the analysis of impedance data and the design of experiments. Identification of the various components of the error can help guide the design of experiments because one can thus minimize the source of error. The model for the error structure can also be used to weight data during regression of a model to impedance data.

Proper weighting of data is crucial during non-linear regression of a model to impedance data in order to get unbiased estimates of the parameters. In the absence of explicit weighting, the objective function J minimized by the regression algorithm for complex fitting is given by

$$J = \sum_k (Z_{r,k} - \hat{Z}_{r,k})^2 + \sum_k (Z_{j,k} - \hat{Z}_{j,k})^2 \qquad (6)$$

The objection to the "no-weighting" approach is that the largest magnitude terms contribute the greatest amount to the objective function, and potentially important information at high frequency (where Z_j tends towards zero and Z_r becomes small) can often be lost.

The most commonly used weighting strategy found in the literature is "proportional weighting", either using the experimental data:

$$J = \sum_k \frac{(Z_{r,k} - \hat{Z}_{r,k})^2}{Z_{r,k}^2} + \sum_k \frac{(Z_{j,k} - \hat{Z}_{j,k})^2}{Z_{j,k}^2} \qquad (7)$$

or, as suggested by Macdonald and Potter,[17] using model estimates. The most defensible weighting approach is to weight the regression by the measured variance of the data σ^2, i.e.

$$J = \sum_k \frac{(Z_{r,k} - \hat{Z}_{r,k})^2}{\sigma_{r,k}^2} + \sum_k \frac{(Z_{j,k} - \hat{Z}_{j,k})^2}{\sigma_{j,k}^2} \qquad (8)$$

The model for the error structure given by equation (5) provides an accurate estimate for the variance and can be used to weight the regression.

Bias Contributions to the Error Structure.

Having a viable approach for obtaining the stochastic contribution to the error structure and viable models for some specific experimental designs, the next step was to identify the bias error of the measurement. If the models to be used are stationary, a quantitative measure of the consistency with the Kramers Kronig relations would provide evidence that a given data set was unaffected by nonstationary behavior or instrumental artifacts. The Kramers-Kronig relations have not found widespread use in the analysis and interpretation of electrochemical impedance spectroscopy data due to difficulties with their application. The integral relations require data for frequencies ranging from zero to infinity; whereas, the experimental frequency range is often constrained by instrumental limitations or by the instability of the electrode.

In this work, measurement models are used to check for the consistency of the experimental data with the Kramers-Kronig relations. The methodology takes advantage of the fact that electrical circuits composed of passive elements must satisfy the Kramers-Kronig relations. Since, by including a sufficient number of lineshapes, a measurement model can provide an adequate fit to stationary electrochemical impedance data, an inability to fit an impedance spectrum can be attributed to the failure of the data to conform to the assumptions of the Kramers-Kronig relations rather than the failure of the model.

The algorithm used to check data consistency takes advantage of the Kramers-Kronig equations in that the equations relate the real part of the impedance spectra to the imaginary part, i.e. the real part of the spectra is constrained by the imaginary part and vice versa. The measurement model is regressed to the real (or imaginary) part of the spectra and the parameters obtained from the regression are used to predict the imaginary (or real) part of the spectra. Experimental data always have random or stochastic errors associated with it. The presence of these random errors gives rise to an uncertainty in the prediction of parameters in a regression. This uncertainty in the parameter estimation is quantified by the standard deviation (σ) of the parameters, i.e. one can say with 95.4% certainty that the parameter estimates lie within 2σ of the value calculated by regression. Due to this uncertainty in the parameter estimation, there is uncertainty in any prediction that is made using these parameters. A Monte-Carlo simulation is used to determine the 95.4% confidence interval for the prediction. Calculation of the 95.4% confidence interval takes into account the stochastic component of measurement error. Hence, one can say with 95.4% certainty that the data points which lie outside this predicted confidence interval are corrupted by systematic error, i.e. they are inconsistent with the Kramers-Kronig relations.

In principle, regression can be performed on the real or imaginary part of the spectra to obtain the same information, but in practice, due to stochastic errors, the information content of the

real and imaginary part of the spectra can differ. For example, impedance data typically exhibit a high frequency asymptote, i.e. at the high frequency the real part of the impedance tends towards a constant but finite value and the imaginary part tends towards zero. It was shown in the previous section that the absolute values of the stochastic error in the real and the imaginary part of impedance are equal. The implication of this result is that at high frequency, as the imaginary part of the impedance goes to zero and the real part goes to a finite non zero value, the stochastic error is finite and non zero, i.e. the percentage error in the imaginary part tends to infinity at high frequency. Hence, at high frequency the imaginary part of the impedance has very little information content compared to the real part of the impedance because the imaginary part of the data is corrupted by stochastic error. Due to experimental difficulties (such as the time required to collect low frequency data), typical impedance spectra often do not exhibit low frequency asymptotic behavior. At the low frequency end, since the stochastic errors in the real part are equal to stochastic errors in the imaginary part, both the real and imaginary data are equally reliable. At low frequency, the real part of a deconvolution of the measurement model does not have significant frequency dependence; whereas, a significant change is observed in the imaginary part of the deconvolution. Hence, we can conclude that the imaginary part of an impedance spectra usually has higher information content at low frequencies.

While in principle, a complex fit of the measurement model could be used to assess the consistency of impedance data, sequential regression to either the real or the imaginary can provide a greater sensitivity to lack of consistency. The preferred approach can be determined by trial and error, but the selection should be guided by use of the real part of the measurement to assess consistency in the frequency limit (high or low) where the asymptotic behavior of the imaginary impedance is seen. Conversely, the imaginary part of the measurement should be used to assess consistency in the frequency limit where the asymptotic behavior of the imaginary impedance is not seen. For example, if the imaginary part of impedance approaches asymptotic behavior at high frequency but is finite at low frequency, the following algorithm is proposed:

Step 1: Check for consistency at the high frequency end.
    a) Regress the measurement model to the real part of the data.
    b) Predict the imaginary part and the 95.4% confidence interval through Monte-Carlo simulation.
    c) High frequency data that lie outside the 95.4% confidence interval are deemed inconsistent. Delete the inconsistent data points.
Step 2: Check for consistency at the low frequency end.
    a) Regress the measurement model to the imaginary part of the truncated data set.
    b) Predict the real part and the 95.4% confidence interval through Monte-Carlo simulation.
    c) Low frequency data that lie outside the 95.4% confidence interval are deemed inconsistent. Delete the inconsistent data points.

Conclusions

The development and application of mathematical models for the interpretation of electrochemical impedance data requires both physical insight and a quantitative assessment of the fundamental characteristics of the measurement. The synergistic implementation of experiment, measurement model and process model can enhance the information content of impedance spectra in terms of physically meaningful parameters.

Acknowledgment

References

1. Agarwal, M. E. Orazem, and L. H. Garcia-Rubio, *J. Electrochem. Soc.* **139** (1992), 1917-1927.
2. Agarwal, M. E. Orazem, and L. H. Garcia-Rubio, in *Electrochemical Impedance: Analysis and Interpretation, ASTM STP*, J. Scully, D. Silverman, M. Kendig, Editors, American Society for Testing and Materials, Philadelphia, 1993, p 115.
3. E. Orazem, P. Agarwal, A. N. Jansen, P. T. Wojcik, and L. H. Garcia-Rubio, *Electrochimica Acta* **38** (1993), 1903-1911.
4. R. Macdonald, editor, *Impedance Spectroscopy Emphasizing Solid Materials and Analysis*, John Wiley and Sons, New York, 1987.
5. T. Sah, *Proc. IEEE* **55** (1967), 654-671.
6. R. Macdonald, *J. Appl. Phys.* **62** (1987), R51-R62.
7. R. Macdonald, *Electrochimica Acta* **35** (1990), 1483-1492.
8. Gabrielli, M. Keddam and H. Takenouti, *Electrochimica Acta* **35** (1990), 1553-1557.
9. M. Peter, J. Li, R. Peat, H. J. Lewerenz, and J. Stumper, *Electrochimica Acta* **35** (1990), 1657-1664.
10. Delouis and B. Tribollet, *Electrochimica Acta* **35** (1990), 1637-1648.
11. Aaboubi, J. P. Chopart, J. Douglade and A. Olivier, *J. Electrochem. Soc.* **137** (1990), 1796-1804.
12. Aaboubi, A. Olivier, E. Merienne, J. P. Chopart, J. P. Chopart, C. Delouis and B. Tribollet, presented at the Second International Symposium on Electrochemical Impedance Spectroscopy, Santa Barbara, California.
13. Bourkane, C. Gabrielli and M. Keddam, *Electrochimica Acta* **34** (1989), 1081-1092.
14. Cordoba-Torresi, C. Gabrielli, M. Keddam, H. Takenouti and R. Torresi, *J. Electroanal. Chem.* **290** (1990), 269-274.
15. George E. P. Box and Norman R. Draper, *Empirical Model-Building and Response Surfaces*, John Wiley & Sons, Inc., 1987.
16. P. Agarwal, O. C. Moghissi, M. E. Orazem, L. H. Garcia-Rubio, *Corrosion*, **49**, 278 (1993).
17. J. R. Macdonald and L. D. Potter, Jr., *Solid State Ionics*, **23**, 61 (1987).