

On the Propagation of Errors from the Time Domain to the Frequency Domain

Mark E. Orazem and Oscar D. Crisalle
Department of Chemical Engineering, University of
Florida, Gainesville, FL, 32611

Interpretation of impedance spectra requires, in addition to an adequate quantitative deterministic model, quantitative assessment of measurement characteristics. The error structure of the measurement is used implicitly in regression analysis and has a significant influence on the quality and amount of information that can be extracted from impedance data. The variance of the stochastic error can be incorporated explicitly into the weighting strategy for the regression and can provide a means to determine whether observed features lie outside the noise-level of the measurement. The stochastic errors can also influence the use of the Kramers-Kronig relations for determining the internal consistency of the data.

Three approaches have been documented in the literature for incorporating the error structure of impedance data into interpretation strategies. One approach has been to assume a standard form for the stochastic errors.^{1,2} One assumed error structure requires that the real and imaginary parts of the impedance have the same variance;¹ whereas, the other allows the variances to be different.² A second approach has been to use the regression procedure to obtain an estimate for the error structure of the data.³ The error structure obtained by simultaneous regression is severely constrained by the assumed form of the error-variance model. Independent of the assumed form of the error variance model, the assumption that the error variance model can be obtained by minimizing the objective function ignores the different sources of contributions to the residual errors.

A third approach, developed for impedance spectroscopy by Agarwal, *et al.*,^{4,5} entailed experimental identification of the different contributions to the residual errors. The error analysis used a measurement model approach to estimate the standard deviation of the stochastic part of the measurement from imperfectly replicated impedance measurements. A general structure for the errors in impedance measurements was identified. An important result was that the variance of the real part of the impedance response was equal to that of the imaginary part for data that conformed to the Kramers-Kronig relations.

A more comprehensive understanding of the error structure of impedance measurements requires a different approach. The discussion of impedance measurement errors found in the literature has centered on assumptions made in the frequency domain, *e.g.*, that stochastic errors in the impedance are normally distributed. Such a perspective ignores the fact that the fundamental measured quantities in impedance spectroscopy are time-domain signals, and the frequency-domain result is a derived quantity. Thus, while the literature to date has made assumptions about the structure of frequency domain errors, the manner in which these frequency-domain errors develop from time-domain measurements has not been analyzed in detail.

The objective of this work was to investigate the manner in which frequency-domain errors arise from time-domain measurements. The propagation of errors from time-domain measurements to the desired complex variables in

the frequency domain was analyzed for the two dominant algorithms used in spectroscopy measurements: frequency response analysis (FRA) and phase-sensitive detection (PSD). The influence of the electrochemical cell impedance was investigated by allowing the ratio of the faradaic impedance to the electrolyte resistance to vary from 1 to 10,000. The work represents an extension of the approach presented by Carson.⁶ The principal results were:

- Both the FRA and the PSD algorithms provided accurate estimations for the impedance response. Neither algorithm introduced significant bias errors.
- For both the PSD and FRA techniques, errors in the frequency domain were normally distributed, even when the errors in the time-domain were not normally distributed.
- The impedance measurements were heteroskedastic, which means that the variance of the stochastic errors is a strong function of frequency.
- The standard deviations were not proportional to the magnitude of the impedance, suggesting that a more sophisticated model of the form suggested by Orazem *et al.*⁷ is needed to describe the error structure.
- The errors in the real and imaginary impedance obtained using FRA technique were uncorrelated (*i.e.*, $\mathbf{s}_{z_r z_j} = 0$), and the variances of the real and imaginary parts of the complex impedance were equal, $\mathbf{s}_{z_r}^2 = \mathbf{s}_{z_j}^2$.
- In contrast, when using the PSD technique, $\mathbf{s}_{z_r z_j} \neq 0$ and $\mathbf{s}_{z_r}^2 \neq \mathbf{s}_{z_j}^2$.
- For both the PSD and FRA techniques, errors in phase angle and magnitude were not correlated, *i.e.*, $\mathbf{s}_{|z| \angle} = 0$.
- The relationship $\mathbf{s}_{|z|}^2 - |Z|^2 \mathbf{s}_{\angle}^2 = 0$ was satisfied for the FRA technique, but not for the PSD technique.
- A series of necessary and sufficient conditions were established under which $\mathbf{s}_{z_r z_j} = 0$, and $\mathbf{s}_{z_r}^2 = \mathbf{s}_{z_j}^2$.
- A series of sufficient-only conditions were established under which $\mathbf{s}_{z_r z_j} = 0$, and $\mathbf{s}_{z_r}^2 = \mathbf{s}_{z_j}^2$. These conditions may be particularly useful for instrument development because they are functions only of the statistics of the measured current and potential signals.

References

1. P. Zoltowski, *J. Electroanal. Chem.*, **178** (1984), 11.
2. J. R. Macdonald and J. L. D. Potter, *Solid State Ionics*, **23** (1987), 61.
3. J. R. Macdonald, *Electrochim. Acta*, **35** (1990) 1483.
4. P. Agarwal, M. E. Orazem, and L. H. García-Rubio, *J. Electrochem. Soc.*, **139** (1992), 1917.
5. P. Agarwal, O. D. Crisalle, M. E. Orazem, and L. H. García-Rubio, *J. Electrochem. Soc.*, **142** (1995), 4149.
6. S. L. Carson, Ph.D. dissertation, University of Florida (1999).
7. M. E. Orazem, T. E. Moustafid, C. Deslouis, and B. Tribollet, *J. Electrochem. Soc.*, **143** (1996) 3880.