

Error Analysis for Interpretation of Impedance Data using Mathematical Models

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In the field of impedance spectroscopy, mathematical models are commonly used in conjunction with measurements to extract physical parameters or to identify physical phenomena. In the early years, the comparison between deterministic process models and experiment was largely qualitative. Application of complex nonlinear regression algorithms, coupled with increases in computation speed, has enabled quantitative comparison based on minimization of fitting errors. The development, over the past 25 years, of increasingly accurate impedance measurements and of correspondingly detailed deterministic models raises several important questions. Can the data be used to discriminate between different models? Do the data justify development of refined models? Are the parameters obtained statistically significant? The answers to these questions require an understanding of the error structure of the measurement.

Interpretation of impedance spectra requires, in addition to an adequate quantitative deterministic model, quantitative assessment of measurement characteristics. For the purposes of the discussion presented here, the errors in an impedance measurement are expressed in terms of the difference between the observed value $Z_{ob}(\mathbf{w})$ and a model $Z_{mod}(\mathbf{w})$ as

$$\begin{aligned} \mathbf{e}_{resid}(\mathbf{w}) &= Z_{ob}(\mathbf{w}) - Z_{mod}(\mathbf{w}) \\ &= \mathbf{e}_{fit}(\mathbf{w}) + \mathbf{e}_{stoch}(\mathbf{w}) + \mathbf{e}_{bias}(\mathbf{w}) \end{aligned} \quad (1)$$

where $\mathbf{e}_{resid}(\mathbf{w})$ represents the residual error, $\mathbf{e}_{fit}(\mathbf{w})$ is the systematic error that can be attributed to inadequacies of the model, $\mathbf{e}_{stoch}(\mathbf{w})$ is the stochastic error with expectation $E\{\mathbf{e}_{stoch}(\mathbf{w})\} = 0$, and $\mathbf{e}_{bias}(\mathbf{w})$ represents the systematic experimental bias error that cannot be attributed to model inadequacies. Typically, the impedance is a strong function of frequency and can vary over several orders of magnitude over the experimentally accessible frequency range. The stochastic errors of the impedance measurement are strongly heteroskedastic, which means that the variance of the stochastic errors is also a strong function of frequency.

A distinction is drawn, in the present work, between stochastic errors that are randomly distributed about a mean value of zero, errors caused by the lack of fit of a model, and experimental bias errors that are propagated through the model. The problem of interpretation of impedance data is therefore defined as consisting of two parts: one of identification of experimental errors, which includes assessment of consistency with the Kramers Kronig relations, and one of fitting, which entails model identification, selection of weighting strategies, and examination of residual errors. The error analysis provides information that must be incorporated into regression of process models. The experimental bias errors, as referred

to here, may be caused by a changing base line or by instrumental artifacts.

While the inability to replicate impedance measurements has made it difficult to distinguish contributions to the error structure, the recent development of measurement model tools for impedance spectroscopy has made such a detailed experimental identification of error structure possible.¹⁻³ Measurement model approaches have been used to identify the stochastic and experimental bias errors, and this information was used to filter data, to design experiments, and to assess the validity of regression assumptions.

This work provides a demonstration of the manner in which error analysis can be incorporated into the interpretation of impedance data using deterministic process models. Models are developed and applied for data obtained on a rotating disk electrode, for which detailed models of convective diffusion are available.⁴ The approach taken is general and can be applied to a wide variety of electrochemical and non-electrochemical spectroscopy measurements.

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References

1. P. Agarwal, M. E. Orazem and L. H. García-Rubio, *J. Electrochem. Soc.*, **139** (1992), 1917.
2. P. Agarwal, O. D. Crisalle, M. E. Orazem and L. H. García-Rubio, *J. Electrochem. Soc.*, **142** (1995), 4149.
3. P. Agarwal, M. E. Orazem and L. H. García-Rubio, *J. Electrochem. Soc.*, **142** (1995), 4159.
4. B. Tribollet and J. Newman, *J. Electrochem. Soc.*, **130**, 2016, (1983).