The global and local impedance response of a blocking disk electrode with local constant-phase-element behavior.

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Numerical methods were used to calculate the influence of geometry-induced current and potential distributions on the impedance response of a blocking disk electrode with a local constant-phase element behavior. While the calculated global impedance is purely capacitive, the local impedance has high-frequency inductive loops that were observed in experiments conducted on a stainless steel electrode in 0.05 M NaCl + 0.005 M Na2SO4 electrolyte. The calculated global impedance responses are in good agreement with experimental results obtained using both the steel electrode and a glassy-carbon disk in KCl electrolytes of differing concentrations. The computed local and both local and global ohmic impedances are shown to provide insight into the frequency dispersion associated with the geometry of disk electrodes.

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The term constant-phase element (CPE) is used in impedance spectroscopy to describe the impedance that, for a blocking circuit, follows a form such as,

\[ Z(\omega) = R_0 + \frac{1}{(j\omega)^n Q} \]  

where the parameters \( R_0 \) and \( Q \) are constant with respect to frequency. When \( n = 1 \), \( Q \) has units of a capacitance, i.e., \( \mu \text{F/cm}^2 \), and represents the capacity of the interface. When \( n \neq 1 \), the system shows behavior that has been attributed to surface heterogeneity or to continuously distributed time constants for charge-transfer reactions. Independent of the origin of the behavior, the phase angle associated with a CPE is independent of frequency.

CPE behavior may arise from a variation of properties in the direction that is normal to the electrode surface. Such variability may arise, for example, from changes in the conductivity of oxide layers or from porosity or surface roughness. This CPE behavior is said to arise from a 3D distribution, with the third direction being the normal direction to the plane of the electrode. For a blocking electrode, a 3D distribution should yield a local impedance that shows CPE behavior at low frequencies. As discussed by Huang et al., local impedance measurements can be easily used to distinguish CPE behavior that has an origin with a 3D distribution from one that arises from a 2D distribution of properties along the surface of the electrode.

Using both global and local impedance measurements on a disk made of AZ91 magnesium alloy, Jorcin et al. found CPE behavior that was attributed to a 2D distribution, which yielded locally a pure capacitive response coupled with a radial distribution of local resistance. Jorcin et al. have also found CPE behavior on a pure aluminum disk in which the local impedance response showed a CPE which was modified only slightly by an apparent 2D distribution.

The disk geometry is well-defined and amenable to numerical calculation of the impedance response. Newman developed both numerical and analytic treatments for the impedance response of a faradaic reaction on a nonpolarizable disk electrode. A similar approach was taken by Nisancioglu. Their work is closely related to numerical solutions for the transient response of a disk electrode to current and/or potential transients. None of the work developed to date addresses the coupling of 2D and 3D distributions, and apart from the previous paper in this series, none of the previous works links the global impedance response to the local impedance.

The objective of the present work was to explore the role of current and potential distribution on the global and local impedance response of a blocking electrode exhibiting a local CPE behavior. In this sense, the objective was to explore the role of coupled 2D and 3D distributions on the global impedance response of a disk electrode and to relate this response to the local impedance. This work follows a mathematical treatment of the apparent CPE behavior of an ideally polarized disk electrode. A subsequent paper addresses the influence of current and potential distributions on the global and local impedance response of systems exhibiting faradaic reactions.

** Mathematical Development

The mathematical development follows that presented by Newman. Laplace’s equation in cylindrical coordinates was expressed in rotational elliptic coordinates, i.e.,

\[ y = r_0 \xi \eta \]  

and

\[ r = r_0 \sqrt{(1 + \xi^2)(1 + \eta^2)} \]  

Thus

\[ \frac{\partial}{\partial \xi} \left[ (1 + \xi^2) \frac{\partial \Phi}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[ (1 + \eta^2) \frac{\partial \Phi}{\partial \eta} \right] = 0 \]  

A discussion of the relationship between the transformed coordinates and the original coordinate system is presented elsewhere. The potential \( \Phi \) was separated into steady and time-varying parts as

\[ \Phi = \Phi_0 + \text{Re} \{ \Phi_1 \exp(j\omega t) \} \]  

where \( \Phi_0 \) is the steady-state solution for potential and \( \Phi_1 \) is the complex oscillating potential. Thus, Eq. 4 could be written as

\[ 2\xi \frac{\partial \Phi_0}{\partial \xi} + (1 + \xi^2) \frac{\partial^2 \Phi_0}{\partial \xi^2} - 2\eta \frac{\partial \Phi_0}{\partial \eta} + (1 + \eta^2) \frac{\partial^2 \Phi_0}{\partial \eta^2} = 0 \]  

and
\[2\xi^{2}\frac{\partial^{2}\Phi_{j}}{\partial \xi^{2}} + (1 + \xi^{2})^{2}\frac{\partial^{2}\Phi_{j}}{\partial \eta^{2}} - 2\eta \frac{\partial \Phi_{j}}{\partial \eta} + (1 - \xi^{2})^{2}\frac{\partial^{2}\Phi_{j}}{\partial \eta^{2}} = 0 \quad [7] \]

where \(\Phi_{j}\) and \(\Phi_{i}\) refer to the real and imaginary parts of the complex oscillating potential, respectively.

The flux boundary condition at the electrode surface \(\xi = 0\) was written in frequency-domain as

\[K\left[ (V_{0} - \Phi_{i}) \cos \frac{\alpha \pi}{2} + \Phi_{j} \sin \frac{\alpha \pi}{2} \right] = -\frac{1}{\eta} \frac{\partial \Phi_{j}}{\partial \eta} \quad |\xi = 0\]  

[8]

and

\[K\left[ V_{0} \sin \frac{\alpha \pi}{2} - \Phi_{i} \cos \frac{\alpha \pi}{2} - \Phi_{j} \sin \frac{\alpha \pi}{2} \right] = -\frac{1}{\eta} \frac{\partial \Phi_{i}}{\partial \eta} \quad |\xi = 0\]  

[9]

where \(V_{0}\) represents the imposed perturbation in the electrode potential referenced to an electrode at infinity, and \(K\) is the dimensionless frequency

\[K = \frac{Q\omega^{2}r_{0}}{\kappa} \quad [10] \]

As seen in Eq. 10, the dimensionless frequency \(K\) includes the CPE coefficient \(Q\), the frequency \(\omega\) raised to the power of the CPE exponent \(\alpha\), the disk radius \(r_{0}\), and the electrolyte conductivity \(\kappa\). This equation is consistent with the dimensionless frequency defined in the case of a pure capacitor.

At \(\eta = 0\) and \(\eta = 1\), zero-flux conditions impose that

\[\frac{\partial \Phi_{i}}{\partial \eta} = 0 \quad [11] \]

and

\[\frac{\partial \Phi_{j}}{\partial \eta} = 0 \quad [12] \]

At the far boundary condition \(\xi \rightarrow \infty\)

\[\Phi_{j} = 0 \quad [13] \]

and

\[\Phi_{i} = 0 \quad [14] \]

The equations were solved under the assumption of uniform CPE parameters \(Q\) and \(\alpha\). The simulations were performed using the collocation package PDE2D developed by Sewell.\(^{30}\) Calculations were performed for differing domain sizes, and the results reported here were obtained by extrapolation to an infinite domain size.

The equations were also solved in the cylindrical coordinates using a finite-elements package FEMLAB. The results obtained by the two packages were in excellent agreement for dimensionless frequencies \(K < 100\). As discussed in the previous paper,\(^{22}\) the calculated results are believed to be incorrect for frequencies \(K > 100\) due to the presence of a singular perturbation problem, identified by Newman,\(^{23}\) that arises at the periphery of the electrode at high frequencies.

Results and Discussion

In the previous article in this series, Huang et al.\(^{22}\) presented a notation that addressed the concept of a global impedance, which involved quantities averaged over the electrode surface, a local interfacial impedance, which involved both a local current density and the local potential drop across the diffuse double layer, a local impedance, which involved a local current density and the potential of the electrode referenced to a distant electrode, and a local ohmic impedance, which involved a local current density and potential drop from the outer region of the diffuse double layer to the distant electrode. The local impedance \(z\) can be represented by the sum of local interfacial impedance \(z_{0}\) and local ohmic impedance \(z_{e}\) as

\[z = z_{0} + z_{e} \quad [15] \]

Huang et al.\(^{22}\) demonstrated for an ideally polarized disk electrode that, while the local interfacial impedance represents the behavior of the system unaffected by the current and potential distributions along the surface of the electrode, the local impedance shows significant frequency dispersion. The local and global ohmic impedances were shown to contain the influence of the current and potential distributions.

The calculated results for global, local, local interfacial, and both local and global ohmic impedances are presented in this section. A list of symbols used in the present work is provided in Table I of Huang et al.\(^{22}\)

Global impedance.— The calculated dimensionless impedance response is presented in Fig. 1 with \(\alpha\) as a parameter. The complex-impedance-plane representation given in Fig. 1 applies for all values of electrolyte conductivity \(\kappa\) and disk radius \(r_{0}\), but different values are obtained for different values of \(\alpha\). The impedance was made dimensionless according to \(Z\kappa/k\), where the units of impedance \(Z\) are used to be scaled by area and to have, for example, units of \(\Omega \text{ cm}^{2}\).

The frequency dependence of the impedance response can be seen more clearly in Fig. 2a and b, where the real and imaginary parts of the impedance, respectively, are presented as functions of dimensionless frequency \(K\). The real part of the dimensionless impedance, plotted in Fig. 2a, approaches the expected theoretical value of 1/4 at high frequency.\(^{25}\) The low-frequency behavior depends on the value of \(\alpha\). When plotted against dimensionless frequency \(K\), the values of the dimensionless imaginary impedance in Fig. 2b superpose for all values of \(\alpha\). This superposition is made possible by the inclusion of \(\alpha\) in the definition of frequency \(K\) in Eq. 10.

Orazem et al.\(^{31}\) cite the utility of logarithmic plots of imaginary impedance as a function of frequency for identifying CPE behavior. The calculated slope of \(\log(Z\kappa/k\pi)\) with respect to \(\log(K)\) (Fig. 2b) is presented in Fig. 3. The slope of plots such as Fig. 2b is related to the presence of CPE behavior. Due to the definition of \(K\), the slope at low frequencies of the logarithmic plots of imaginary impedance as a function of \(K\) is equal to \(-1\). At frequencies \(K > 1\), the slope increases to around \(-0.85\). When expressed in terms of these dimensionless parameters, the low-frequency response is independent of \(\alpha\), but the results obtained at higher frequencies depend on \(\alpha\).
The frequency $K = 1$ at which the current distribution influences the impedance response can be expressed as

$$f = \frac{1}{2\pi} \left( \frac{\kappa}{Qr_0} \right)^{\frac{1}{\alpha}}$$ \hspace{1cm} [16]$$

This characteristic frequency can be well within the range of experimental measurements. For conductivities of $0.001$ $\Omega^{-1}$ cm$^{-1}$, CPE coefficient $Q = 10^{-5}$ s/cm$^2$, CPE exponent $\alpha = 0.9$, and disk radius $r_0 = 0.25$ cm, Eq. 16 yields a frequency of 124 Hz. This frequency decreases to 10 Hz if a CPE coefficient of $Q = 10^{-4}$ s/cm$^2$ is used.

The calculation of effective CPE coefficient $Q_{\text{eff}}$ provides further evidence that the low-frequency behavior is unaffected by the current and potential distribution. The effective CPE coefficient $Q_{\text{eff}}$ for electrochemical systems can be obtained from the imaginary part of the impedance as

$$Q_{\text{eff}} = \sin \left( \frac{\alpha \pi}{2} \right) \frac{1}{Z_{\text{j}}(\omega)}$$ \hspace{1cm} [17]$$

The CPE coefficient obtained from Eq. 17 scaled by the input value is presented in Fig. 4 as a function of frequency with $\alpha$ as a parameter. Equation 17 yields the input value for the CPE coefficient at low frequencies, but this calculation is influenced by the current distributions at frequencies $K > 1$. From an experimental perspective, the evaluation of the influence of 3D distributions on impedance response should use data collected at frequencies smaller than $K = 1$. From the numerical examples given above, it appears that the pure 3D distribution can be observed only by performing impedance analysis in the low-frequency range.

Local interfacial impedance.—The calculated local interfacial impedance at $\alpha = 0.8$ is presented in Fig. 5 as a function of dimensionless frequency $K$: (a) real part and (b) imaginary part.

The calculated slope of $\log(Z_K/r_0 \pi)$ with respect to $\log(K)$ (Fig. 2b) as a function of $\log(K)$ with $\alpha$ as a parameter.

The results presented in Fig. 5 and 6 show that the calculated local interfacial impedance is, as would be expected from the boundary
conditions employed, independent of 2D distributions.

Local impedance.—The calculated local impedance response for \( \alpha = 0.8 \) is presented in Fig. 7 with normalized radial position as a parameter. The dimensionless impedance is scaled to the disk area \( \pi r_0^2 \) in order to show the comparison with the asymptotic value of 0.25 for the real part of the dimensionless global impedance. The impedance is largest at the center of the disk and smallest at the periphery, reflecting the greater accessibility of the periphery of the disk electrode. Inductive loops are seen at high frequencies, and these were obtained by both methods of calculation.

The real and imaginary parts of the local impedance are presented in Fig. 8a and b, respectively, with radial position as a parameter. The real and imaginary parts of the local impedance presented in Fig. 8 show a pure CPE behavior at low frequencies and a geometry-induced dispersion at high frequencies. The absolute value of the imaginary part presented in Fig. 8b shows peaks caused by the change of sign associated with the inductive features seen in Fig. 7. The changes in sign occur at frequencies well below \( K = 100 \), showing that the inductive loop cannot be ascribed to a calculation artifact.

Local ohmic impedance.—The local ohmic impedance \( z_e \) accounts for the difference between the local interfacial and the local impedances. The calculated local ohmic impedance for \( \alpha = 0.8 \) is presented in Fig. 9 in Nyquist format with radial position as a parameter. The results obtained here for the local ohmic impedance are very similar to those reported for the ideally polarized electrode. \(^{22} \)

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**Figure 5.** Calculated local interfacial impedance as a function of frequency with position as a parameter: (a) real part and (b) imaginary part. All four curves indicated are superposed.

**Figure 6.** Calculated local interfacial impedance as a function of position with frequency as a parameter: (a) real part and (b) imaginary part. All four curves indicated are superposed.

**Figure 7.** The local impedance in Nyquist format with radial position as a parameter.
At the periphery of the electrode, two time constants (inductive and capacitive loops) are seen, whereas at the electrode center only an inductive loop is evident. These loops are distributed around the asymptotic real value of 1/4.

The influence of $\alpha$ on the local ohmic impedance response is seen in Fig. 10a and b, respectively, for positions at the center and at the periphery of the disk. The inductive feature dominates at the center of the disk, whereas both capacitive and inductive features are evident at the periphery. Both Fig. 9 and 10 show that the magnitude of the local ohmic impedance is about twice as large at the electrode center than it is close to the periphery.

The calculated values for real and imaginary parts of the local ohmic impedance are presented in Fig. 11a and b, respectively, as functions of frequency with radial position as a parameter. The local ohmic impedance has only real values at $K \to 0$ and $K \to \infty$, but in the frequency range $10^{-2} < K < 100$, $z_\alpha$ has both real and imaginary components. A similar behavior for $z_\alpha$ was observed for a pure capacitor. From these results, it is clear that using a single representation of impedance diagrams can lead to misinterpretations.

**Global interfacial and global ohmic impedance.**— The local interfacial impedance is associated with an ideal CPE according to Eq. 1 that is independent of radial position. Thus, the global interfacial impedance is given by

$$Z_0 = \frac{1}{j\omega\alpha}$$.  

The global ohmic impedance $Z_e$ is obtained from the global impedance $Z$ by the expression

$$Z_e = Z - Z_0$$.  

or, in the dimensionless terms used in the present work

$$Z_e \kappa/\rho_0 \pi = \frac{Z \kappa}{\rho_0 \pi} - \frac{1}{j\pi\kappa}$$.

The real part of $Z_e$ is given in Fig. 12a, and the imaginary part of $Z_e$ is given in Fig. 12b as functions of dimensionless frequency $K$ with $\alpha$ as a parameter. In the low frequency range $Z_e \kappa/\rho_0 \pi$ is a pure resistance equal to 0.27, and in the high frequency range, $Z_e \kappa/\rho_0 \pi$ tends towards 1/4. The imaginary part of the global ohmic imped-

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Figure 8. Calculated local impedance as a function of frequency with $\alpha$ as a parameter: (a) real part and (b) absolute value of the imaginary part.

Figure 9. The local ohmic impedance in Nyquist format with radial position as a parameter.

Figure 10. Calculated values for local ohmic impedance in Nyquist format with $\alpha$ as a parameter: (a) at $r/r_0 = 0$ and (b) at $r/r_0 = 0.96$. 

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ance shows a nonzero value in the frequency range that is influenced by the current and potential distributions. Figure 12 shows that all the effects of the current and potential distribution appears in the global ohmic impedance.

Experimental

The predictions made by these calculations can be compared to experimental observations. In the present work, comparison is made to the impedance response for two systems. The influence of electrolyte conductivity on global impedance response was explored for a glassy-carbon-disk electrode in KCl electrolyte. A comparison of local and global impedance measurements was obtained for a stainless steel disk.

Glassy-carbon electrode.—Experiments were conducted on a glassy-carbon-disk electrode to explore the influence of electrolyte conductivity on global impedance response.

Experimental procedure.—Electrochemical measurements were performed with a three-electrode cell; the reference electrode and the counter electrode were a silver/silver chloride electrode (Ag/AgCl) and a large-area platinum grid (10 cm²), respectively. The working electrode consisted of a 5 mm diameter glassy-carbon rod, laterally insulated by a cataphoretic paint and embedded in an epoxy resin to form a 0.2 cm² planar-disk electrode. Before the experiment, the carbon electrode was polished with SiC polishing paper (from grade 1200 to grade 4000) and then thoroughly washed with deionized water.

The electrochemical experiments were carried out with a CH Instrument setup (IJJ Cambria). Impedance diagrams were performed at room temperature (about 20°C) with a potentiostatic regulation in a frequency range varying from 100 kHz to 10 mHz, with a 20 mV peak-to-peak sinusoidal perturbation and recording 12 points per frequency decade. Electrolytic solutions were prepared from analytical-grade chemicals (KCl) purchased from Sigma and used as-received in deionized and bidistilled water.

Experimental results.—Impedance measurements were made at three different concentrations of KCl. The results obtained in 0.5, 0.06, and 0.0065 M KCl are presented in Fig. 13 with concentration as a parameter. Differences among the results are most apparent at high frequencies, as shown in Fig. 13b. The results are consistent with a blocking, but not ideally polarized, electrode. A high-frequency feature is evident in Fig. 13b, and this feature appears at lower frequencies for the smaller values of concentration.

Under the assumption that glassy carbon in KCl solutions can be represented as a blocking electrode with local capacity dispersion, a sequential graphical method was used to extract parameters from the experimental data. The real and imaginary impedance data are presented in Fig. 14 as a function of frequency. As shown in Fig. 14a, the high-frequency value for the real part of the dimensionless impedance is independent of parameters α, r₀, and κ; thus, a value for the solution conductivity can be extracted from the real part of the impedance following

\[ \kappa = \left[ \frac{4 r_0 \lim_{f \to \infty} Z_r}{f} \right]^{-1} \tag{23} \]

The real part of the impedance corresponding to the values obtained from Eq. 23 are presented in Fig. 14a as dashed lines. The resulting values for conductivity are presented in Table I.
At low frequencies, the slope of the imaginary part of the impedance plotted in logarithmic scales as a function of frequency has a value of −1 when dimensionless frequency $K$ is used as defined in Eq. 10. When plotted against frequency, $f$, the low-frequency slope has a value of $-1/9251$. Thus, the data presented in Fig. 14b can be used to obtain values of the CPE exponent $\alpha$ (see Eq. 1). The values of $\alpha$ obtained from Fig. 14b are presented in Table I.

A value for the CPE coefficient $Q$ was obtained from the low-frequency asymptotic behavior where the current and potential distributions associated with the geometry do not influence the impedance response. The resulting values obtained from Eq. 17 are presented in Fig. 15 as a function of frequency for each of the electrolyte concentrations. At lower values of concentration and, therefore, at lower values of conductivity, an asymptotic value for $Q$ can be readily identified at low frequencies. The values extracted are marked by dashed lines in Fig. 15 and reported in Table I.

Following the assumption that glassy carbon in KCl solutions can be represented as a blocking electrode with local time-constant dispersion, the graphical methods described above are sufficient to extract all relevant physical parameters. A note of caution is introduced, however, by the Bode representation presented in Fig. 16. The modulus corrected for electrolyte resistance presented in Fig. 16a shows the expected behavior, but the phase angle given as Fig. 16b does not show a constant value at low frequencies. The low-frequency data shown in Fig. 16b suggests that Eq. 1 provides only an approximate model for the capacity dispersion on a glassy-carbon electrode.

The values of $\alpha$, $\kappa$, and $Q$ presented in Table I were used to calculate, using Eq. 16, the frequency at which $K = 1$. These results are consistent with the results presented in Fig. 13b. The values of $\alpha$, $\kappa$, and $Q$ presented in Table I were also used to calculate dimensionless values for impedance and frequency. The comparison between these results and the curves presented in the preceding section provide a test of the suitability of the theory for explaining the experimental results.

The dimensionless imaginary part of the impedance is presented in Fig. 17a as a function of dimensionless frequency. The superposition of data for the three values of conductivity is in excellent agreement with Fig. 2b, and the change in slope from a value of −1 appears at frequencies higher than $K = 1$.

The derivative of the logarithm of the dimensionless imaginary part of the impedance with respect to the logarithm of dimensionless frequency is presented in Fig. 17b. The dispersion of the data apparent in Fig. 17b can be attributed to the fact that the derivative cal-

<table>
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<th>Concentration (M)</th>
<th>$\alpha$ (M$^{-1}$ cm$^2$ s$^{-1}$)</th>
<th>$\kappa$ (cm$^{-1}$)</th>
<th>$f$ (Hz at $K = 1$)</th>
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<td>22.5</td>
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<td>0.0065</td>
<td>0.861</td>
<td>9.2</td>
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</table>

Table I. Parameter values for experimental results extracted from Fig. 14a, 14b, and 15. The frequency at which $K = 1$ was obtained from Eq. 16.
Calculations were performed on experimental data (12 points per decade). The superposition of data for the three values of conductivity is in excellent agreement with Fig. 3 with $\alpha = 0.9$, and the transitional frequency between low and high-frequency response is in good agreement with the theoretical value of $K = 1$.

Stainless steel disk.— Stainless steel electrodes covered by a passive layer exhibit a small dissolution current, but this anodic current is approximately independent of potential. The impedance at zero frequency tends toward infinity, and the local and global impedance at high frequency exhibit CPE behavior unaffected by the dissolution current. Thus, the steel electrode under passivating conditions provides a suitable system for examining the predictions made by the model.

**Experimental procedure.**— The Fe–17Cr (wt %) stainless steel electrode was a disk of 4.5 mm diameter. Before the experiment, the electrode surface was mechanically polished with diamond paste down to 1 μm. The bielectrode consisted of two platinum wires (40 μm in diameter). A deposit of Pt black from hydrogen hexachloroplatinate(IV) was performed daily on each microdisk. The distance between the bielectrode and the steel disk was estimated to be about 100 μm. The experiment was performed with a classical three-electrode cell at room temperature. The counter electrode was a large platinum grid, and the potentials were measured with respect to a saturated sulfate electrode (SSE). The electrolyte was aerated, pH 4, 0.05 M NaCl + 0.005 M Na₂SO₄ (total ionic concentration of 0.055 M).

The experimental setup consisted of a homemade potentiostat coupled with a Solartron 1254 four-channel frequency response analyzer, allowing both global and local impedances to be recorded simultaneously. A homemade analog differential amplifier (gain 10) was used to record the local current and potential variations. The
The hypothesis that the steel system exhibits CPE behavior in the experimental frequency range is confirmed for both the global and local impedance in Fig. 18b. The plot of \( \log |Z| \) as a function of \( \log(f) \) exhibits a straight line at low frequencies, yielding, for the global impedance, a CPE exponent \( \alpha = 0.86 \). At higher frequencies, the impedance deviates from the ideal CPE behavior. The methods described in the previous section were employed to calculate a characteristic frequency of 130 Hz for inception of geometry-induced distortions to the impedance. This value is in good agreement with the impedance response presented in Fig. 18b.

The local impedance shows CPE behavior at low frequencies and a change in sign for the imaginary part of the impedance at high frequencies. This appearance of high-frequency inductive loops is consistent with the calculated local impedance presented in Fig. 8b. The appearance of inductive loops in the local impedance is influenced by the distance between the probe and the disk electrode. The influence of the finite gap between the impedance probe and the electrode surface on the striking inductive features of local impedance measurements will be reported separately.

The agreement between the model presented here and the experimental results obtained for the steel electrode illustrates the utility of the model for describing features of systems that exhibit CPE behavior even over a limited range of frequency.

Conclusions

Geometry-induced current and potential distributions modify the global impedance response of a blocking electrode subject to both 2D and 3D distributions. The characteristic transition frequency at which the geometry plays a role is well within experimental range. The predicted behavior of the blocking disk electrode was in good agreement with global impedance measurements made with a glassy-carbon disk in an inert electrolyte and with a stainless steel disk.

While the calculated global impedance is purely capacitive, the local impedance has high-frequency inductive loops. These inductive features were observed in experiments conducted on a stainless steel electrode. The calculated local and ohmic impedances are shown to provide insight into the frequency dispersion associated with the geometry of disk electrodes.

The calculations show that local impedance provides a means for understanding the role of 2D current and potential distributions on impedance response. While the calculated local interfacial impedance showed idealized CPE behavior, the local impedance showed inductive behavior at high frequency and idealized CPE behavior at low frequency. The local impedance is influenced by the local ohmic impedance, which has complex behavior near dimensionless frequency \( K = 1 \). The imaginary part of both the local and global ohmic impedance is equal to zero at both high and low frequencies where the ohmic impedances have purely resistive character.

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