On the Error Structure of Impedance Measurements

Simulation of FRA Instrumentation

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A new paradigm is introduced for the investigation of errors in frequency-domain measurements. The propagation of errors from time-domain measurements to the desired complex variables in the frequency domain was analyzed for the frequency response analysis (FRA) algorithm, one of two techniques commonly used for spectrscopy measurements. Errors in the frequency domain were found to be normally distributed, even when the errors in the time-domain were not normally distributed and when the measurement technique introduced bias errors. For additive errors in time-domain signals, the errors in the real and imaginary impedance were found to be uncorrelated, and the variances of the real and imaginary parts of the complex impedance were equal. The equality of variances was realized except for cases where the time-domain signals contained proportional errors. The statistical characteristics of the results were in good agreement with experimental observations.

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Weighted complex nonlinear regression techniques are typically used to extract information from electrochemical impedance data. 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 for determining 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.

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 $Z_{\text{obs}}(\omega)$ and a model value $Z_{\text{mod}}(\omega)$ as

$$e_{\text{res}}(\omega) = Z_{\text{obs}}(\omega) - Z_{\text{mod}}(\omega) = e_{\text{stoch}}(\omega) + e_{\text{bias}}(\omega)$$  \[1\]

where $e_{\text{res}}$ represents the residual error, $e_{\text{stoch}}(\omega)$ is the systematic error that can be attributed to inadequacies of the model, $e_{\text{bias}}(\omega)$ represents the systematic experimental bias error that cannot be attributed to model inadequacies, and $e_{\text{stoch}}(\omega)$ is the stochastic error with expectation $E(e_{\text{stoch}}(\omega)) = 0$. The experimental bias errors, as referred to here, may be caused by a nonstationary behavior or by instrumental artifacts.

Typically, the impedance is a strong function of frequency and can vary over several orders of magnitude through 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. Selection of an appropriate weighting strategy is, therefore, critical for interpretation of data.

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. 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 can be incorporated into regression of process models.

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. Two models are commonly used. Zoltowski and Boukamp advocated use of modulus weighting under the assumption that the standard deviation is proportional to the frequency-dependent modulus $|Z(\omega)|$ of the impedance, i.e.

$$\sigma_{Z}^2(\omega) = \sigma_{Z}^2 F(|\omega, \theta|^\xi)$$  \[2\]

where $\sigma_{Z}^2(\omega)$ and $\sigma_{Z}^2 F(|\omega, \theta|^\xi)$ represent the standard deviation of the real and imaginary parts of the impedance, respectively. The parameter $\sigma_{stoch}$ is assumed to be independent of frequency and is often arbitrarily assigned a value based on an assumed noise level of the measurement. Macdonald et al. advocated use of a modified proportional weighting strategy, i.e.

$$\sigma_{Z}^2(\omega) = \alpha^2 + \sigma^2 F(|\omega, \theta|^\xi)$$  \[3\]

and

$$\sigma_{Z}^2 F(|\omega, \theta|^\xi) = \alpha^2 + \sigma^2 F(|\omega, \theta|^\xi)$$  \[4\]

where $\alpha$, $\sigma$, and $\xi$ are error-structure parameters, $F(|\omega, \theta|^\xi)$ are real and imaginary parts of the model immittance function, respectively, and $\theta$ is a vector of model parameters.

Equations 3 and 4 are applied to a general immittance function, but, for comparison to Eq. 2, $F$ could be considered to be the impedance function $Z$.

There are fundamental differences between the two commonly used standard weighting strategies. Under Eq. 2, $\sigma_{Z}^2 = \sigma_{Z}^2 F(|\omega, \theta|^\xi)$ whereas, Eq. 3 and 4 state that, in general, $\sigma_{Z}^2 \neq \sigma_{Z}^2$ unless errors are assumed to be independent of frequency (i.e., $\sigma = 0$) or unless $F(|\omega, \theta|^\xi) = F(|\omega, \theta|^\xi)$.

A second approach has been to use the regression procedure to obtain an estimate for the error structure of the data. A sequential regression is employed in which the parameters for an assumed error structure model, e.g., Eq. 3 and 4 are obtained directly from regression to the data. In more recent work, the error variance model was replaced by

$$\sigma_{Z}^2(\omega) = \alpha^2 + |F(|\omega, \theta|^\xi)$$  \[5\]

and

$$\sigma_{Z}^2 F(|\omega, \theta|^\xi) = \alpha^2 + |F(|\omega, \theta|^\xi)$$  \[6\]
where parameters $\alpha$ and $\xi$ are obtained by regression, and an extension of modulus weighting can be obtained by replacing the functions $F'(\omega, \theta)$ and $F''(\omega, \theta)$ with $|F(\omega, \theta)|$. 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 differences among the contributions to the residual errors shown in Eq. 1.

The approach, developed for impedance spectroscopy by Agarwal et al.,[9,11] 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 standard deviation of the real part of the impedance response was equal to the imaginary part for data that conformed to the Kramers-Kronig relations. The finding that the standard deviations of the real and imaginary parts of the impedance were equal for systems that satisfied the Kramers-Kronig relations was verified both experimentally and analytically.[4,12,17] Nevertheless, Macdonald and Piterbarg suggested that the equality of standard deviation in the stochastic errors in the real and imaginary impedance observed by Orazem et al.[4,12,17] was "probably associated with the specifics of the frequency response analyzer used and unlikely to be an intrinsic property of immittance spectroscopy measurements."[14] It is important to note that the observations reported by Orazem et al. were obtained using frequency response analyzer (FRA) instrumentation.

A different approach is required to address the question of whether the observed statistical properties are in fact an intrinsic property of transfer-function measurements. The discussion of errors in impedance measurement 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.

Some preliminary evaluations of the transformation of errors from time to frequency domain have been reported. Milocco and Biagiola showed that, when noise was transferred from the time domain, the variance of the real and imaginary parts of the impedance were equal; however, they did not account for the correlation of input and output errors through the cell impedance, and they did not address the effects of the distinguishing features of the frequency analysis instrumentation.[19] The relationship between time-domain noise and cell impedance has been developed with application to electrochemical noise analysis, but the statistical properties of the resulting impedance were not developed.[20,21]

The objective of the present work is to explore the manner in which stochastic errors in time-domain signals propagate through the instrumentation to the frequency domain. The approach presented is intended to serve as a paradigm for analyzing the propagation of error, and is applicable to arbitrary instruments (either currently available or in the design phase) and to arbitrary electrochemical cells. To retain the focus of the present presentation, the propagation-of-noise analysis is presented in detail for frequency-response analysis. A separate paper addresses phase-sensitive detection.[22] In this way, the error propagation treatment was applied to the two dominant techniques in the field. For simplicity, and without loss of generality, the electrochemical cell considered is represented by a single V oigt element. While the complex quantity simulated in this work is electrical impedance, the approach is general and applies to the measurement of other material properties such as the complex dielectric function, the complex viscosity, and acoustic impedance.

**Figure 1.** Schematic representation of an electrochemical cell under potentiostatic regulation, with sources of potential noise indicated as shaded circles and sources of current noise indicated as shaded double circles (see Fig. A.2 given by Gabrielli et al.[20]).

**Origins of Noise in Time-Domain Signals**

Stochastic signals in electrochemical measurements can originate from instrumental sources, thermal fluctuations of resistivity, thermal fluctuations of the concentration of species, and the rates of electrochemical reactions, and macroscopic events such as pitting and bubble nucleation. Only high-frequency noise is considered in the present work; therefore the influence of macroscopic noise events is not considered.

The origin of noise can be traced to specific components of the electrochemical cell and instrumentation. A detailed analysis of the sources of noise in standard systems under galvanostatic or potentiostatic regulation reveals that the instrumental and electrochemical noise appear as stochastic perturbations about average values. For example, Gabrielli et al.[20] considered that the potential imposed between the working electrode and the reference electrode $E_{\text{ref}} = E_{\text{reg}} + \epsilon_{\text{reg}}$ [7] contains a stochastic noise $\epsilon_{\text{reg}}$, shown schematically in Fig. 1. The noise in the regulation signal can be expressed in the frequency domain as

$$
\epsilon_{\text{reg}} = \frac{Z_{\text{WE}}}{Z_{\text{WE}} A_v + Z_{\text{ref}} + R_{\text{m}} + Z_{\text{CE}}} \left\{ A_v (v_e + v_p + R_{\text{m}} i_n + v_{\text{ref}}) - v_{\text{ref}} - (R_{\text{m}} + Z_{\text{CE}})(i - i_n) + R_{\text{m}} i_{\text{ref}} \right\}
$$  

[8]

where $Z_{\text{WE}}$ is the impedance of the working electrode, $Z_{\text{CE}}$ is the impedance of the counter electrode, $Z_{\text{ref}}$ is the impedance of the reference electrode, $A_v$ is the gain of the operational amplifier, $R_{\text{m}}$ is the resistance of the current measurement circuit, $R_{\text{m}}$ is the resistance of the potential control circuit, $v_e$, $v_p$, $v_{\text{ref}}$, $v_{\text{WE}}$, and $v_{\text{CE}}$ represent voltage noise contributions shown as shaded circles in Fig. 1, and $i$, $i_n$, $i_{\text{ref}}$, and $i_{\text{ref}}$ represent current noise contributions shown as shaded double circles in Fig. 1. The electrochemical noise $i$ arises from molecular-scale fluctuations.[23,24] The current noise contributions act through resistors $R_{\text{m}}$ and $R_{\text{m}}$ to generate voltage noise contributions.

Under the assumptions that the gain of the operational amplifier $A_v$ is large and that the reference electrode impedance $Z_{\text{ref}}$ is small, the stochastic contribution to the regulation signal consists of additive contributions from reference electrodes and the operational amplifiers as
The regulation noises induce, through the electrochemical cell impedance, a parasitic current fluctuation \( i_{reg}(t) \) which can be calculated from

\[
e_{reg} = v_e + v_p + R_d i_n + v_{ref} \tag{9}
\]

As Eq. 9 is not a function of frequency, it applies in both time and frequency domains. In principle, \( e_{reg} \) will be autocorrelated due to the impedance of the instrumentation. The autocorrelation function decays according to \( \exp(-\beta t) \). If the time constant \( \tau \) is small, the noise appears as an impulse.\(^{25}\)

The regulation noise induces, through the electrochemical cell impedance, a parasitic current fluctuation \( i_{reg}(t) \) which can be calculated from

\[
i_{reg}(t) = IFT[FT[e_{reg}(t)]/Z(\omega)] \tag{10}
\]

where \( IFT[x] \) represents the inverse Fourier transform (IFT) of the function \( x \), and \( FT[x] \) represents the Fourier transform of the function \( x \). Thus, the potential difference across the inputs to the current follower is given as

\[
S_m = \overline{S_m} + s_m \tag{11}
\]

where

\[
s_m = v_m + v_{R_m} + R_m(i + i_{reg} - i_n - i_{in}) \tag{12}
\]

The response of the current measurement channel is given by \( E_{out} = G_e S_m \), and the noise in the current measurement channel is given by

\[
e_{out} = G_{en} v_m + v_{R_m} + R_m(i + i_{reg} - i_n - i_{in}) \tag{13}
\]

Thus, the noise in both current and potential measurement channels consists of sums of noise contributions. A similar development has been presented for zero resistance ammeters.\(^{21}\)

The investigation of noise sources suggests that instrumental and electrochemical noise can be represented by stochastic signals added to the time-averaged measured and controlled signals. The present work is based on the assumption of an idealized instrumentation, such that the instrumental noise is unautocorrelated, identically distributed, and has only high-frequency components. Thus, the evaluation of the instrumental noise at any two instances in time \( t \) and \( t + \tau \) can be assumed to be uncorrelated. The added signals should be statistically independent, with the exception of the term \( i_{reg}(t) \), which is correlated both with \( e_{reg}(t) \) and \( i_{reg}(t + \tau) \). To address situations where the instrument generates autocorrelated noise, the first task is to model the autocorrelation function. Then the analysis of propagation of error from time-domain to frequency domain would proceed as outlined in this paper, provided that at every step where noise is injected the appropriate autocorrelation relation is respected.

For most potentiostats, the assumption \( A_1 \gg 1 \) becomes invalid at frequencies above 1 to 10 kHz. In this case, the noise terms are still additive, but the interaction between the gain of the operational amplifier and the cell impedance results in additional correlation between the input and output channels.

Another source of a stochastic error can be traced to the finite precision of analog-to-digital samplers. Such errors are the result of a rounding or chopping operation, and hence have zero mean, are independently distributed, and are uncorrelated.\(^{26}\) Furthermore, these discretization errors are rather small. For example, a 16-bit converter introduces errors whose magnitude is bounded by \( r/2 \), where \( r \) is the range of the sampled signal (the difference between the maximum and minimum values that can be observed by the converter). Given that these errors are so small, in general they may be neglected from the analysis. In the rather unlikely case where the instrument in question features a converter with very poor resolution, then the effect of such errors can be quantified following the paradigm proposed in this paper, namely, by explicitly including the magnitude of the discretization errors as part of the stochastic error.

### Frequency Response Analysis

Frequency response analysis (FRA) makes use of the orthogonality of sines and cosines to determine the complex impedance representing the ratio of the response to a single-frequency input signal.\(^{27-30}\) The current and potential signals can be expressed by

\[
I(t) = I_0 \sin(\omega t + \phi_i) \tag{14}
\]

and

\[
V(t) = V_0 \sin(\omega t + \phi_v) \tag{15}
\]

respectively, where the constant coefficients \( I_0 \) and \( V_0 \) represent the amplitudes of the respective signals.

The formulation presented here, strictly valid only for input signals expressed in terms of a sine function, follows that used for a commercial instrument.\(^{28}\) The mapping of the time-domain signals, Eq. 14 and 15, to the frequency domain is done via a complex Fourier representation where the real part of the current signal is

\[
I_1(\omega) = \frac{1}{T} \int_0^T I_0 \sin(\omega t + \phi) \sin(\omega t) dt \tag{16}
\]

and the imaginary part of the current signal is

\[
I_2(\omega) = \frac{1}{T} \int_0^T I_0 \sin(\omega t + \phi) \cos(\omega t) dt \tag{17}
\]

Analogously, the real part of the voltage signal is

\[
V_1(\omega) = \frac{1}{T} \int_0^T V_0 \sin(\omega t + \phi) \sin(\omega t) dt \tag{18}
\]

and the imaginary part of the voltage signal is

\[
V_2(\omega) = \frac{1}{T} \int_0^T V_0 \sin(\omega t + \phi) \cos(\omega t) dt \tag{19}
\]

The integration procedure converts the time-domain quantities into the respective frequency-domain quantities. Integration is carried out over a period \( T \) comprising an integer number of cycles to filter errors in the measurement.

The impedance \( Z(\omega) = Z_r(\omega) + jZ_i(\omega) \) is calculated as the complex ratio of the complex representations of the output signal to the input signal. Thus

\[
Z_r(\omega) = \text{Re}\left[\frac{V_i + jV_r}{I_i + jI_r}\right] \tag{20}
\]

and

\[
Z_i(\omega) = \text{Im}\left[\frac{V_i + jV_r}{I_i + jI_r}\right] \tag{21}
\]

The real and imaginary parts of the impedance are thereby extracted from a common set of complex numbers.

### Simulation of Impedance Systems

Code was written in the LabVIEW® G Language to simulate impedance measurements. Bode quadrature, which is an order \( \Delta \chi \) algorithm, was employed for signal integration.\(^{31}\) The electrochemical cell was assumed to be a single Voigt element consisting of a leading 1 \( \Omega \) resistor \( R_e \) in series with a parallel combination of a resistor \( R \) and a capacitor \( C \). The value of \( R/R_e \) was allowed to vary between 1 and 10\(^3\), and the capacitance \( C \) was adjusted such that the RC time constant was always 10\(^{-4}\) s.
Figure 2. Schematic representation of the algorithm for incorporation of errors in the synthetic impedance calculations.

**Time-domain signals.**—Three forms of time-domain signals were considered in the simulation study. The signal influenced by additive errors was described by

\[ A(t) = A_0 \sin(\omega t + \phi_A) + e(t) \]  

where \( A(t) \) represents either a potential or current signal, and \( e(t) \) is a stochastic error which was added to the error-free value. Proportional errors were considered following

\[ A(t) = A_e [1 + e_2(t)] \sin(\omega t + \phi_A) \]  

Introduction of errors into the argument of the sine function posed serious problems for both the FRA algorithm considered in the present work and the phase sensitive detection (PSD) algorithm treated separately.\(^{22}\) Such errors in the argument of the sine can be considered to result from uncertainty in frequency or time. Use of Eq. 22 and 23 is predicated on the assumption that errors in measurement of frequency or time are sufficiently small that they can be neglected.

Equation 22 has sufficient flexibility to describe the nonautocorrelated noise distribution in electrochemical measurements corresponding to the discussion of Fig. 1 and originating from instrumental sources, thermal fluctuations of resistivity, and thermal fluctuations of the concentration of species and the rates of electrochemical reactions. The calculation algorithm, described in the subsequent section, accounts for the propagation of input noise through the cell impedance into the output signal.

**Simulation of measurement techniques.**—The algorithm for the calculation of the impedance response, represented in Fig. 2 and summarized below, was implemented for a given model impedance transfer function \( Z_{mod}(\omega) \):

1. One cycle of the clean perturbation signal was constructed for a galvanostatic modulation following Eq. 14 with 1024 points per cycle.
2. Noise was added to the input signal, following Eq. 22 or 23, yielding the input current \( i_{in}(t) \).
3. The Fourier transform (FT) of the input signal was calculated. The time-domain response signal was obtained from the real inverse FT of the product of the perturbation signal and the impedance transfer function, i.e.

\[ I(t) = I_0 \sin(\omega t + \phi_I) \]

\[ V(t) = IFT\{FT[i_{in}(t)] \cdot Z_{mod}(\omega)\} \]

Note that \( V(t) \) contains noise that has been transformed through the impedance transfer function. The effective digital sample rate, \( s = 1024 \omega \), provided an upper frequency limit on the FT of the sampled signal.

4. Noise was added to the response signal, following Eq. 22 or 23, yielding the output potential \( V_{out}(t) \). The noise distributions used were uncorrelated such that the only correlation between input and output signals resulted from step 3.

5. The impedance spectra were calculated following the FRA algorithm.

The calculations were repeated over a number of cycles sufficient to allow the autointegration criterion to be achieved. After three cycles of measurement were completed, convergence was considered to be achieved when the ratio of the standard deviation of the estimation of the magnitude to the magnitude over all cycles on the selected channel was less than 0.01. The impedance was taken to be the mean of the impedance values calculated at all cycles for the given frequency. Details on the calculation procedure are presented elsewhere.\(^{32,33}\)

Step 3 represents the propagation of input noise through the cell, a critical step in the procedure that merits further discussion. Under the approach described above, noise added to the input caused the response signal to contain noise transformed through the impedance transfer function. When noise was added to both the perturbation and response signals, the latter signal contained both transformed noise and additive noise. This method of introducing noise is in full agreement with Eq. 9 and 13, obtained under the assumption that \( A_v \gg 1 \). This method applies as well to the more general case where \( A_v \gg 1 \) because the impedance function can be modified to account for correlation between input and output caused by the instrument so long as the system continues to satisfy the Kramers-Kronig relations. Thus, in contrast to the previous applications of system identification techniques to propagation of noise through impedance measurements,\(^{19}\) the influence of the transfer function on the transformation of noise was taken explicitly into account.

Since the cell considered in this case is a Voigt element, i.e., a linear model, the inverse Fourier transform method adopted in step 3 is an adequate technique for calculating the cell response to the noisy input signal. An equivalent alternative would be to simulate the time-domain response of the cell using the corresponding convolution formula.\(^{25,26}\) The results of the former and latter methods are numerically identical, given that a convolution in the time domain is equivalent to the frequency-domain multiplication done in the argument of the IFT operation shown on the right side of Eq. 24.\(^{26}\) It is important, however, to ensure that the time-domain step size is sufficiently small such that the numerical value of the continuous response is adequately captured. In the present paper, the time-domain step size was set at a small value, \( T/1024 \), where \( T \) is the period of the signal.

It is worth noting that, in cases where the electrochemical cell must be represented via a time-varying or a nonlinear model, the cell response must be calculated using an appropriate technique for solving differential equations. Finally, when the goal is to investigate the effect of the discrete-sampling operation on the propagation of error, the cell response in step 3 must be calculated using a time step-size that is smaller than the sampling period. This ensures that the intersample response of the cell is appropriately simulated. The impedance calculated in step 5 would then make use of only the sampled values, ignoring all intersample calculations and hence effectively emulating the physical sampling process. In this case the user must take precautions to select an adequately small sampling period to minimize the aliasing effect.

**Results**

Four cases were considered in the present study. Noise-free signals were first treated to verify that the algorithms yielded the ex-
pected theoretical results. Three time-domain signals were then considered, including normally distributed additive errors, skewed additive errors, and proportional errors, as described by Eq. 22 and 23.

Normally distributed additive time-domain errors.—Simulation of normally distributed additive errors, following Eq. 22, resulted in an input signal such as shown in Fig. 3a. The solid line shown in Fig. 3b represents a normal distribution. The stochastic error added to Eq. 22 conformed to a normal distribution and had a mean value equal to zero.

A set of 500 calculations were performed for different cell impedance values to explore the distribution of impedance errors realized in the frequency domain. The results were used to assess the dependence of standard deviation on frequency and cell impedance, to assess the accuracy of the FRA algorithm, to test the validity of the assumption that errors in the measured impedance are normally distributed, and to identify statistical relationships among impedance components.

Dependence of standard deviation on frequency and cell impedance.—The standard deviation of the impedance results obtained for the FRA simulation are presented in Fig. 4 as a function of frequency with $R/R_e$ as a parameter. The propagation of errors from time to frequency domain is seen to yield results that are strongly heteroskedastic, i.e., the standard deviations are strong functions of frequency, particularly as $R/R_e$ becomes large.

The standard deviations reported in Fig. 4 were normalized by the magnitude of the impedance and expressed in Fig. 5 as a percentage, with $R/R_e$ as a parameter. As seen in Fig. 5, the frequency dependence of the standard deviation was, to a first approximation, proportional to the modulus $|Z|$ of the impedance. The results shown in Fig. 5, therefore, support the use of modulus weighting as a preliminary strategy in regression of impedance data obtained by the
FRA algorithm. The magnitude of the error observed, roughly 0.1% of the modulus, is consistent with the experimental values reported in Fig. 3 of Orazem et al. A refined error structure model, such as that proposed by Orazem et al., was required to account for departures from proportionality with the impedance modulus.

The decrease of standard deviation shown in Fig. 4 at frequencies below 10 Hz is seen more clearly in Fig. 5. This result and the observation that the decrease was seen for \( R/R_e > 10 \), but not for \( R/R_e = 1 \), seems counterintuitive, given that the same algorithm was used for all simulations. However, as will be discussed later (see Fig. 20), a similar decrease in standard deviation was seen in experimental values for large values of cell impedance. We hypothesize that the decrease in standard deviation at low frequencies, where the cell impedance must be purely resistive, may be related to the use of a minimum of three cycles before applying the autointegration convergence criterion.

Error in impedance simulation.—The percent error in the evaluation of real and imaginary parts of the impedance is presented in Fig. 6 as a function of frequency, with \( R/R_e \) as a parameter. The bias errors were largest for the imaginary part of the impedance at high frequency, but the errors were always less than 0.07% of the magnitude of the impedance.

Distribution of impedance errors.—The concept that errors in the measured impedance are normally distributed represents a fundamental assumption in using regression to interpret spectra. A test of this assumption is seen in Fig. 7 for real and imaginary parts of the impedance at a frequency of 1 Hz for a cell impedance characterized by:

\[
\sigma = \alpha |Z_j| + \beta |Z_i - R_c| + \gamma \frac{|Z|^2}{R_m} + \delta
\]  

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\]
by $R/Re = 100$. The lower plot in Fig. 7a provides the histogram and the upper plot in Fig. 7a provides the estimated cumulative distribution function (i.e., a probability plot) for the random variable $100(Z_r - Z_{r,mod})/|Z|$ featured in the abscissa. The ordinate of the histogram shows the number of counts, defined as the number of realizations of the random variable that occur within a given bin. The data in the upper plot of Fig. 7a were obtained by summing the counts of successive bins and carrying out a straightforward normalization to yield probability estimates in the range of 0 to 100%. A most important feature of the cumulative-counts plot in Fig. 7a is that the scale of the ordinate is chosen such that a normally distributed random variable would yield a straight line. Therefore, a cumulative-counts plot that follows a straight line provides an indication that the distribution can be considered to be normal. A second indication of the normality of the distribution is provided by the bell-shaped curve superimposed on the histogram, which is a normal distribution with a mean and a variance equal to the sample mean and sample variance of the data. Figure 7b was constructed analogously.

The straight line in the cumulative probability plots in Fig. 7a and b indicate that the distributions can be considered to be normal. Both real and imaginary impedance values were normally distributed about zero with a standard deviation of 0.03% of the modulus, a value that is consistent with the standard deviations for impedance measurements reported by Orazem et al.\textsuperscript{12}

One measure of the presence of outliers in the distribution is the kurtosis $E((x - \mu)^4)/\sigma^4 - 3$, presented in Fig. 9 as a function of frequency with $R/Re$ as a parameter. The kurtosis has an expected value of zero for a normal distribution. The kurtosis of the impedance

![Figure 8](image.png)

**Figure 8.** Distribution of calculated impedance errors, obtained under the assumption of normally distributed errors in the time-domain signals at a frequency of 1.259 kHz for $R/Re = 100$, as a function of the normalized difference between calculated and the model value for the impedance of the cell: (a, left) real part and (b, right) imaginary part. The sample size was 500.

![Figure 9](image.png)

**Figure 9.** Kurtosis of the distributions of real and imaginary parts of the impedance for normally distributed errors in the time-domain signals as a function of frequency with $R/Re$ as a parameter. The symbols are as given in Fig. 4.
Statistical relationships among impedance components.—A comparison of the standard deviations of real and imaginary impedance components in Fig. 4 and the histograms presented in Fig. 7 and 8 would suggest that the real and imaginary parts of the FRA-determined impedance have the same variance. Given the controversy found in the literature over the appropriate relationship between the variances of real and imaginary components, it is worthwhile to identify a test of whether such an observation has statistical significance.

One possible approach would be to use the F-test which provides, in the present case, a frequency-by-frequency test of the hypothesis that the variances are equal. Given the controversy found in the literature over the appropriate relationship between the variances of real and imaginary components, it is worthwhile to identify a test of whether such an observation has statistical significance.

The use of a Student’s $t$-test as a statistical evaluation of the hypothesis that the variances are equal is predicated on the assumption that calculations performed at each frequency can be considered independent samples of the ratio of variances. Such a test provides a statistically justifiable rejection of the hypothesis that the variances of real and imaginary parts of the impedance are unequal.

The Student’s $t$-test statistical analysis of the conjecture $x = 0$ at a significance level of $\alpha = 0.05$ is presented in Table I for normally distributed errors in the time-domain signals. In Table I, $\bar{x}$ represents the mean observed value, which should be compared to the hypothesis data had a mean value of $-0.00483$ with a standard deviation of 0.21, which is comparable to the kurtosis of 0.0053 ± 0.23 obtained for a normal distribution of the same sample size. There is no influence of frequency or cell impedance evident in the distribution of kurtosis, which further supports the observation that errors in impedance measurement are normally distributed.

![Figure 10](image)

**Figure 10.** Calculated ratio of variances for the real and imaginary parts of the impedance distribution obtained under assumption of normally distributed errors in the time-domain signals as a function of frequency and with cell impedance $R/R_e$ as a parameter. Symbols are as presented in Fig. 4. The outer dashed lines provide the $F$ statistic at a 99% confidence level for 500 samples, and the inner dash-dot lines provide the $F$ statistic at a 95% confidence level for 500 samples.

![Figure 11](image)

**Figure 11.** Distribution of the logarithm of ratio of variances of the stochastic errors for the real and imaginary impedance calculated using the FRA with Gaussian noise added to the input and output signals in the time domain. The sample set includes calculations for all 61 frequencies and five cell impedances.

<table>
<thead>
<tr>
<th>Test $x = 0$</th>
<th>$R/R_e$</th>
<th>$\bar{x}$</th>
<th>$\sigma_x$</th>
<th>$P_{\text{obs}}$</th>
<th>$t/t_{\text{crit}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\log_{10}(\sigma^2_{Z_r}/\sigma^2_{Z_j}) = 0$</td>
<td>$1$</td>
<td>$0.0025$</td>
<td>$0.038$</td>
<td>$0.62$</td>
<td>$0.25$</td>
</tr>
<tr>
<td></td>
<td>$10$</td>
<td>$0.00040$</td>
<td>$0.39$</td>
<td>$0.948$</td>
<td>$0.039$</td>
</tr>
<tr>
<td></td>
<td>$10^2$</td>
<td>$0.0029$</td>
<td>$0.373$</td>
<td>$0.54$</td>
<td>$0.31$</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>$-0.0047$</td>
<td>$0.337$</td>
<td>$0.32$</td>
<td>$0.50$</td>
</tr>
<tr>
<td></td>
<td>$10^6$</td>
<td>$-0.0075$</td>
<td>$0.047$</td>
<td>$0.22$</td>
<td>$0.62$</td>
</tr>
<tr>
<td>2. $\sigma_{Z_r}/(\sigma_{Z_r}/\sigma_{Z_j}) = 0$</td>
<td>$1$</td>
<td>$-0.0076$</td>
<td>$0.044$</td>
<td>$0.18$</td>
<td>$0.67$</td>
</tr>
<tr>
<td></td>
<td>$10$</td>
<td>$0.000055$</td>
<td>$0.45$</td>
<td>$0.92$</td>
<td>$0.49$</td>
</tr>
<tr>
<td></td>
<td>$10^2$</td>
<td>$0.00023$</td>
<td>$0.45$</td>
<td>$0.97$</td>
<td>$0.20$</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>$0.00079$</td>
<td>$0.051$</td>
<td>$0.90$</td>
<td>$0.06$</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>$0.0028$</td>
<td>$0.045$</td>
<td>$0.63$</td>
<td>$0.24$</td>
</tr>
<tr>
<td>3. $\sigma_{</td>
<td>Z_r</td>
<td>}/(\sigma_{</td>
<td>Z_r</td>
<td>}/\sigma_{</td>
<td>Z_j</td>
</tr>
<tr>
<td></td>
<td>$10$</td>
<td>$0.0015$</td>
<td>$0.044$</td>
<td>$0.79$</td>
<td>$0.13$</td>
</tr>
<tr>
<td></td>
<td>$10^2$</td>
<td>$-0.0012$</td>
<td>$0.044$</td>
<td>$0.84$</td>
<td>$0.10$</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>$-1.4 \times 10^{-5}$</td>
<td>$0.049$</td>
<td>$0.999$</td>
<td>$0.001$</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>$0.0062$</td>
<td>$0.040$</td>
<td>$0.23$</td>
<td>$0.60$</td>
</tr>
<tr>
<td>4. $(\sigma^2_{</td>
<td>Z_r</td>
<td>} -</td>
<td>Z</td>
<td>^2)/\sigma^2_{</td>
<td>Z_r</td>
</tr>
<tr>
<td></td>
<td>$10$</td>
<td>$0.0016$</td>
<td>$0.073$</td>
<td>$0.86$</td>
<td>$0.09$</td>
</tr>
<tr>
<td></td>
<td>$10^2$</td>
<td>$0.0041$</td>
<td>$0.071$</td>
<td>$0.66$</td>
<td>$0.22$</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>$-0.013$</td>
<td>$0.079$</td>
<td>$0.20$</td>
<td>$0.65$</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>$0.021$</td>
<td>$0.098$</td>
<td>$0.11$</td>
<td>$0.82$</td>
</tr>
</tbody>
</table>
The symbols are as presented in Fig. 10.

Figure 12. Scaled covariance for real and imaginary parts of the impedance distribution as a function of frequency for simulation of the FRA techniques with additive errors in the time domain signals. The symbols are as presented in Fig. 10.

Figure 13. Scaled covariance for phase angle and magnitude as a function of frequency for simulation of the FRA techniques with additive errors in the time domain signals. The symbols are as presented in Fig. 10.

Figure 14. Calculated values for $\sigma_{\Delta Z_\phi}^2 / |Z|\sigma_{\Delta Z_r}^2$ as a function of frequency for simulation of the FRA techniques with additive errors in the time domain signals. The symbols are as presented in Fig. 10.
\[ t \text{-test} \] indicated that \( \log_{10} \left( \frac{s^2_Z r}{s^2_Z j} \right) \approx 0 \) for \( R/R_e > 10 \). The F-test shown in Fig. 16c could not be used to support the hypothesis that \( s^2_Z r \approx s^2_Z j \) on a frequency-by-frequency basis. The covariance relationships \( s^2_Z r = s^2_Z j = 0 \) were satisfied for all \( R/R_e \). The relationship \( s^2_Z r / (s^2_Z r + s^2_Z j) = 0 \) was not satisfied for values of \( R/R_e > 10 \). The impedance values were found to be normally distributed, with kurtosis values centered about zero.

**Table II. Student's \( t \)-test statistical analysis of the conjecture \( x = 0 \) at a significance level of \( \alpha = 0.05 \) for skewed-distributed errors in the time-domain signals.**

<table>
<thead>
<tr>
<th>Test</th>
<th>( R/R_e )</th>
<th>( \bar{x} )</th>
<th>( s_x )</th>
<th>( p_{0.05} )</th>
<th>( t/1_{\text{crit}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \log_{10}(\sigma^2_Z r / \sigma^2_Z j) = 0 )</td>
<td>1</td>
<td>-0.0099</td>
<td>0.040</td>
<td>0.056</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.013</td>
<td>0.034</td>
<td>0.045</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.0069</td>
<td>0.043</td>
<td>0.056</td>
<td>1.57</td>
</tr>
<tr>
<td>2. ( \sigma^2_{X^2} / (\sigma^2_{Z r}) = 0 )</td>
<td>1</td>
<td>-0.0080</td>
<td>0.041</td>
<td>0.13</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.0041</td>
<td>0.048</td>
<td>0.51</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-0.0073</td>
<td>0.050</td>
<td>0.26</td>
<td>0.56</td>
</tr>
<tr>
<td>3. ( \sigma^2_{Z r} / (\sigma^2_{Z j}) = 0 )</td>
<td>1</td>
<td>-0.0086</td>
<td>0.043</td>
<td>0.12</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.0073</td>
<td>0.050</td>
<td>0.26</td>
<td>0.56</td>
</tr>
<tr>
<td>4. ( (\sigma^2_Z r -</td>
<td>Z</td>
<td>^2 \sigma^2_Z j) / \sigma^2_Z j = 0 )</td>
<td>1</td>
<td>-0.027</td>
<td>0.091</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.027</td>
<td>0.068</td>
<td>0.003</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-0.017</td>
<td>0.084</td>
<td>0.12</td>
<td>0.79</td>
</tr>
</tbody>
</table>

**Figure 15.** Simulation of a skewed and biased distribution of additive errors: (a, top) input signal as a function of time (represented by a solid line) and errors (represented by open circles) and (b, bottom) histogram showing a typical distribution of skewed and biased additive errors with a sample size of \( 3 \times 10^4 \).

**Figure 16.** Calculated results as a function of frequency obtained for a skewed noise input using the FRA with \( R/R_e \) as a parameter: (a, top) errors in simulated measurement of impedance and (b, bottom) ratio of variances for real and imaginary parts of the impedance.
presented in Fig. 16a as a function of frequency. When proportional errors were incorporated according to Eq. 23 the bias errors in the calculated result were much smaller than observed with the skewed error distribution, but, as seen in Fig. 18b, the ratio of variances deviated significantly from unity at $R/R_e = 10$.

The conclusion that $\sigma^2_Z \neq \sigma^2_{\bar{Z}}$ for $R/R_e = 10$ is supported by the analysis of statistical relationships among impedance components shown in Table III. The relationship $\log_{10} (\sigma^2_Z / \sigma^2_{\bar{Z}}) = 0$ was not satisfied for $R/R_e = 10$. The covariance relationships $\sigma_{Z\bar{Z}} = 0$ and $\sigma_{Z\bar{Z}0} = 0$ were also not satisfied, nor was the relationship $\sigma^2_{\bar{Z}1} - |\bar{Z}|^2 \alpha^2_0 = 0$. The impedance values were, nevertheless, found to be normally distributed, with kurtosis values centered about zero.

For proportional errors, the FRA yielded variances for real and imaginary parts of the impedance that were not equal. This result, which is counter to the experimental and theoretical results of Orazem et al. $^4,12,13$ lends significant support to the conjecture that the noise in the signals present in the above references $^3,12,13$ were not of the proportional type.

Comparison to Experiment

It should be noted that the present simulation was based on the assumption of an idealized instrumentation, and that actual instrumentation introduces errors, such as those associated with nonopti-

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**Figure 17.** Simulation of normally distributed proportional errors: (a, top) input signal as a function of time (represented by a solid line) and errors (represented by open circles) and (b, bottom) histogram showing a typical distribution proportional errors with a sample size of $3 \times 10^24$.

**Figure 18.** Calculated results as a function of frequency obtained for a proportional noise input using the FRA with $R/R_e$ as a parameter: (a, top) errors in simulated measurement of impedance and (b, bottom) ratio of variances for real and imaginary parts of the impedance.

---

**Table III.** Student’s $t$-test statistical analysis of the conjecture $x = 0$ at a significance level of $\alpha = 0.05$ for proportionally distributed errors in the time-domain signals.

<table>
<thead>
<tr>
<th>Test</th>
<th>$R/R_e$</th>
<th>$\bar{x}$</th>
<th>$\sigma_x$</th>
<th>$P_{0.05}$</th>
<th>$t/t_{\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\log_{10}(\sigma^2_Z / \sigma^2_{\bar{Z}}) = 0$</td>
<td>1</td>
<td>0.011</td>
<td>0.042</td>
<td>0.043</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.11</td>
<td>0.20</td>
<td>0.0011</td>
<td>2.1</td>
</tr>
<tr>
<td>2. $\sigma_{Z\bar{Z}1}/(\sigma_{Z\bar{Z}})$ = 0</td>
<td>1</td>
<td>–0.0082</td>
<td>0.039</td>
<td>0.11</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>–0.14</td>
<td>0.16</td>
<td>$3.3 \times 10^{-4}$</td>
<td>3.5</td>
</tr>
<tr>
<td>3. $\sigma_{Z\bar{Z}0}/(\sigma_{Z\bar{Z}})$ = 0</td>
<td>1</td>
<td>–0.0079</td>
<td>0.038</td>
<td>0.11</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>–0.088</td>
<td>0.13</td>
<td>$1.5 \times 10^{-4}$</td>
<td>2.7</td>
</tr>
<tr>
<td>4. $(\sigma^2_{\bar{Z}1} -</td>
<td>\bar{Z}</td>
<td>^2 \alpha^2_0) / \sigma^2_{\bar{Z}1}$ = 0</td>
<td>1</td>
<td>0.021</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.19</td>
<td>0.30</td>
<td>$8.6 \times 10^{-4}$</td>
<td>2.4</td>
</tr>
</tbody>
</table>
mal selection of current measurement circuitry, that are not simulated here. Thus, it cannot be expected that the simulations presented here would provide exact predictions of experimental observations. Nevertheless, general observations have been made that merit comparison with experimental data reported in the literature.4,12,13

The impedance data presented in Fig. 19 represent the mean values for 5 replicated spectra that were obtained using a commercial frequency response analyzer for a n-GaAs/W Schottky diode held at fixed temperatures ranging from 320 to 400 K. The experimental system is described by Jansen and Orazem.35 The experimental data presented in Fig. 19 show great sensitivity to temperature and cover a broad range of impedance values.

The measurement model methods of Agarwal et al.9-11 were used to filter minor systematic variations among measurements taken at each temperature. The resulting standard deviations are presented in Fig. 20a as a function of frequency. These results show that the impedance data are strongly heteroskedastic, as predicted by the simulation and presented in Fig. 4. The larger scatter in the standard deviations reported in Fig. 20a, as compared to that seen in Fig. 4, can be attributed to the fact that five replicates were used to obtain Fig. 20a as compared to 500 for Fig. 4. The standard deviations obtained by direct calculation showed the same behavior, but application of the measurement model tools developed by Agarwal et al.9-11 improved the statistics by reducing the bias contribution.

The standard deviations were scaled by the magnitude of the impedance and presented as a percentage in Fig. 20b. Clearly, changes in the magnitude of the impedance cannot account completely for the heteroskedasticity of the data, a result that is again consistent with the results of the simulations presented in Fig. 5. It may be worth observing that the simulations predict a decrease in standard deviation at low frequencies which is enhanced at large cell impedance values. Such a decrease is evident in Fig. 20 for the results obtained at a temperature of 320 K.

The ratio of the variances of real and imaginary parts of the impedance is presented in Fig. 21 as a function of frequency for all temperatures. It is clear that, despite the large dependence of the

**Figure 19.** Mean value of impedance as a function of frequency with temperature as a parameter. Five replicated measurements were obtained for a n-GaAs Schottky diode using an FRA. (a, top) Real part and (b, bottom) imaginary part. Data taken from Jansen and Orazem15 and reproduced by permission of the publisher, The Electrochemical Society.

**Figure 20.** Standard deviations for the real and imaginary parts of the impedance reported in Fig. 19 as a function of frequency with temperature as a parameter: (a, top) standard deviations and (b, bottom) standard deviations normalized by the magnitude of the impedance.
standard deviation on frequency and temperature, the ratio of the variances of real and imaginary parts of the impedance have similar values that are distributed about unity. The histogram of the combined data set is presented in Fig. 21b. The results are consistent with the results of the simulation.

The results of the t-test, presented in Table IV, are consistent with the F-test presented in Fig. 21b. At temperatures of 320, 360, 380, and 400 K, the conjecture \( \log_{10}(\sigma^2_{Z_r}/\sigma^2_{Z_j}) = 0 \) was satisfied far beyond the \( \alpha = 0.05 \) confidence level. At a temperature of 340 K, the conjecture \( \log_{10}(\sigma^2_{Z_r}/\sigma^2_{Z_j}) = 0 \) was not satisfied at the \( \alpha = 0.05 \) confidence level; nevertheless, it was satisfied at the \( \alpha = 0.019 \) confidence level. The last line of Table IV shows that the conjecture \( \log_{10}(\sigma^2_{Z_r}/\sigma^2_{Z_j}) = 0 \) was satisfied at the 0.39 confidence level for the ensemble of data collected at all temperatures. The large value for the corresponding \( p \)-statistic indicates a high probability that the null hypothesis that \( \log_{10}(\sigma^2_{Z_r}/\sigma^2_{Z_j}) \neq 0 \) can be rejected for the ensemble of data.

Discussion

The calculations presented here provide insight into the manner in which frequency-domain errors originate from errors in the time-domain signals. Some key conclusions can be drawn concerning the nature of the distribution of frequency-domain errors and the relationship between the variance of the real and imaginary parts of the impedance obtained from FRA measurements.

Distribution of spectroscopy errors.—The assumption that errors in the frequency domain are normally distributed is fundamental to the statistical analysis of spectroscopy measurements. This work shows that errors, proportional time-domain errors, propagated through the measurement techniques, yield frequency domain errors that are, in fact, normally distributed. This result was found when the errors added to the time-domain signals were normally distributed and when the errors followed a skewed distribution. A normal distribution of frequency-domain errors was found even when the measurement technique introduced a small bias error in the frequency-domain results. The normal distribution of stochastic errors in the frequency-domain may be described as being a consequence of the central limit theorem applied to the methodology used to measure the complex impedance. The statistical properties of the error structure of impedance measurements are influenced by the nature of noise in the time-domain measurements. In fact, the comparison between simulations and experimental results obtained via FRA support the suggestion that the nature of experimental time-domain errors is likely to be additive rather than proportional. For additive time-domain errors, the variances for real and imaginary components were found to be equal. The equality of variance for real and imaginary parts of the impedance does not require, however, that the real and imaginary errors be correlated. Indeed, the covariances between real and imaginary impedance and between magnitude and phase angle were found to be equal to zero for additive time-domain errors.

The results of the present simulation do not, in themselves, answer fully the question of whether the statistical properties reported by Orazem et al.4,10,12,17 are in fact an intrinsic property of transfer-function measurements. Nevertheless, the present results go a long way in resolving this issue. The propagation of additive time-domain errors through the frequency-response instrumentation yields impedance spectra with the property that the variance of real and imaginary parts of the impedance are equal. The fact that the simulations provide, as well, real and imaginary components that are uncorrelated, and even modulus and phase angle components that are uncorrelated, demonstrates that the FRA algorithm does not introduce undesired correlations.

There remains work to be done. The present simulations were performed under galvanic modulation. It would be worthwhile to perform simulations under potentiostatic modulation to assess differences in the resulting frequency-domain error structure. A similar analysis using phase-sensitive detection is reported separately,22 and a set of sufficient-only and necessary-and-sufficient conditions for \( \sigma^2_{Z_r} = \sigma^2_{Z_j} \) and \( \sigma_{Z_r}^2 \sigma_{Z_j}^2 = 0 \) have been identified.26

<table>
<thead>
<tr>
<th>Test</th>
<th>x = 0</th>
<th>Temperature (K)</th>
<th>( \bar{x} )</th>
<th>( \sigma_x )</th>
<th>( p_{0.05} )</th>
<th>( t_{crit} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \log_{10}(\sigma^2_{Z_r}/\sigma^2_{Z_j}) = 0 )</td>
<td>320</td>
<td>-0.076</td>
<td>0.46</td>
<td>0.24</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>340</td>
<td>-0.23</td>
<td>0.67</td>
<td>0.019</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>360</td>
<td>0.11</td>
<td>0.45</td>
<td>0.095</td>
<td>0.848</td>
</tr>
<tr>
<td></td>
<td></td>
<td>380</td>
<td>0.027</td>
<td>0.57</td>
<td>0.74</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>0.025</td>
<td>0.44</td>
<td>0.69</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>All</td>
<td>-0.029</td>
<td>0.53</td>
<td>0.39</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Figure 21. Ratio of the variance of the real and imaginary parts of the impedance reported in Fig. 19: (a, top) distribution as a function of frequency (F-test) where the upper and lower dashed lines provide the F statistic at a 99% confidence level and (b, bottom) histogram for all data (Student’s t-test).
Conclusions

The objective of this work was to investigate the manner in which frequency-domain errors arise from time-domain measurements. This work provides a new approach for the analysis of impedance errors through the cell impedance.

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 analysis model of the form suggested by Orazem et al. 12 is needed to describe the error structure.

The results of the simulations demonstrated that, in the absence of bias errors, the errors in the real and imaginary impedance are uncorrelated and the variances of the real and imaginary parts of the complex impedance are equal. This work also showed that, independent of the distribution function for stochastic errors in the time-domain, stochastic errors in the frequency-domain have a normal distribution. The normal distribution of stochastic errors in the frequency-domain is a consequence of the central limit theorem applied to the methodology used to measure the complex impedance.

The approach presented here was based on the equations for the frequency-domain errors arising from time-domain measurements to electrochemical impedance spectroscopy, it can be applied to the methodology used to measure the complex impedance.

Acknowledgments

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References