



HAL
open science

Physical properties obtained from measurement model analysis of impedance measurements

Hangqi Liao, William Watson, Arthur Dizon, Bernard Tribollet, Vincent
Vivier, Mark Orazem

► **To cite this version:**

Hangqi Liao, William Watson, Arthur Dizon, Bernard Tribollet, Vincent Vivier, et al.. Physical properties obtained from measurement model analysis of impedance measurements. *Electrochimica Acta*, 2020, 354, pp.136747. 10.1016/j.electacta.2020.136747 . hal-02907090

HAL Id: hal-02907090

<https://hal.sorbonne-universite.fr/hal-02907090>

Submitted on 27 Jul 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Physical Properties Obtained from Measurement Model Analysis of Impedance Measurements

Hangqi Liao^a, William Watson^a, Arthur Dizon^a, Bernard Tribollet^b, Vincent Vivier^b, Mark E. Orazem^{a,*}

^aDepartment of Chemical Engineering, University of Florida, Gainesville, FL 32611

^bSorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electroniques (LISE), 4 place Jussieu, F-75005, Paris, France

Abstract

The Voigt measurement model is regressed to synthetic data to demonstrate its ability to extract capacitance, ohmic resistance, and polarization resistance values from impedance data. The systems explored include a Randles circuit, films with exponential and power-law distributions of resistivity, systems exhibiting geometric capacitance, and systems showing geometry-induced frequency dispersion. The Voigt measurement model is also regressed to complex capacitance to identify the high-frequency limit in Cole-Cole plots. The measurement model is shown to provide a useful means to estimate properties characteristic of electrochemical systems.

Keywords: simulation, regression, complex capacitance, frequency dispersion

1. Introduction

The measurement model was developed in the early 1990s as a means to quantify the error structure of electrochemical impedance spectroscopy measurements. Agarwal et al.¹ demonstrated that a Voigt series can provide an adequate fit to impedance spectra and could therefore serve as a generalized measurement model. By filtering lack of replication of similar impedance spectra, the measurement model was used to identify the standard deviation representing the stochastic error of impedance measurements.² The measurement model was also used to identify the frequency range of impedance measurements that was consistent with the Kramers-Kronig relations.^{3,4} The theoretical justification for the use of RC elements to approximate impedance spectra was provided by Schönleber and Ivers-Tiffée.⁵ The measurement model approach for assessing consistency was also explored by Boukamp and Macdonald,⁶ and Boukamp developed a linear regression of the Voigt series in which time constants are assigned values based on measured frequencies, leaving a simple linear regression for the corresponding values of resistances.⁷ Schönleber et al.⁸ provided a program that refines the selection of time constants in Boukamp's linear regression approach.⁷

The measurement model concept was explored by Blajiev et al.,^{9,10} who suggested that a rational model similar to those used in signal analysis¹¹ could be a suitable measurement model. Shukla et al.¹² used both rational and Voigt measurement models to show that the stochastic error structure identified was independent of the form of the measurement model used. You et al.¹³ showed that the Voigt measurement model as developed by Agarwal et al.^{1,2,3,4} was more sensitive to failures of causality associated with nonstationary behavior than was the linear regression approach pioneered by Boukamp⁷ and implemented by Gamry instruments.

Given that the measurement model could easily fit impedance data that are consistent with the Kramers-Kronig relations, significant effort was made to identify useful information that could be extracted from a measurement model fit to the data. Orazem et al.¹⁴ showed that the measurement model could yield

*Corresponding author

Email address: meo@che.ufl.edu (Mark E. Orazem)

estimates for the polarization and ohmic resistances. Their approach was applied, for example, to estimate an upper bound for the rate of corrosion of copper in anaerobic water.¹⁵ Orazem et al.¹⁶ used regression of the Voigt measurement model as a means of deconvolution to identify underlying distributions in impedance spectra, and Chen et al.¹⁷ explored the use of the Voigt measurement model to identify resistivity distributions in oxide films. Indeed the measurement model was used to determine that a power-law distribution of resistivity in a film gives rise to constant-phase-element (CPE) behavior.^{18,19}

It would be useful if the measurement model could also extract capacitance values for electrochemical systems. The evaluation of capacitance is somewhat critical because most electrochemical systems exhibit distributed-time-constant behavior. Often, the analysis of such data employs constant-phase elements (CPE), e.g.,

$$Z_{\text{CPE}} = \frac{1}{(j\omega)^\alpha Q} \quad (1)$$

where $j = \sqrt{-1}$ is the imaginary number, ω is the angular frequency [s^{-1}], and, as shown by Córdoba-Torres et al.,²⁰ the CPE parameters α and Q [$\text{F}/\text{cm}^2\text{s}^{1-\alpha}$] are highly correlated. The interpretation of the constant-phase element in terms of capacitance requires, in principle, an understanding of the nature of the associated time-constant distribution.²¹ Brug et al.²² developed an expression for a surface distribution of time constants that can be expressed as²³

$$C_{\text{eff,surf}} = Q^{1/\alpha} \left(\frac{R_c R_t}{R_c + R_t} \right)^{(1-\alpha)/\alpha} \quad (2)$$

where R_c [Ωcm^2] is the ohmic resistance and R_t [Ωcm^2] represents the charge-transfer resistance. Hirschorn et al.²⁴ showed that equation (2) applies for geometry-induced frequency dispersion associated with nonuniform current and potential distributions. Hirschorn et al.^{18,19} developed an expression for a distribution of time constants through a film as

$$C_{\text{eff,PL}} = gQ (\rho_\delta \varepsilon \varepsilon_0)^{1-\alpha} \quad (3)$$

where ε is the dielectric constant, $\varepsilon_0 = 8.8542 \times 10^{-14}$ F/cm is the permittivity of vacuum, ρ_δ [Ωcm] is the resistivity at film-electrolyte interface, and

$$g = 1 + 2.88(1 - \alpha)^{2.375} \quad (4)$$

Orazem et al.²³ showed that equation (3) applies for a perpendicular distribution of time-constants in a film.

A third approach for interpretation of the CPE parameters can be expressed as

$$C_{\text{eff,norm}} = Q^{1/\alpha} R_{\parallel}^{(1-\alpha)/\alpha} \quad (5)$$

where R_{\parallel} [Ωcm^2] is the resistance associated with the arc of the depressed semicircle. Equation (5) is equivalent to equation (3) in the work of Hsu and Mansfeld,²⁵ presented in terms of the characteristic angular frequency ω_{max} . Equation (5) may be applied only under conditions in which the resistance R_{\parallel} is due solely to the properties of the film. In many cases, however, the resistance R_{\parallel} is affected by other factors such as electrochemical reactions or open pores. Orazem et al.²³ showed that equation (5) did not apply to the apparent CPE response of human skin and oxides on steel; whereas, application of equation (3) yielded values for film thickness that agreed with surface analysis with oxides on free-machining 18/8 and martensitic steels. The power-law model has also been applied successfully to characterize oxides on ASTM A416 steels,²⁶ oxides on carbon steel,²⁷ properties of organic coatings,^{28,29,30,31,32} and properties of oxides on aluminum.³³

Not all time-constant distributions give rise to a constant-phase element. Young, for example, showed that the impedance of oxides on valve metals can be explained in terms of an exponential distribution of resistivity.^{34,35} Cole-Cole plots,^{36,37} used to extract limiting values for complex relative permittivity, can sometimes be applied to identify capacitance for electrochemical systems.^{38,39}

The objective of the present work was to explore the extent to which measurement models may be used to provide a reliable value for the capacitance, ohmic resistance, and polarization resistance of electrochemical systems. The measurement model is applied to synthetic data to explore the conditions under which it will yield reliable values.

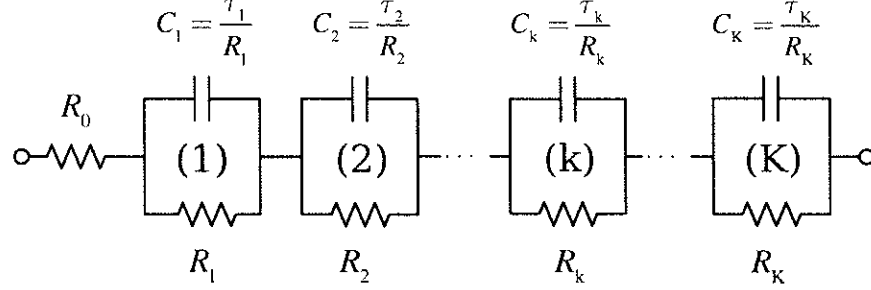


Figure 1: A schematic representation of a Voigt circuit used by Agarwal et al.^{1,2,4} as a measurement model.

65 2. Method

66 The measurement model proposed by Agarwal et al.¹ comprises Voigt elements in series with a solution
 67 resistance, shown in Figure 1. The impedance of the Voigt circuit can be expressed as

$$Z = R_0 + \sum_{k=1}^K \frac{R_k}{1 + j\omega\tau_k} \quad (6)$$

68 where the resistance R_k has units of $[\Omega]$ or $[\Omega\text{cm}^2]$ and τ_k has units of $[\text{s}]$. Agarwal et al.¹ showed that, by
 69 including a sufficient number of terms, a general measurement model based on equation (6) can fit impe-
 70 dance data for typical stationary electrochemical systems. The number of Voigt elements K was increased
 71 sequentially under the constraint that the 95.4% ($\pm 2\sigma$) confidence interval for each regressed parameter does
 72 not include zero. The same value for K can be obtained by minimization of the Akaike information criterion,
 73 which penalizes each additional parameter.⁴⁰

74 A capacitance for each element k can be expressed as

$$C_k = \frac{\tau_k}{R_k} \quad (7)$$

75 where capacitance C_k has units of F or F/cm^2 . In the limit that frequency tends toward infinity,

$$\lim_{\omega \rightarrow \infty} Z = R_0 + \sum_{k=1}^K \frac{R_k}{j\omega\tau_k} = R_0 - j \sum_{k=1}^K \frac{1}{\omega C_k} = R_0 - j \frac{1}{\omega C_{\text{eff}}} \quad (8)$$

76 where the effective capacitance can be obtained as

$$\frac{1}{C_{\text{eff}}} = \sum_k \frac{1}{C_k} \quad (9)$$

77 In the limit that frequency tends toward zero, the polarization resistance may be obtained as

$$\lim_{\omega \rightarrow 0} Z = R_p = R_0 + \sum_{k=1}^K R_k \quad (10)$$

78 The confidence intervals for the effective capacitance and polarization resistance can be obtained from the
 79 estimated standard errors of the regressed parameters using a linear propagation of error analysis (see Section
 80 3.2 of Orazem and Tribollet⁴¹).

81 Synthetic data were generated by either analytic expressions (Sections 4.1 and 4.2.1), by numerical
 82 solution of an integral (Section 4.2.2), or solution of Laplace's equation applied to a potential phasor (Sections
 83 4.3 and 4.4). Normally distributed noise was added to the synthetic data, i.e.,

$$Z_r = Z_{r,\text{model}} + N_1(\mu, \sigma^2) \quad (11)$$

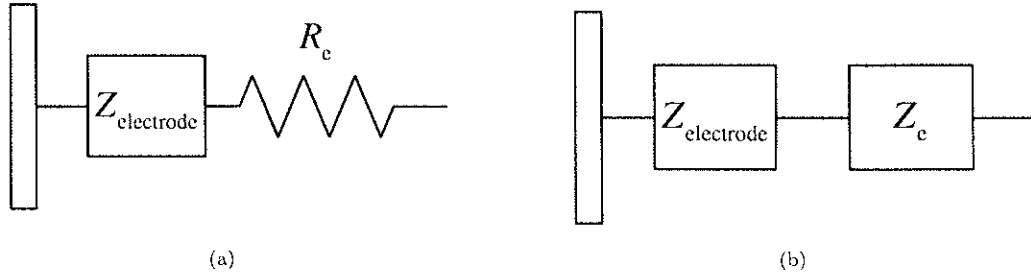


Figure 2: Schematic representation of an electrochemical electrode-electrolyte interface: a) electrode with a uniform current and potential distribution and b) electrode with a nonuniform geometry-induced current and potential distribution.

84 and

$$Z_j = Z_{j,\text{model}} + N_2(\mu, \sigma^2) \quad (12)$$

85 where the means of independent normal distributions N_1 and N_2 had value $\mu = 0$.

86 Equations (11) and (12) are justified by the work of Carson et al.,⁴² who showed that, for propagation of
 87 additive time-domain errors through an electrochemical cell and the Fourier analysis associated with typical
 88 frequency response analyzers, the errors in the real and imaginary impedance were normally distributed,
 89 uncorrelated, and had equal frequency-dependent standard deviations. The statistical results of Carson et
 90 al.⁴² agreed with experimental data collected using a Solartron 1250 frequency response analyzer (FRA)
 91 with a Solartron 1286 electrochemical interface for an n-GaAs/W Schottky diode held at fixed temperatures
 92 ranging from 320 to 400 K.⁴³

93 Carson et al.⁴⁴ also studied propagation of additive time-domain errors through an electrochemical cell
 94 and the mathematics of phase-sensitive detection associated with typical lock-in amplifiers. In contrast to
 95 results obtained using the frequency-response analysis algorithm, errors in the real and imaginary impedance
 96 were found to be correlated, and the variances of the real and imaginary parts of the complex impedance
 97 were not equal under all conditions. For the present work, the standard deviations for the real and imaginary
 98 parts of the impedance were assumed to be equal with a value $\sigma = 0.002|Z|$, in agreement with experimental
 99 observation.^{41,45} Thus, the assumed stochastic error structure was that associated with systems that employ
 100 Fourier analysis, such as the Gamry, Solartron, and Autolab instruments.

101 3. Regression Approach

102 The regressions performed in the present work employed weighted nonlinear complex least-squares regres-
 103 sion using a Levenberg-Marquardt algorithm. The regressions were weighted by the inverse of the variance of
 104 the assumed stochastic error structure. The original measurement model program was written in the 1990s in
 105 a combination of FORTRAN and Matlab programming languages. The present analysis was performed using
 106 a new program written in the Python language and available from the authors as a Windows installation
 107 executable.⁴⁶

108 4. Results

109 Equation (6) was regressed to synthetic data corresponding to a number of typical electrochemical sys-
 110 tems. In principle, an electrochemical system may be described in terms of a electrode impedance and the
 111 contribution of the electrolyte. The electrochemical systems considered are of two types. In the absence of
 112 nonuniform current and potential distributions, the impedance may be expressed as the series combination
 113 of a electrode impedance $Z_{\text{electrode}}$ and an ohmic resistance R_e , as shown in Figure 2(a). In the presence
 114 of nonuniform current and potential distributions, caused, for example, by the geometry of an electrode,
 115 the ohmic contribution must be expressed in terms of an ohmic impedance Z_e , as shown in Figure 2(b).

Table 1: Parameters employed for the electrochemical reaction influenced by mass transfer in a film presented in Figures 3–7.

δ_i	4×10^{-3}	cm
D_i	1×10^{-5}	cm^2/s
C	2×10^{-5}	F/cm^2
R_c	5	Ωcm^2
R_t	2.835	Ωcm^2
R_d	8.504	Ωcm^2

The ohmic impedance may be expressed, as shown by Gharbi et al.,³³ in the form of the Havriliak–Negami equation,⁴⁷ i.e.,

$$Z_o = R_{c,\text{HF}} + \frac{R_{c,\text{LF}} - R_{c,\text{HF}}}{(1 + (j\omega\tau)^\nu)^\beta} \quad (13)$$

where τ is the characteristic time constant of the ohmic impedance and the exponents ν and β dictate the limiting phase angles of the ohmic impedance at high and low frequency. Thus, in the presence of a nonuniform current and potential distribution, the influence of the electrolyte may be expressed in terms of two ohmic resistances: $R_{c,\text{HF}}$ that applies in the high-frequency limit and $R_{c,\text{LF}}$ that applies at lower frequencies.

In Section 4.1, the measurement model is applied for a reaction influenced by mass transfer. This example does not account for the complications associated with a nonuniform current and potential distribution. It serves to demonstrate that the measurement model yields an accurate estimate for the capacitance and ohmic resistance in spite of the interference caused by the mass-transfer term. The results presented in Section 4.2 for the impedance of a film demonstrate that the measurement model can provide accurate values for capacitance, ohmic, and polarization resistances in the presence of frequency dispersion caused by a distribution of properties in a film. Two examples presented in Section 4.2 are not affected by nonuniform current and potential distributions along the surface of the electrodes. The presentation in Section 4.3 of a geometric capacitance for a disk electrode shows that the information to be obtained by use of the measurement model depends on the frequency range used for the regression. At low frequencies, the influence of ohmic impedance associated with nonuniform current and potential distributions must be considered. The results presented in Section 4.4 for a disk electrode demonstrate that the influence of the ohmic impedance may be avoided by limiting the frequency range regressed by the measurement model. The results presented in Sections 4.1 to 4.4 serve to illustrate the power and the limitations of the use of the measurement model to extract physical properties.

4.1. Reaction Influenced by Mass Transfer

Synthetic data were generated for an electrochemical reaction influenced by mass transfer in a film. The parameters used to generate the data are presented in Table 1. The current was assumed to be three quarters of the mass-transfer-limited current. The frequency range was 10 mHz–100 kHz. The charge-transfer resistance was $R_t = 2.835 \Omega\text{cm}^2$ and a diffusion resistance was $R_d = 8.504 \Omega\text{cm}^2$.

The impedance was expressed as

$$Z = R_c + \frac{R_t + Z_d(\omega)}{1 + j\omega(R_t + Z_d(\omega))C} \quad (14)$$

where $Z_d(\omega)$ is the frequency-dependent diffusion impedance. Under the assumption of diffusion through a film, the diffusion impedance can be expressed as

$$Z_d(\omega) = R_d \frac{\tanh \sqrt{j\omega\delta_i^2/D_i}}{\sqrt{j\omega\delta_i^2/D_i}} \quad (15)$$

where R_d is the diffusion resistance. The capacitance, shown in Table 1, was assigned to have a value of $C = 20 \mu\text{F}/\text{cm}^2$. Normally distributed errors were added to the synthetic data with $\sigma_r = \sigma_j = 0.002|Z|$.

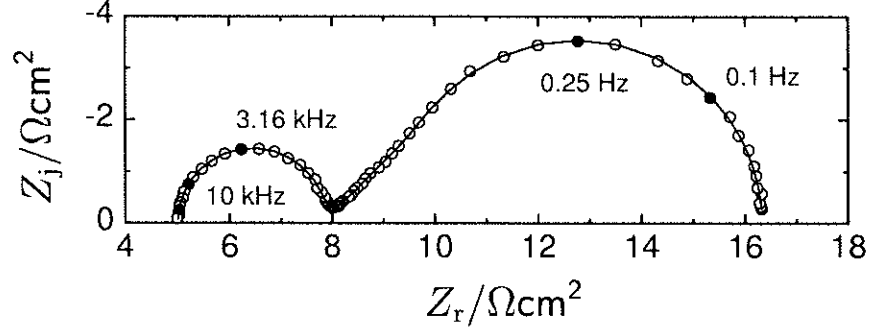


Figure 3: Regression results for synthetic data obtained using the parameters given in Table 1 at three quarters of the mass-transfer-limited current. The line represents the fit of the measurement model with parameters given in Table 2.

Table 2: Regression results for the synthetic data shown in Figure 3. The characteristic frequency for each element is defined as $f_k = 1/(2\pi\tau_k)$.

k	τ_k/s	f_k/Hz	$R_k/\Omega cm^2$	$C_k/\mu F cm^{-2}$	Contribution
0	—	—	5.0065 ± 0.0027	—	—
1	$(5.817 \pm 0.025) \times 10^{-5}$	2736	2.8607 ± 0.0070	20.332 ± 0.099	99.48%
2	$(1.10 \pm 0.12) \times 10^{-3}$	145	0.213 ± 0.014	5180 ± 650	0.39%
3	0.0106 ± 0.0010	15.0	0.422 ± 0.024	25100 ± 2800	0.081%
4	0.0635 ± 0.0029	2.51	0.939 ± 0.024	67800 ± 3500	0.030%
5	0.6490 ± 0.0028	0.245	6.887 ± 0.017	94320 ± 440	0.021%

148 The resulting synthetic data are presented in Figure 3. The fit of the measurement model to the synthetic
 149 data shown in Figure 3 is presented as a solid line, and the resulting parameters are presented in Table
 150 2. The ohmic resistance and capacitance extracted from the regressed parameters are presented in Table
 151 3. The capacitance obtained from the measurement model was $C = 20.226 \pm 0.098 \mu F/cm^2$ and the ohmic
 152 resistance was $5.0065 \pm 0.0027 \Omega cm^2$. The error in estimation of capacitance was 1.1 percent and the error
 153 in estimation of ohmic resistance was 0.13 percent.

154 Five Voigt elements were used to obtain the fit shown in Figure 3 and Table 2. Use of an additional
 155 Voigt element resulted in parameter estimates that included zero in the 95.4% confidence interval. Following
 156 equations (7) and (9), each Voigt element contributes to the estimated capacitance, but the Voigt elements
 157 used to fit the low-frequency diffusion impedance yielded large capacitances and, as shown in Table 2,
 158 correspondingly small contributions to the estimated capacitance. The 1.1 percent error in estimation of
 159 capacitance can be attributed largely to the added noise in the synthetic data. Regression of the measurement
 160 model to synthetic data without added noise yielded seven Voigt elements and an estimated capacitance of
 161 $20.019 \pm 0.038 \mu F/cm^2$ with an error of 0.093 percent.

162 The normalized residual errors for the regression shown in Figure 3 and Table 2 are presented in Figure

Table 3: Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figures 3, 5, and 7. Input parameters are given in Table 1.

Parameter	Input	Measurement Model	Data Type	Figure	Frequency Range
$R_c/\Omega cm^2$	5	5.0065 ± 0.0027	Impedance	3	10 MHz–100kHz
$C/\mu F cm^{-2}$	20	20.226 ± 0.098	Impedance	3	10 MHz–100kHz
$C/\mu F cm^{-2}$	20	20.115 ± 0.025	Capacitance	5	1Hz–10kHz
$R_c/\Omega cm^2$	5	5.0061 ± 0.0027	Impedance	7	1kHz–100kHz
$C/\mu F cm^{-2}$	20	20.33 ± 0.10	Impedance	7	1kHz–100kHz

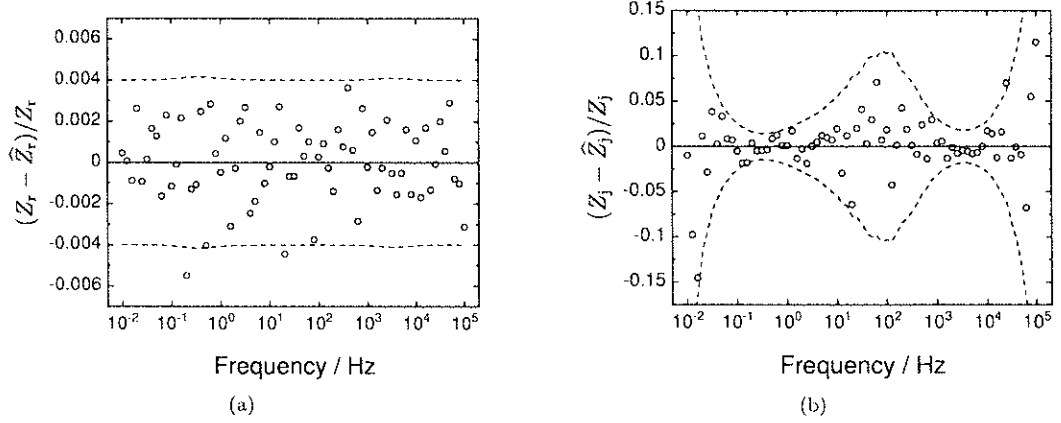


Figure 4: Normalized residual errors for the regression shown in Figure 3 with parameters shown in Table 2: a) real part of the impedance and b) imaginary part of the impedance. Dashed lines represent the 95.4% interval for the assumed stochastic error structure, i.e., $\pm 2\sigma/Z_r$ or $\pm 2\sigma/Z_j$, where $\sigma = 0.002|Z|$.

163 4 as functions of frequency. The residual errors generally fell within the 95.4% interval for the assumed error
 164 structure. The large values for the normalized residual errors for the imaginary part of the impedance at
 165 high and low frequencies, shown in Figure 4(b), can be attributed to the small magnitudes of the imaginary
 166 part of the impedance. For this regression, the weighted chi squared statistic was close to the degree of
 167 freedom ν , i.e., $\chi^2/\nu = 0.89$, also suggesting an excellent fit. Boukamp⁴⁸ provided an analytic expression
 168 for the time constants of a Voigt element applied to a finite-length Warburg impedance as

$$\tau_m = \frac{\tau_0}{\pi^2(m - 0.5)^2} \quad (16)$$

169 where $\tau_0 = \delta^2/D_i$ and the order of the index m is inverted from that shown for the index k in Table 2,
 170 i.e., the index $m = 1$ corresponds to the largest time constant. The value $\tau_5 = 0.6490 \pm 0.0028$ s given
 171 in Table 2 is in good agreement with the value $\tau_1 = 0.648$ calculated from equation (16). The resistance
 172 $R_5 = 6.887 \pm 0.017 \Omega\text{cm}^2$ is in agreement with Figure 7 of Boukamp.⁴⁸

173 The Cole–Cole representation³⁶ provides an alternative method to extract capacitance. The complex
 174 capacitance, obtained as

$$C^* = \frac{1}{j\omega(Z - R_c)} \quad (17)$$

175 requires, however, a good estimate for ohmic resistance.³² The complex capacitance is presented in Figure 5
 176 with ohmic resistance used in equation (17) as a parameter. The ohmic resistance was varied by $\pm 5\%$ from
 177 the input value of $R_c = 5 \Omega\text{cm}^2$. The calculation of complex capacitance yielded scattered results at low
 178 frequency due to the noise in the synthetic data, and these low-frequency results are not shown in Figure 5.
 179 The trending at high-frequency may be attributed in part to the noise in the measurement under conditions
 180 that $Z \approx R_c$. In addition, the noise is very large on the imaginary part of the impedance for frequencies
 181 above 10 kHz. An extrapolation of the complex capacitance to the real axis suggests that an uncertainty of
 182 5 percent in ohmic resistance yields an uncertainty of 20 percent in the capacitance.

183 The complex capacitance calculated for the input value of $R_c = 5 \Omega\text{cm}^2$ is presented in Figure 6.
 184 An asymptotic approach to a capacitance near $20 \mu\text{F}/\text{cm}^2$ is evident at high frequencies. To facilitate
 185 extrapolation of the Cole–Cole plot to the high-frequency limit, the measurement model given as equation
 186 (6) was modified for complex capacitance as

$$C = C(\infty) + \sum_{k=1}^K \frac{C_k}{1 + j\omega\tau_k} \quad (18)$$

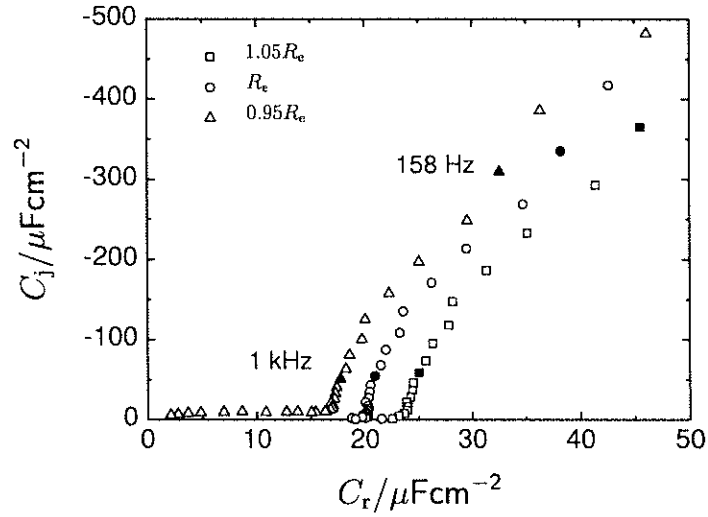


Figure 5: Complex capacitance obtained from the impedance data shown in Figure 3 with assumed ohmic resistance as a parameter. The maximum frequency shown is 100 kHz.

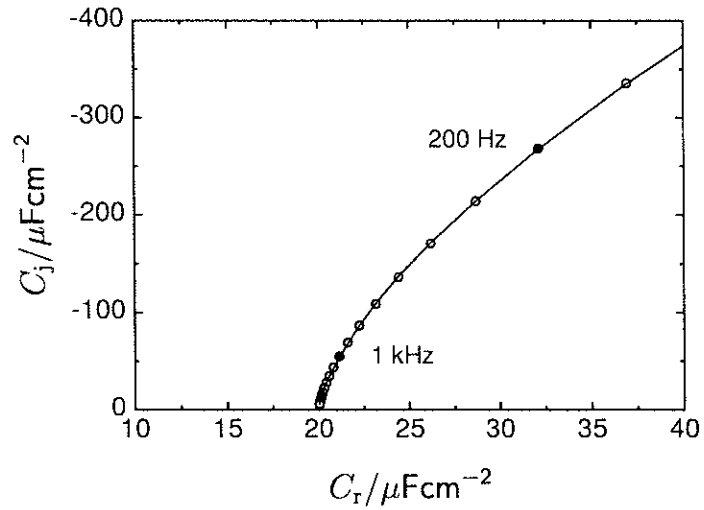


Figure 6: Complex capacitance obtained from the impedance data shown in Figure 3. The maximum frequency shown is 10 kHz. An asymptotic approach at high frequencies yields a capacitance near $20 \mu\text{F}/\text{cm}^2$. The line is the fit by a modified measurement model given as equation (18) to frequencies between 1 Hz and 10 kHz.

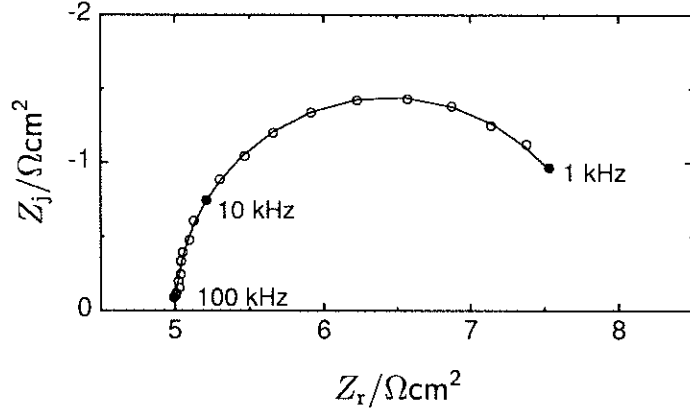


Figure 7: Regression results for synthetic data obtained using the parameters given in Table 1 at three quarters of the mass-transfer-limited current. The data were truncated to minimize the contribution of the diffusion impedance. The frequency range was 1–100 kHz, and $\chi^2/\nu = 0.86$. The line represents the fit of the measurement model with parameters given in Table 4.

Table 4: Regression results for a truncated spectrum shown in Figure 7. Input parameters for R_o (see R_0) and R_t (see R_1) are given in Table 1.

k	τ/s	f_k/Hz	$R_k/\Omega\text{cm}^2$	$C_k/\mu\text{Fcm}^{-2}$	Contribution
0	—	—	5.0061 ± 0.0027	—	—
1	$(5.868 \pm 0.025) \times 10^{-5}$	2712	2.8866 ± 0.0075	20.33 ± 0.10	100%

and fit to the synthetic data shown in Figure 6. The fit with four Voigt elements to frequencies between 1 Hz and 10 kHz is presented as a line in Figure 6. The capacitance estimate from equation (18) was $C(\infty) = 20.115 \pm 0.052 \mu\text{F}/\text{cm}^2$ with an error of 0.58 percent.

The low-frequency part of the synthetic data shown in Figure 3 was truncated to emphasize the high-frequency part of the measurement. The resulting spectrum, spanning a frequency range from 1 kHz to 100 kHz, is presented in Figure 7. Regression of the measurement model to the high-frequency data shown in Figure 7 yielded a single Voigt element, as would be expected for a reaction unaffected by mass transfer. The fit is shown as a line in Figure 7, and the resulting regressed parameters are presented in Table 4. The results are included in the summary presented in Table 3. The capacitance obtained from the measurement model was $C = 20.33 \pm 0.10 \mu\text{F}/\text{cm}^2$. The error in estimation of capacitance was 1.6 percent. The ohmic resistance was estimated as $R_o = 5.0061 \pm 0.0027 \Omega\text{cm}^2$, in good agreement with the value obtained by regression to the complete spectrum shown in Table 2. The value $R_1 = 2.8866 \pm 0.0075 \Omega\text{cm}^2$ corresponds to the input value of $R_t = 2.835 \Omega\text{cm}^2$ given in Table 1.

4.2. Distribution of Time Constants in a Film

Two models are often used to account for frequency dispersion associated with a perpendicular distribution of time constants in a film. Young³⁴ applied an exponential distribution of resistivity with respect to the normal distance to the electrode, and Hirschorn et al.^{18,19} developed a model based on a power-law distribution of resistivity.

4.2.1. Exponential Resistivity Distribution in a Film

The impedance of the film can be written for an arbitrary resistivity distribution $\rho(y)$ as

$$Z_t(f) = \int_0^\delta \frac{\rho(y)}{1 + j\omega\epsilon\epsilon_0\rho(y)} dy \quad (19)$$

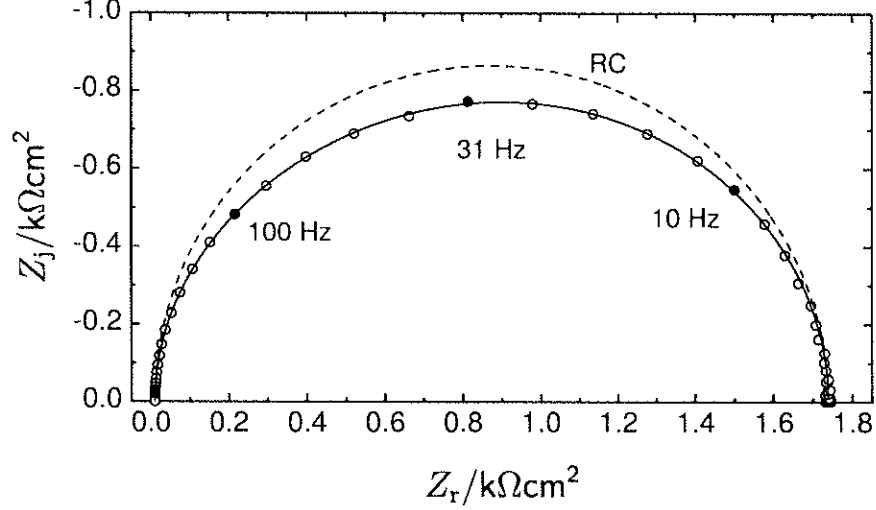


Figure 8: Young impedance given by equation (21) in Nyquist format with $R_c = 10 \text{ } \Omega\text{cm}^2$, $\varepsilon = 12$, $\lambda = 2 \text{ nm}$, $\delta = 4 \text{ nm}$, and $\rho_0 = 10^{10} \text{ } \Omega\text{cm}$. The line represents the measurement model fit with three Voigt elements. The dashed line represents a perfect RC behavior and is presented to highlight the distortion caused by the Young resistivity distribution. The frequency range was 10 mHz to 100 kHz and $\chi^2/\nu = 1.23$.

207 Young³⁴ assumed that the nonstoichiometry of an oxide layer resulted in an exponential variation of the
 208 conductivity with respect to the normal distance to the electrode. This assumption may be expressed in
 209 terms of resistivity as

$$\rho(y) = \rho_0 \exp(-y/\lambda) \quad (20)$$

210 The Young impedance for the gradient presented in equation (20) is^{24,49,50}

$$Z_Y = \frac{\lambda}{j\omega\varepsilon\varepsilon_0} \ln \left(\frac{1 + j\omega\rho_0\varepsilon\varepsilon_0}{1 + j\omega\rho_0\varepsilon\varepsilon_0 \exp(-\delta/\lambda)} \right) \quad (21)$$

211 In the low-frequency limit, application of L'Hôpital's rule yields

$$\lim_{\omega \rightarrow 0} Z_Y = \lambda\rho_0 (1 - \exp(-\delta/\lambda)) \quad (22)$$

212 which corresponds to a resistor. This result is in agreement with the direct integration of resistivity. In the
 213 high-frequency limit,

$$\lim_{\omega \rightarrow \infty} Z_Y = -j \frac{\delta}{\omega\varepsilon\varepsilon_0} \quad (23)$$

214 which corresponds to the impedance of the capacitor

$$C_Y = \frac{\varepsilon\varepsilon_0}{\delta} \quad (24)$$

215 The measurement model was applied to synthetic data for a film following the Young impedance.

216 The impedance was calculated as

$$Z = R_c + Z_Y \quad (25)$$

217 and normally distributed stochastic errors were added following equations (11) and (12). The calculated
 218 impedance response for $R_c = 10 \text{ } \Omega\text{cm}^2$, $\varepsilon = 12$, $\lambda = 2 \text{ nm}$, $\delta = 4 \text{ nm}$, and $\rho_0 = 10^{10} \text{ } \Omega\text{cm}$ is shown in
 219 Figure 8, where the line represents the measurement model fit using three Voigt elements. The dashed line
 220 represents a perfect RC behavior and is presented to highlight the distortion caused by the Young resistivity
 221 distribution.

Table 5: Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figure 8.

Parameter	Input	Source	Measurement Model
$R_c/\Omega\text{cm}^2$	10	–	9.9915 ± 0.0062
$Z_Y(0)/\Omega\text{cm}^2$	1729.33	Equation (22)	1728 ± 158
$C/\mu\text{Fcm}^{-2}$	2.65626	Equation (24)	2.66 ± 0.29

A summary is presented in Table 5 of values extracted from the measurement model regression to the synthetic data presented in Figure 8. The measurement model results are in excellent agreement to the input parameters. The error for determination of ohmic resistance was 0.085%, the error for determination of $Z_Y(0)$ was 0.039%, and the error for determination of capacitance was 0.020%.

4.2.2. Power-Law Resistivity Distribution in a Film

Hirschorn et al.^{18,19} showed that a power-law distribution of resistivity corresponds to a constant-phase element, i.e.,

$$\frac{\rho}{\rho_\delta} = \xi^{-\gamma} \quad (26)$$

where $\xi = y/\delta$, y represents the position through the depth of the film, and δ is the film thickness. The parameter ρ_δ is the resistivity at $y = \delta$, and γ is a constant indicating the sharpness of the variation of resistivity. A distribution of resistivity that provides a bounded value for resistivity at $\xi = 0$ was proposed to be

$$\frac{\rho}{\rho_\delta} = \left(\frac{\rho_\delta}{\rho_0} + \left(1 - \frac{\rho_\delta}{\rho_0} \right) \xi^\gamma \right)^{-1} \quad (27)$$

where ρ_0 and ρ_δ are the boundary values of resistivity at the respective interfaces. By integration of equation (19), Hirschorn et al.^{18,19} showed that

$$Q = \frac{(\varepsilon\varepsilon_0)^\alpha}{g\delta\rho_\delta^{1-\alpha}} \quad (28)$$

and

$$\alpha = \frac{\gamma - 1}{\gamma} \quad (29)$$

where g , defined by equation (4), provided a relationship between the constant-phase-element parameters and the power-law model.

The impedance was calculated following

$$Z = R_c + Z_f \quad (30)$$

and normally distributed stochastic errors were added following equations (11) and (12). The simulations presented in Figure 9 represent the integration of equations (19) and (27) with $\rho_0 = 10^{14} \Omega\text{cm}$, $\rho_\delta = 5 \times 10^6 \Omega\text{cm}$, $\gamma = 6 + 2/3$, $\varepsilon = 12$, and $\delta = 2 \text{ nm}$. The ohmic resistance, $R_c = 10 \Omega\text{cm}^2$, was added following equation (30).

The results presented in Figure 9(a) suggest a constant-phase-element behavior as suggested by equation (29), from which a value $\alpha = 0.85$ is obtained. The impedance response has two characteristic frequencies:

$$f_{c,0} = \frac{1}{2\pi\varepsilon\varepsilon_0\rho_0} = 1.50 \text{ Hz} \quad (31)$$

and

$$f_{c,\delta} = \frac{1}{2\pi\varepsilon\varepsilon_0\rho_\delta} = 29.96 \text{ kHz} \quad (32)$$

The high-frequency region, presented in Figure 9(b), indicates that the impedance deviates from pure CPE behavior near $f_{c,\delta}$, at which a capacitive behavior is identified. The measurement model results are compared

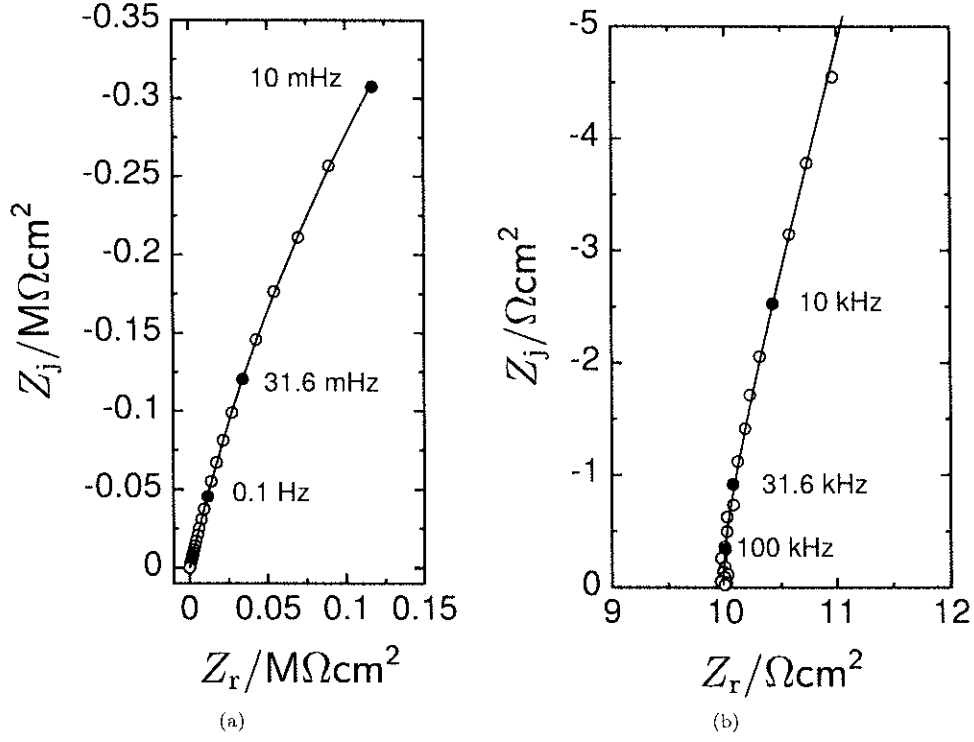


Figure 9: Impedance given by equations (30) and (19) for the resistivity given by equation (27) with $R_c = 10 \Omega cm^2$, $\rho_0 = 10^{14} \Omega cm$, $\rho_s = 5 \times 10^6 \Omega cm$, $\gamma = 6 + 2/3$, $\epsilon = 12$, and $\delta = 2 \text{ nm}$: a) complete frequency range and b) high frequency range. The line represents the measurement model fit with eleven Voigt elements. The frequency range was 10 mHz to 100 kHz and $\chi^2/\nu = 1.09$.

Table 6: Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figure 9.

Parameter	Input	Source	Measurement Model
$R_c / \Omega cm^2$	10	–	9.9965 ± 0.0079
$C / \mu F cm^{-2}$	5.313	equation (24)	5.45 ± 0.22

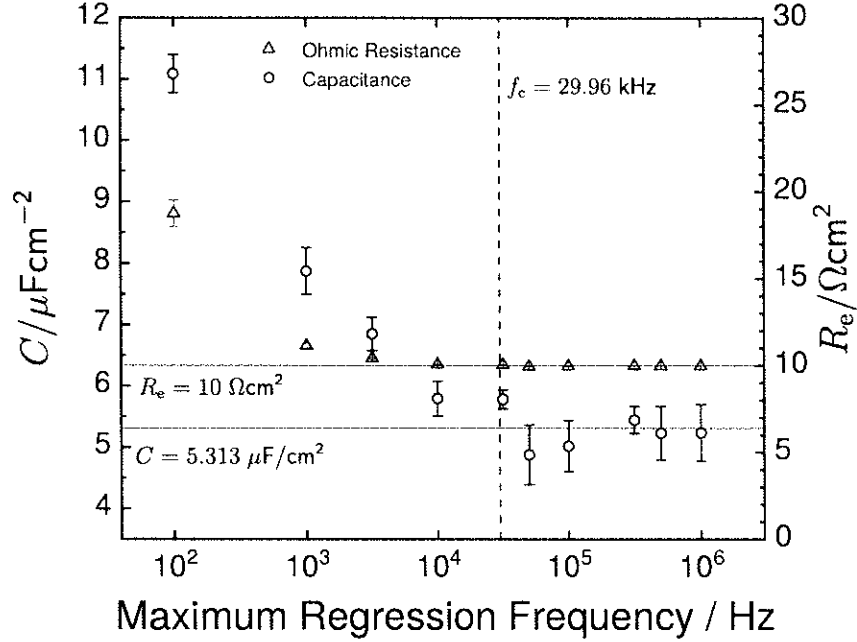


Figure 10: Capacitance obtained by regression of equation (6) to the complex impedance for truncated frequency ranges as functions of the maximum regression frequency of the regressed data. For example, the values of capacitance and ohmic resistance for a maximum regression frequency of 100 Hz were obtained by regression to data encompassing the frequency range of 10 mHz to 100 Hz.

248 to the input values in Table 6. The error for determination of ohmic resistance was -0.14% and the error
 249 for determination of capacitance was -1.38% .

250 Determination of capacitance was made possible by the high-frequency capacitive behavior seen in Figure
 251 9(b). For systems in which the characteristic frequency defined by equation (32) is larger than the measured
 252 frequency range, the impedance has the character of a constant-phase element for which a capacitance cannot
 253 be obtained. Thus, capacitance values extracted from the measurement model analysis will be incorrect.
 254 Equation (6) was regressed to the complex impedance for truncated frequency ranges. The results are
 255 presented in Figure 10. A capacitance of $11.09 \pm 0.31 \mu\text{F}/\text{cm}^2$, shown for a maximum regression frequency of
 256 100 Hz, was obtained by regression to data encompassing frequencies from 10 mHz to 100 Hz. The maximum
 257 frequency analyzed was smaller than the characteristic frequency given by equation (32), and the resulting
 258 capacitance had an error of 109%. Larger errors may be obtained by regression to spectra with still smaller
 259 maximum frequencies. A similar error was found for the estimation of the ohmic resistance. The ohmic
 260 resistance of $18.74 \pm 0.76 \Omega\text{cm}^2$, shown for a maximum regression frequency of 100 Hz, had an error of 87%.

261 4.3. Geometric Capacitance

262 Numerical simulations using finite elements were performed for a disk electrode embedded in an insulating
 263 plane. The numerical method employed in the present work is described by Dizon and Orazem for interdig-
 264 itated electrodes.⁵¹ The appearance of a high-frequency loop associated with the geometric capacitance can
 265 be attributed to treatment of displacement as well as electrical currents.

266 The governing equation was conservation of current density

$$\nabla \cdot \mathbf{i} = 0 \quad (33)$$

267 where the current density vector \mathbf{i} comprised both electrical and displacement currents, i.e.,

$$\mathbf{i} = \kappa \mathbf{E} + \frac{d\mathbf{D}}{dt} \quad (34)$$

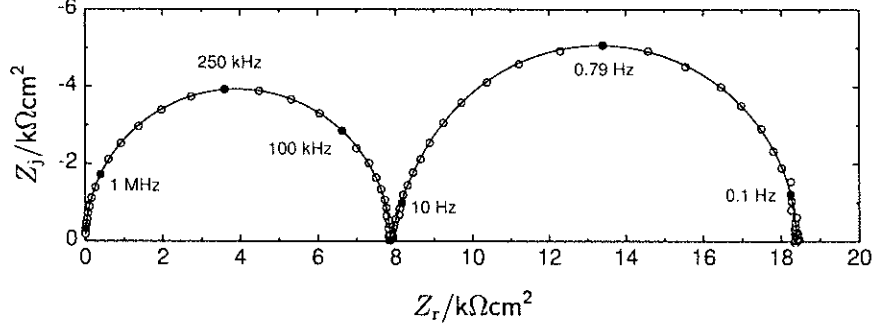


Figure 11: Simulated impedance response for a disk electrode with parameters $r_0 = 0.1$ cm, $\rho = 10^5$ Ωcm , $\epsilon = 78$, $C_{dl} = 20$ $\mu\text{F}/\text{cm}^2$, and $R_t = 10^4$ Ωcm^2 . The line represents the fit by the measurement model with four Voigt elements. The frequency range was 1 mHz – 1 MHz, and $\chi^2/\nu = 1.29$.

where κ is the electrical conductivity, \mathbf{E} is the electric field vector, and \mathbf{D} is the electrical displacement vector. The electrical displacement vector was obtained from the constitutive relationship

$$\mathbf{D} = \epsilon\epsilon_0\mathbf{E} \quad (35)$$

and the electric-field vector was related to the electrical potential Φ by

$$\mathbf{E} = -\nabla\Phi \quad (36)$$

Equations (33)-(36) are straightforward applications of Maxwell's equations.⁵²

The electric potential and current were represented in phasor notation as

$$\Phi = \bar{\Phi} + \text{Re}\{\tilde{\Phi}e^{j\omega t}\} \quad (37)$$

and

$$\mathbf{i} = \bar{\mathbf{i}} + \text{Re}\{\tilde{\mathbf{i}}e^{j\omega t}\} \quad (38)$$

where $\bar{\Phi}$ and $\bar{\mathbf{i}}$ are the steady-state electrical potential and current density, respectively, and $\tilde{\Phi}$ and $\tilde{\mathbf{i}}$ are complex potential and current density phasors, respectively. The phasors $\tilde{\Phi}$ and $\tilde{\mathbf{i}}$ are functions of frequency and position, but are independent of time.

Under assumptions of a steady state and uniform properties, substitution of equations (34) to (38) into equation (33) yields

$$\nabla \cdot \tilde{\mathbf{i}} = -\kappa\nabla^2\tilde{\Phi} = 0 \quad (39)$$

The conservation of current under a sinusoidal steady-state may be expressed as

$$(1 + j\omega\epsilon\epsilon_0\rho)\nabla^2\tilde{\Phi} = 0 \quad (40)$$

As the permittivity of vacuum $\epsilon_0 = 8.8542 \times 10^{-14}$ C/V cm is a very small number, equation (40) shows that, for electrolytes of modest resistivity, the contribution of the displacement current can be neglected for impedance measurements in the usual 10 mHz–100 kHz range. The displacement current plays an important role for measurements performed in high-resistivity electrolytes such as organic liquids.^{53,54}

Synthetic data are presented in Figure 11 for a disk electrode with parameters $r_0 = 0.1$ cm, $\rho = 10^5$ Ωcm , $\epsilon = 78$, $C_{dl} = 20$ $\mu\text{F}/\text{cm}^2$, and $R_t = 10^4$ Ωcm^2 . Normally distributed stochastic errors were added following equations (11) and (12). The synthetic data reveal a high-frequency loop that can be attributed to the geometric capacitance. The geometric capacitance for a disk electrode may be expressed as

$$C_g = \frac{4\epsilon\epsilon_0}{\pi r_0} \quad (41)$$

Table 7: Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figures 3, 5, and 7.

Parameter	Input	Measurement Model	Figure	Frequency Range
C_g/nFcm^{-2}	0.08793	0.088008 ± 0.000067	11	1 mHz–10 MHz
$R_{e,\text{HF}}/\Omega\text{cm}^2$	7,854	$7,855.3 \pm 3.0$	11	1 mHz–10 MHz
$C_{\text{dl}}/\mu\text{Fcm}^{-2}$	20	12.0 ± 1.2	12(a)	1 mHz–100 Hz
$R_{e,\text{HF}}/\Omega\text{cm}^2$	7,854	$7,879.2 \pm 8.3$	12(a)	1 mHz–100 Hz
$R_t/\Omega\text{cm}^2$	10,000	$10,519 \pm 81$	12(a)	1 mHz–100 Hz
$C_{\text{dl}}/\mu\text{Fcm}^{-2}$	20	19.50 ± 0.40	12(b)	1 mHz–0.79 Hz
$R_{e,\text{LF}}/\Omega\text{cm}^2$	–	$8,268 \pm 45$	12(b)	1 mHz–0.79 Hz
$R_t/\Omega\text{cm}^2$	10,000	$10,131 \pm 43$	12(b)	1 mHz–0.79 Hz

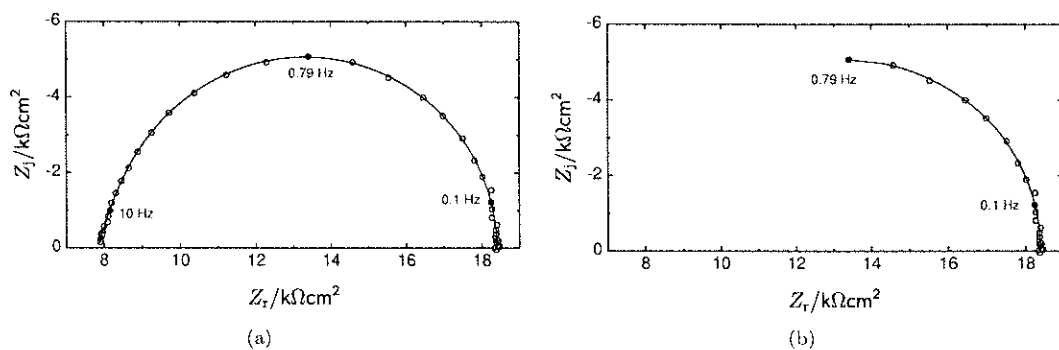


Figure 12: Truncated impedance taken from Figure 11: a) synthetic data with a frequency range of 1 mHz to 100 Hz and b) synthetic data with a frequency range of 1 mHz to 0.79 Hz. The lines represent measurement model fits using, respectively, three or one Voigt element, and the respective values of χ^2/ν were 1.14 and 1.06.

288 where the characteristic dimension for the disk electrode is $\pi r_0/4$.

289 Regression of the measurement model to the complete spectrum shown in Figure 11 required four Voigt
 290 elements. The results are presented in Table 7. The capacitance was $C_g = 0.088008 \pm 0.000067$ nF/cm², in
 291 good agreement with the value of 0.08793 nF/cm² calculated from equation (41). The geometric capacitance
 292 loop was fit by a single Voigt element, and the high-frequency ohmic resistance could be obtained from
 293 associated resistance value as $R_{e,\text{HF}} = 7,855.3 \pm 3.0$ Ωcm², in good agreement with the value of 7,854 Ωcm²
 294 calculated from input parameters.

295 Regression of the measurement model to the low-frequency capacitive loop, shown in Figure 12(a), re-
 296 quired three Voigt elements. The regressed frequency range was 1 mHz–100 Hz. The results are presented
 297 in Table 7. The ohmic resistance obtained was $7,879.2 \pm 8.3$ Ωcm², which was close to the high-frequency
 298 ohmic resistance estimated from input parameters to be 7,854 Ωcm². The regression allowed estimation of
 299 capacitance, but the value obtained, 12.0 ± 1.2 μFcm⁻², was substantially smaller than the input double
 300 layer capacitance of 20 μFcm⁻². Similarly, the charge-transfer resistance was slightly larger than the input
 301 value.

302 The error in estimation of double-layer capacitance and, to a lesser degree, the error in estimation of
 303 charge-transfer resistance can be attributed to the frequency dispersion caused by the nonuniform current
 304 and potential distribution associated with the disk geometry. The characteristic frequency associated with
 305 frequency dispersion has a value⁵⁵

$$f_c = \frac{1}{8R_{e,\text{HF}}C_{\text{dl}}} = 0.796 \text{ Hz} \quad (42)$$

306 based on input values of $R_{e,\text{HF}}$ and C_{dl} . The results of the regression of the measurement model to the
 307 data with frequencies in the range 1 mHz–0.79 Hz are shown in Figure 12(b). Only a single Voigt element
 308 could be extracted, as would be expected in the absence of frequency dispersion. The capacitance was

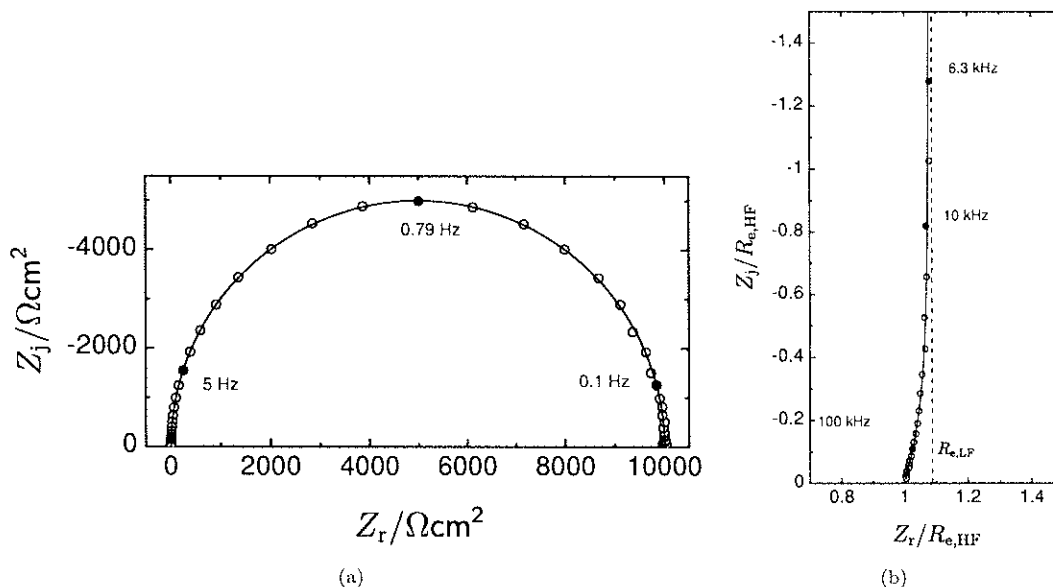


Figure 13: Simulated impedance response for a disk electrode with parameters $r_0 = 0.1$ cm, $\rho = 12.67$ Ωcm , $\varepsilon = 78$, $C_{dl} = 20$ $\mu\text{F}/\text{cm}^2$, and $R_t = 10^4$ Ωcm^2 . Normally distributed stochastic error was added to the impedance with standard deviation equal to 0.2% of the modulus: a) full spectrum and b) scaled impedance in the high-frequency region. The line represents the fit by the measurement model with three Voigt elements and $\chi^2/\nu = 0.94$.

309 19.50 ± 0.40 μFcm^{-2} , in good agreement with the input value of 20 μFcm^{-2} . The charge-transfer resistance
 310 was $10,131 \pm 43$ Ωcm^2 , in good agreement with the input value of $10,000$ Ωcm^2 . The ohmic resistance of
 311 $8,268 \pm 45$ can be considered the low-frequency ohmic resistance $R_{c,LF}$. The ratio $R_{c,LF}/R_{c,HF} = 1.053$ is
 312 less than the value of 1.08 calculated for capacitive behavior on disk electrodes^{56,55} and is in good agreement
 313 with Figure 13.13 in Orazem and Tribollet⁴¹ for $J = 4R_c/\pi R_t = 1$.

314 4.4. Surface Distribution of Time Constants

315 Newman showed, in 1966, that the electrode-insulator interface gives rise to nonuniform current and
 316 potentials distributions for currents that are below the mass-transfer-limited current.^{57,58} Newman also
 317 reported that the capacity and ohmic resistance were functions of frequency above a critical value of fre-
 318 quency.⁵⁶ Huang et al.⁵⁵ showed that the geometry-induced frequency dispersion distorts the impedance
 319 response above a critical frequency. Hirschorn et al.²⁴ reported that the geometry induced frequency dis-
 320 persion could be modeled approximately by a constant-phase element and that the Brug formula²² given as
 321 equation (2) provided a good means of extracting the capacitance from the resulting constant-phase-element
 322 parameters.

323 Synthetic data were obtained by finite-element solution of Laplace's equation for a disk electrode embed-
 324 ded in an insulating plane. The boundary condition for the electrode included the influence of a faradaic
 325 reaction. The numerical methods used were described by Gharbi et al.³³ Normally distributed stochastic
 326 errors were added following equations (11) and (12). The resulting synthetic data are presented in Figure
 327 13(a) for a disk electrode with parameters $r_0 = 0.1$ cm, $\rho = 12.57$ Ωcm , $\varepsilon = 78$, $C_{dl} = 20$ $\mu\text{F}/\text{cm}^2$, and
 328 $R_t = 10^4$ Ωcm^2 . The influence of geometry-induced frequency dispersion is seen in Figure 13(b).

329 The characteristic frequency associated with frequency dispersion was calculated from equation (42) to be
 330 6.3×10^3 Hz. Above this frequency, the nonuniform current and potential distributions associated with the
 331 electrode geometry causes frequency dispersion. The capacitance obtained by regression of the measurement
 332 model to the complete spectrum was $C = 11.8 \pm 0.75$ $\mu\text{F}/\text{cm}^2$, substantially smaller than the input value of
 333 20 $\mu\text{F}/\text{cm}^2$.

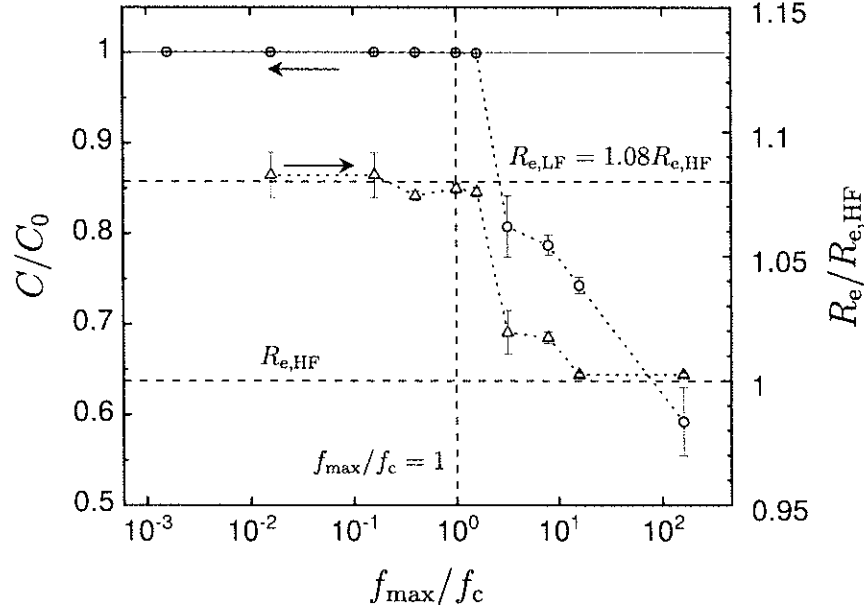


Figure 14: Scaled capacitance and scaled ohmic resistance obtained by regression of equation (6) to the complex impedance shown in Figure 13 for truncated frequency ranges as functions of the maximum frequency of the regressed data scaled to the characteristic frequency given by equation (42).

Table 8: Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figures 13 and 14.

Parameter	Input	Measurement Model	Frequency Range
$R_{c,HF}/\Omega\text{cm}^2$	0.99472	0.99708 ± 0.00084	1 mHz–1 MHz
$R_t/\Omega\text{cm}^2$	10,000	$10,002.4 \pm 3.6$	1 mHz–1 MHz
$C/\mu\text{Fcm}^{-2}$	20	11.85 ± 0.75	1 mHz–1 MHz
$R_{c,LF}/\Omega\text{cm}^2$	–	1.0715 ± 0.0019	1 mHz–6.31 kHz
$R_t/\Omega\text{cm}^2$	10,000	$10,002.0 \pm 3.8$	1 mHz–6.31 kHz
$C/\mu\text{Fcm}^{-2}$	20	19.996 ± 0.013	1 mHz–6.31 kHz

334 The capacitance values obtained by regression of equation (6) to the complex impedance for truncated
335 frequency ranges are presented in Figure 14 as functions of the maximum regressed frequency. Capacitance
336 values were normalized by the input value for double-layer capacitance. A correct value for the capacitance
337 was obtained for regression to a maximum frequency equal to that obtained by equation (42). Regression
338 of the measurement model to the complete spectrum shown in Figure 13 required three Voigt elements, and
339 regression to the truncated spectrum from 1 mHz–6.31 kHz required one Voigt element. The results are
340 presented in Table 8.

341 Regression to maximum frequencies an order of magnitude larger than the characteristic frequency given
342 by equation (42) yielded good estimates for the high-frequency ohmic resistance $R_{c,HF}$. Regression to maxi-
343 mum frequencies below the characteristic frequency yielded values of $R_c/R_{c,HF}$ that were close to the value
344 of 1.08 calculated for $J = 4R_c/\pi R_t$ approaching zero.^{56,55,41} For the present simulations, $J = 1.3 \times 10^{-4}$.
345 As the value of the ohmic resistance is much smaller than the charge-transfer resistance, both the regression
346 to the complete spectrum and regression to the truncated spectrum yielded good approximations for the
347 charge-transfer resistance. The regression to the 1 mHz–6.31 kHz frequency range yielded accurate values
348 for the double-layer capacitance because regression to a maximum frequency of 6.31 kHz eliminated most of
349 the confounding influence of the ohmic impedance.

5. Conclusions

The measurement model provides a powerful tool for the identification of the error structure of impedance measurements, including determination of the frequency-dependent standard deviation of the measurements and the frequency range that is consistent with the Kramers–Kronig relations. The present work demonstrates that the measurement model also serves as a useful means to provide quantitative estimates for parameters relevant to impedance spectroscopy data, including ohmic resistance, polarization resistance, and capacitance.

The ability to extract capacitance by use of the measurement model is important, because most impedance systems show distributed-time-constant behavior that is often fit by use of the CPE. The CPE parameters are related to the capacitance of the electrode, but extraction of a capacitance requires different approaches depending on the nature of the underlying distribution. For example, the Brug formula²² is used in cases of a surface distribution of time constants, and the power-law model^{18,19} applies for a distribution through a film. Not all distributed-time-constant behaviors are represented by a CPE, and formulas like the Brug and Power-Law equations do not exist for such systems. Furthermore, the measurement model provides a unique ability to extract the high-frequency and low-frequency ohmic resistances for systems exhibiting an ohmic impedance.

The application of the measurement model to extract parameters for experimental impedance data depends on the nature of the electrochemical system under investigation. For systems that have a uniform current and potential on the electrode surface, the ohmic resistance and capacitance may be extracted by regression of the measurement model to the part of the impedance spectrum that is found to be consistent with the Kramers–Kronig relations. The polarization resistance corresponding to the zero-frequency limit may also be estimated. For systems that have a nonuniform current and potential distribution, a characteristic frequency can be identified above which the impedance is influenced by the associated frequency dispersion. This characteristic frequency may be estimated for general systems using

$$f_c = \frac{1}{2\pi R_{c,\text{HF}} C} \quad (43)$$

where values of C and $R_{c,\text{HF}}$ are estimated by regression of the measurement model to the impedance spectrum that is found to be consistent with the Kramers–Kronig relations. The estimate for C may be updated by eliminating the frequencies above f_c . The new value of C is used to calculate a new estimate for the characteristic frequency. This iterative process is completed when the estimated characteristic frequency is larger than the maximum frequency used in the regression. The iterative process will yield estimates for C and $R_{c,\text{LF}}$. The iterative process may fail to yield a suitable convergence for cases in which $R_t < R_{c,\text{HF}}$.

The use of the measurement model to extract physical properties of electrochemical systems are guided by four caveats:

1. In the presence of geometry-induced frequency dispersion, the capacitance obtained by the measurement model was smaller than the input double-layer capacitance. The measurement model can be made to yield an accurate capacitance by removing the contribution of the ohmic impedance from the regressed data.
2. High-frequency and low-frequency ohmic resistances are defined for systems showing the presence of geometry-induced frequency dispersion. The low-frequency ohmic resistance may be quantified by regression to data that are below the characteristic frequency defined by equation (42).
3. For systems that exhibit the influence of geometric capacitance, the capacitance obtained by the measurement model is the geometric capacitance, independent of the value of the double layer capacitance. The double-layer capacitance and low-frequency ohmic resistance may be extracted from regression to data that are below the characteristic frequency defined by equation (42). The high-frequency ohmic resistance may be obtained by regression to data that are at frequencies below that affected by the geometric capacitance loop.
4. For systems that show pure constant-phase-element behavior, a capacitance cannot be identified, either by the measurement model or by extrapolation of the Cole-Cole plot.

398 Used wisely, the measurement model may be a powerful tool for extracting the capacitance, ohmic resistance,
399 and polarization resistance for impedance data. It can be applied both for systems exhibiting normal
400 distributions of time constants and, if applied to frequencies sufficiently below the characteristic frequency
401 for geometry-induced dispersion, for systems showing surface distributions of time-constants. Used in this
402 way, the measurement model provides a powerful complement to the development of system-specific process
403 models.

404 6. Acknowledgments

405 Mark Orazem acknowledges financial support from the University of Florida Foundation Preeminence
406 and the Dr. and Mrs. Frederick C. Edie term professorships.

407 References

- 408 [1] P. Agarwal, M. E. Orazem, L. H. García-Rubio, Measurement models for electrochemical impedance
409 spectroscopy: 1. Demonstration of applicability, *Journal of the Electrochemical Society* 139 (1992)
410 1917–1927.
- 411 [2] P. Agarwal, O. D. Crisalle, M. E. Orazem, L. H. García-Rubio, Measurement models for electrochemical
412 impedance spectroscopy: 2. Determination of the stochastic contribution to the error structure, *Journal*
413 *of the Electrochemical Society* 142 (1995) 4149–4158.
- 414 [3] P. Agarwal, M. E. Orazem, L. H. García-Rubio, Application of the kramers kronig relations to elec-
415 trochemical impedance spectroscopy, in: J. Scully, D. Silverman, M. Kendig (Eds.), *Electrochemical*
416 *Impedance: Analysis and Interpretation*, Vol. ASTM STP 1188, American Society for Testing and
417 Materials, Philadelphia, 1993, pp. 115–139.
- 418 [4] P. Agarwal, M. E. Orazem, L. H. García-Rubio, Measurement models for electrochemical impedance
419 spectroscopy: 3. Evaluation of consistency with the kramers-kronig relations, *Journal of the Electro-*
420 *chemical Society* 142 (1995) 4159–4168.
- 421 [5] M. Schönleber, E. Ivers-Tiffée, Approximability of impedance spectra by rc elements and
422 implications for impedance analysis, *Electrochemistry Communications* 58 (2015) 15 – 19.
423 doi:<https://doi.org/10.1016/j.elecom.2015.05.018>.
424 URL <http://www.sciencedirect.com/science/article/pii/S1388248115001502>
- 425 [6] B. A. Boukamp, J. R. Macdonald, Alternatives to kronig-kramers transformation and testing, and
426 estimation of distributions, *Solid State Ionics* 74 (1994) 85–101.
- 427 [7] B. A. Boukamp, A linear kronig-kramers transform test for immittance data validation, *Journal of the*
428 *Electrochemical Society* 142 (1995) 1885–1894.
- 429 [8] M. Schönleber, D. Klotz, E. Ivers-Tiffée, A method for improving the robustness of linear Kramers-
430 Kronig validity tests, *Electrochimica Acta* 131 (2014) 20–27, *electrochemical Impedance Spectroscopy*.
- 431 [9] L. Pauwels, W. Simons, A. Hubin, J. Schoukens, R. Pintelon, Key issues for reproducible impedance
432 measurements and their wellfounded error analysis in a silver electrodeposition system, *Electrochimica*
433 *Acta* 47 (2002) 2135–2141.
- 434 [10] O. Blajiev, T. Breugelmans, R. Pintelon, A. Hubin, Improvement of the impedance measurement reli-
435 ability by some new experimental and data treatment procedures applied to the behavior of copper in
436 neutral chloride solutions containing small heterocycle molecules, *Electrochimica Acta* 51 (8-9) (2006)
437 1403–1412. doi:10.1016/j.electacta.2005.02.113.
- 438 [11] R. Pintelon, J. Schoukens, *System Identification: A Frequency Domain Approach*, John Wiley & Sons,
439 2001.

- 440 [12] P. K. Shukla, M. E. Orazem, O. D. Crisalle, Validation of the measurement model concept for error
441 structure identification, *Electrochimica Acta* 49 (2004) 2881–2889.
- 442 [13] C. You, M. A. Zabara, M. E. Orazem, B. Ulgut, Application of the kramers–kronig relations to multi-sine
443 electrochemical impedance measurements, *Journal of The Electrochemical Society* 167 (2020) 020515.
- 444 [14] M. E. Orazem, P. T. Wojcik, M. Durbha, I. Frateur, L. H. García-Rubio, Application of measurement
445 models for interpretation of impedance spectra for corrosion, *Materials Science Forum* 289-292 (1998)
446 813–828.
- 447 [15] C. Cleveland, S. Moghaddam, M. E. Orazem, Nanometer-scale corrosion of copper in deaer-
448 ated deionized water, *Journal of the Electrochemical Society* 161 (3) (2014) C107–C114.
449 arXiv:<http://jes.ecsdl.org/content/161/3/C107.full.pdf+html>, doi:10.1149/2.030403jes.
450 URL <http://jes.ecsdl.org/content/161/3/C107.abstract>
- 451 [16] M. E. Orazem, P. K. Shukla, M. A. Membrino, Extension of the measurement model approach for
452 deconvolution of underlying distributions for impedance measurements, *Electrochimica Acta* 47 (2002)
453 2027–2034.
- 454 [17] Y.-M. Chen, A. S. Nguyen, M. E. Orazem, B. Tribollet, N. Pébère, M. Musiani, V. Vivier, Identification
455 of resistivity distributions in dielectric layers by measurement model analysis of impedance spectroscopy,
456 *Electrochimica Acta* 219 (2016) 312–320. doi:<https://doi.org/10.1016/j.electacta.2016.09.136>.
- 457 [18] B. Hirschorn, M. E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, Constant-phase-element
458 behavior caused by resistivity distributions in films: 1. Theory, *Journal of the Electrochemical Society*
459 157 (2010) C452–C457.
- 460 [19] B. Hirschorn, M. E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, Constant-phase-element
461 behavior caused by resistivity distributions in films: 2. Applications, *Journal of the Electrochemical*
462 *Society* 157 (2010) C458–C463.
- 463 [20] P. Córdoba-Torres, T. J. Mesquita, O. Devos, B. Tribollet, V. Roche, R. P. Nogueira, On the in-
464 trinsic coupling between constant-phase element parameters α and q in electrochemical impedance
465 spectroscopy, *Electrochimica Acta* 72 (2012) 172–178.
- 466 [21] J.-B. Jorcin, M. E. Orazem, N. Pébère, B. Tribollet, CPE analysis by local electrochemical impedance
467 spectroscopy, *Electrochimica Acta* 51 (2006) 1473–1479.
- 468 [22] G. J. Brug, A. L. G. van den Eeden, M. Sluyters-Rehbach, J. H. Sluyters, The analysis of electrode
469 impedances complicated by the presence of a constant phase element, *Journal of Electroanalytical*
470 *Chemistry* 176 (1984) 275–295.
- 471 [23] M. E. Orazem, B. Tribollet, V. Vivier, S. Marcelin, N. Pébère, A. L. Bunge, E. A. White, D. P.
472 Riemer, I. Frateur, M. Musiani, Dielectric properties of materials showing constant-phase-element (CPE)
473 impedance response, *Journal of the Electrochemical Society* 160 (2013) C215–C225.
- 474 [24] B. Hirschorn, M. E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, Determination of effective
475 capacitance and film thickness from cpe parameters, *Electrochimica Acta* 55 (2010) 6218–6227.
- 476 [25] C. H. Hsu, F. Mansfeld, Technical note: Concerning the conversion of the constant phase element
477 parameter Y_0 into a capacitance, *Corrosion* 57 (2001) 747–748.
- 478 [26] Y.-M. Chen, N. G. Rudawski, E. Lambers, M. E. Orazem, Application of impedance spectroscopy
479 and surface analysis to obtain oxide film thickness, *Journal of the Electrochemical Society* 164 (2017)
480 C563–C573.
- 481 [27] S. Chakri, I. Frateur, M. E. Orazem, E. M. M. Sutter, T. T. M. Tran, B. Tribollet, V. Vivier, Improved
482 EIS analysis of the electrochemical behaviour of carbon steel in alkaline solution, *Electrochimica Acta*
483 246 (2017) 924–930.

- 484 [28] S. Amand, M. Musiani, M. E. Orazem, N. Pébère, B. Tribollet, V. Vivier, Constant-phase-element
485 behavior caused by inhomogeneous water uptake in anti-corrosion coatings, *Electrochimica Acta* 87
486 (2013) 693–700.
- 487 [29] M. Musiani, M. E. Orazem, N. Pébère, B. Tribollet, V. Vivier, Determination of resistivity profiles
488 in anti-corrosion coatings from constant-phase-element parameters, *Progress in Organic Coatings* 77
489 (2014) 2076–2083.
- 490 [30] A. S. Nguyen, M. Musiani, M. E. Orazem, N. Pébère, B. Tribollet, V. Vivier, Impedance analysis of the
491 distributed resistivity of coatings in dry and wet conditions, *Electrochimica Acta* 179 (2015) 452–459.
- 492 [31] A. S. Nguyen, M. Musiani, M. E. Orazem, N. Pébère, B. Tribollet, V. Vivier, Impedance study of the
493 influence of chromates on the properties of waterborne coatings deposited on 2024 aluminium alloy,
494 *Corrosion Science* 109 (2016) 174–181.
- 495 [32] A. S. Nguyen, N. Causse, M. Musiani, M. E. Orazem, N. Pébère, B. Tribollet, V. Vivier, Determination
496 of water uptake in organic coatings deposited on 2024 aluminium alloy: Comparison between impedance
497 measurements and gravimetry, *Progress in Organic Coatings* 112 (2017) 93–100.
- 498 [33] O. Gharbi, A. Dizon, M. E. Orazem, M. T. T. Tran, B. Tribollet, V. Vivier, From frequency dispersion to
499 ohmic impedance: A new insight on the high-frequency impedance analysis of electrochemical systems,
500 *Electrochimica Acta* 320 (2019) 134609. doi:<https://doi.org/10.1016/j.electacta.2019.134609>.
- 501 [34] L. Young, Anodic oxide films 4: The interpretation of impedance measurements on oxide coated elec-
502 trodes on niobium, *Transactions of the Faraday Society* 51 (1955) 1250–1260.
- 503 [35] L. Young, *Anodic Oxide Films*, Academic Press, New York, 1961.
- 504 [36] K. S. Cole, R. H. Cole, Dispersion and absorption in dielectrics 1: Alternating current characteristics,
505 *Journal of Chemical Physics* 9 (4) (1941) 341–351.
- 506 [37] K. S. Cole, R. H. Cole, Dispersion and absorption in dielectrics 2: Direct current characteristics, *Journal*
507 *of Chemical Physics* 10 (2) (1942) 98–105.
- 508 [38] T. Jansch, J. Wallauer, B. Roling, Influence of electrode roughness on double layer for-
509 mation in ionic liquids, *The Journal of Physical Chemistry C* 119 (2015) 4620–4626.
510 arXiv:<http://dx.doi.org/10.1021/jp512617j>.
- 511 [39] M. Benoit, C. Bataillon, B. Gwinner, F. Miserque, M. E. Orazem, C. M. Sánchez-Sánchez, B. Tribol-
512 let, V. Vivier, Comparison of different methods for measuring the passive film thickness on metals,
513 *Electrochimica Acta* 201 (2016) 340–347.
- 514 [40] Y. Sakamoto, M. Ishiguso, G. Kitigawa, *Akaike Information Criterion Statistics*, D. Reidel, Boston,
515 1986.
- 516 [41] M. E. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy*, 2nd Edition, John Wiley & Sons,
517 Hoboken, 2017.
- 518 [42] S. L. Carson, M. E. Orazem, O. D. Crisalle, L. H. García-Rubio, On the error structure of impe-
519 dence measurements: Simulation of frequency response analysis (fra) instrumentation, *Journal of the*
520 *Electrochemical Society* 150 (2003) E477–E490.
- 521 [43] A. N. Jansen, P. T. Wojcik, P. Agarwal, M. E. Orazem, Thermally stimulated deep-level impedance
522 spectroscopy: Application to an n-gaas schottky diode, *Journal of the Electrochemical Society* 143
523 (1996) 4066–4074.
- 524 [44] S. L. Carson, M. E. Orazem, O. D. Crisalle, L. H. García-Rubio, On the error structure of impedance
525 measurements: Simulation of phase sensitive detection (psd) instrumentation, *Journal of the Electro-*
526 *chemical Society* 150 (2003) E491–E500.

- 527 [45] S. K. Roy, M. E. Orazem, Error analysis for the impedance response of pem fuel cells, *Journal of the*
528 *Electrochemical Society* 154 (8) (2007) B883–B891.
- 529 [46] W. Watson, M. E. Orazem, A Python-based measurement model toolbox for impedance spectroscopy,
530 Tech. rep., University of Florida (2020).
- 531 [47] S. Havriliak, S. Negami, A complex plane representation of dielectric and mechanical relaxation processes
532 in some polymers, *Polymer* 8 (1967) 161–210.
- 533 [48] B. A. Boukamp, Derivation of a distribution function of relaxation times for the (fractal) finite length
534 warburg., *Electrochimica Acta* 252 (2017) 154–163.
- 535 [49] H. Göhr, Contributions of single electrode processes to the impedance, *Berichte der Bunsengesellschaft*
536 *für physikalische Chemie* 85 (1981) 274–280.
- 537 [50] H. Göhr, J. Schaller, C. A. Schiller, Impedance studies of the oxide layer on zircaloy after previous
538 oxidation in water vapor at 400°C, *Electrochimica Acta* 38 (14) (1993) 1961–1964.
- 539 [51] A. R. Dizon, M. E. Orazem, On the impedance response of interdigitated electrodes, *Electrochimica*
540 *Acta* 327 (2019) 135000. doi:<https://doi.org/10.1016/j.electacta.2019.135000>.
- 541 [52] J. C. Maxwell, *A Treatise on Electricity and Magnetism*, Vol. 1, Clarendon Press, Oxford, 1873.
- 542 [53] K. N. Allahar, D. P. Butt, M. E. Orazem, H. A. Chin, G. Danko, W. Ogden, R. E. Yungk, Impedance
543 of steels in new and degraded ester-based lubricating oil, *Electrochimica Acta* 51 (2006) 1497–1504.
- 544 [54] V. F. Lvovich, M. F. Smiechowski, AC impedance investigation of conductivity of automotive lubricants
545 using two- and four-electrode electrochemical cells, *Journal of Applied Electrochemistry* 39 (12) (2009)
546 2439.
- 547 [55] V. M.-W. Huang, V. Vivier, M. E. Orazem, N. Pébère, B. Tribollet, The apparent CPE behavior of
548 an ideally polarized blocking electrode: A global and local impedance analysis, *Journal of the Electro-*
549 *chemical Society* 154 (2007) C81–C88.
- 550 [56] J. S. Newman, Frequency dispersion in capacity measurements at a disk electrode, *Journal of the*
551 *Electrochemical Society* 117 (1970) 198–203.
- 552 [57] J. S. Newman, Resistance for flow of current to a disk, *Journal of the Electrochemical Society* 113 (5)
553 (1966) 501–502.
- 554 [58] J. S. Newman, Current distribution on a rotating disk below the limiting current, *Journal of the Elec-*
555 *trochemical Society* 113 (1966) 1235–1241.

556 **List of Figures**

557 1 A schematic representation of a Voigt circuit used by Agarwal et al.^{1,2,4} as a measurement
558 model. 3

559 2 Schematic representation of an electrochemical electrode–electrolyte interface: a) electrode
560 with a uniform current and potential distribution and b) electrode with a nonuniform geometry-
561 induced current and potential distribution. 4

562 3 Regression results for synthetic data obtained using the parameters given in Table 1 at three
563 quarters of the mass-transfer-limited current. The line represents the fit of the measurement
564 model with parameters given in Table 2. 6

565 4 Normalized residual errors for the regression shown in Figure 3 with parameters shown in
566 Table 2: a) real part of the impedance and b) imaginary part of the impedance. Dashed
567 lines represent the 95.4% interval for the assumed stochastic error structure, i.e., $\pm 2\sigma/Z_r$ or
568 $\pm 2\sigma/Z_j$, where $\sigma = 0.002|Z|$ 7

569 5 Complex capacitance obtained from the impedance data shown in Figure 3 with assumed
570 ohmic resistance as a parameter. The maximum frequency shown is 100 kHz. 8

571 6 Complex capacitance obtained from the impedance data shown in Figure 3. The maximum
572 frequency shown is 10 kHz. An asymptotic approach at high frequencies yields a capacitance
573 near $20 \mu\text{F}/\text{cm}^2$. The line is the fit by a modified measurement model given as equation (18)
574 to frequencies between 1 Hz and 10 kHz. 8

575 7 Regression results for synthetic data obtained using the parameters given in Table 1 at three
576 quarters of the mass-transfer-limited current. The data were truncated to minimize the con-
577 tribution of the diffusion impedance. The frequency range was 1–100 kHz, and $\chi^2/\nu = 0.86$.
578 The line represents the fit of the measurement model with parameters given in Table 4. 9

579 8 Young impedance given by equation (21) in Nyquist format with $R_e = 10 \Omega\text{cm}^2$, $\varepsilon = 12$,
580 $\lambda = 2 \text{ nm}$, $\delta = 4 \text{ nm}$, and $\rho_0 = 10^{10} \Omega\text{cm}$. The line represents the measurement model fit
581 with three Voigt elements. The dashed line represents a perfect RC behavior and is presented
582 to highlight the distortion caused by the Young resistivity distribution. The frequency range
583 was 10 mHz to 100 kHz and $\chi^2/\nu = 1.23$ 10

584 9 Impedance given by equations (30) and (19) for the resistivity given by equation (27) with
585 $R_e = 10 \Omega\text{cm}^2$, $\rho_0 = 10^{14} \Omega\text{cm}$, $\rho_\delta = 5 \times 10^6 \Omega\text{cm}$, $\gamma = 6 + 2/3$, $\varepsilon = 12$, and $\delta = 2 \text{ nm}$: a)
586 complete frequency range and b) high frequency range. The line represents the measurement
587 model fit with eleven Voigt elements. The frequency range was 10 mHz to 100 kHz and
588 $\chi^2/\nu = 1.09$ 12

589 10 Capacitance obtained by regression of equation (6) to the complex impedance for truncated
590 frequency ranges as functions of the maximum regression frequency of the regressed data. For
591 example, the values of capacitance and ohmic resistance for a maximum regression frequency
592 of 100 Hz were obtained by regression to data encompassing the frequency range of 10 mHz
593 to 100 Hz. 13

594 11 Simulated impedance response for a disk electrode with parameters $r_0 = 0.1 \text{ cm}$, $\rho = 10^5 \Omega\text{cm}$,
595 $\varepsilon = 78$, $C_{dl} = 20 \mu\text{F}/\text{cm}^2$, and $R_t = 10^4 \Omega\text{cm}^2$. The line represents the fit by the measurement
596 model with four Voigt elements. The frequency range was 1 mHz – 1 MHz, and $\chi^2/\nu = 1.29$ 14

597 12 Truncated impedance taken from Figure 11: a) synthetic data with a frequency range of
598 1 mHz to 100 Hz and b) synthetic data with a frequency range of 1 mHz to 0.79 Hz. The
599 lines represent measurement model fits using, respectively, three or one Voigt element, and
600 the respective values of χ^2/ν were 1.14 and 1.06. 15

601	13	Simulated impedance response for a disk electrode with parameters $r_0 = 0.1$ cm, $\rho = 12.67$ Ω cm, $\varepsilon = 78$, $C_{dl} = 20$ μ F/cm ² , and $R_t = 10^4$ Ω cm ² . Normally distributed stochastic error was added to the impedance with standard deviation equal to 0.2% of the modulus: a) full spectrum and b) scaled impedance in the high-frequency region. The line represents the fit by the measurement model with three Voigt elements and $\chi^2/\nu = 0.94$	16
602			
603			
604			
605			
606	14	Scaled capacitance and scaled ohmic resistance obtained by regression of equation (6) to the complex impedance shown in Figure 13 for truncated frequency ranges as functions of the maximum frequency of the regressed data scaled to the characteristic frequency given by equation (42).	17
607			
608			
609			

610 **List of Tables**

611	1	Parameters employed for the electrochemical reaction influenced by mass transfer in a film presented in Figures 3-7.	5
612			
613	2	Regression results for the synthetic data shown in Figure 3. The characteristic frequency for each element is defined as $f_k = 1/(2\pi\tau_k)$	6
614			
615	3	Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figures 3, 5, and 7. Input parameters are given in Table 1.	6
616			
617			
618	4	Regression results for a truncated spectrum shown in Figure 7. Input parameters for R_e (see R_0) and R_t (see R_1) are given in Table 1.	9
619			
620	5	Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figure 8.	11
621			
622	6	Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figure 9.	12
623			
624	7	Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figures 3, 5, and 7.	15
625			
626	8	Comparison of values extracted from the measurement model regression to the input parameters for the synthetic data presented in Figures 13 and 14.	17
627			