Impedance of a Disk Electrode with Reactions Involving an Adsorbed Intermediate: Experimental and Simulation Analysis

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A comparison of experimental results with numerical simulations is presented that shows the influence of electrode geometry on the impedance response for reactions involving one adsorbed intermediate. The local electrochemical impedance measurements performed on an iron disk electrode were in qualitative agreement with the numerical calculations. Both the experimental and calculated local impedances exhibit a time-constant dispersion induced by the nonuniform current and potential distributions on a disk electrode. The geometry effects were reflected in the complex local ohmic impedance behavior at low frequencies as well as at high frequencies. It was shown that the low frequency imaginary contribution to the ohmic impedance became more significant at a more anodic potential.

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The current and potential distributions in the electrolyte adjacent to a disk electrode embedded in an insulating plane are constrained by the electrode geometry. Newman showed that the ohmic potential drop in solution causes a nonuniform current distribution at the electrode surface.1 He also calculated the secondary current distribution, which accounts for the additional influence of the charge-transfer resistance.2 Nisancioğlu and Newman3 investigated the transient response of a disk electrode with a single faradaic reaction subject to a step change in applied current. The model did not account for mass-transfer effects, and the analytical solution to the Laplace’s equation was obtained using a transformation to rotational elliptic coordinates with a series expansion in terms of Legendre polynomials.

Geometry-induced current and potential distributions cause a frequency dispersion that distorts the impedance response and reflects a CPE behavior. The frequency or time-constant dispersion was originally attributed to the dispersion of double-layer capacitance or the dependence of capacitance on frequency. It is now generally attributed to the nonuniform current and potential distributions associated with factors such as electrode morphology,4 heterogeneity,5 or composition variation in oxide layers,6 and is generally expressed in terms of a constant-phase element (CPE) in equivalent circuits.7 The frequency dispersion resulting from electrode geometry is apparent in systems where the ohmic resistance dominates, leading to a CPE behavior.

The nonuniform current and potential distributions could lead to an error in the estimation of both the charge-transfer resistance and the interfacial capacitance.8 Huang and co-workers9,10,11 presented a series of papers describing the influence of electrode geometry on the impedance response. They defined three local impedances in addition to the global impedance obtained from the usual impedance measurements. Simulations showed that the local impedance and the local ohmic impedance exhibited time-constant dispersion associated with the disk geometry, and the calculated global impedance had quasi-CPE behavior at high frequencies for blocking electrode resistance.12 electrodes subject to a single faradaic reaction.13 The geometry effect was reflected in the local ohmic impedance in which nonzero imaginary components were observed. These effects can be eliminated by recording the impedance data below the characteristic frequency. Predictions made by Huang et al.10,11 were in agreement with the observations of Frateur et al.13 for the local electrochemical impedance spectroscopy (EIS) measurements on a stainless steel electrode. Jorcin et al.14 also observed a CPE behavior on a disk electrode made of magnesium alloy that may be associated with a radial distribution of local resistance.

Wu et al.15 investigated the geometry-induced current and potential distributions in a faradaic system involving an adsorbed intermediate. The dispersion of impedance response was predicted to be observed not only at high frequencies, but also at low frequencies in which the characteristic frequency for the adsorption reaction was involved. The objective of the present work was to provide an experimental verification of the theoretical results described by Wu et al.15 using the iron dissolution as an example.

Mathematical Development

The approach presented here to account for low frequency impedance loops associated with adsorbed reaction intermediates was pioneered by Epelboin et al.16 The first section demonstrates that such low frequency loops cannot be observed for reactions represented by linear kinetic expressions. The subsequent section provides a model development for the corrosion of iron that shows low frequency loops associated with an adsorbed reaction intermediate.

Linear kinetics near the equilibrium potential.—The general reactions for two successive charge-transfer steps with an adsorbed intermediate can be described by

\[ M \rightleftharpoons X_{ads} + e^- \]  
and \[ X_{ads}^+ = P_{ads} + e^- \]

Reactions near the equilibrium potential can be expressed as linear functions of the surface overpotential. Thus, the current density at the electrode surface for Reactions 1 and 2 can be expressed by

\[ i_M = K_M(1 - \gamma)(b_M + b_M)(V - \Phi_0) \]
and \[ i_X = K_X(\Phi_X + b_X)(V - \Phi_0) \]

where \( K_M \) and \( K_X \) are the effective rate constants, \( \gamma \) is the surface coverage by the adsorbed intermediate \( X_{ads}^+ \), \( V \) is the potential of the electrode, \( \Phi_0 \) is the potential in the solution adjacent to the electrode, and \( b_M \) and \( b_X \) are the Tafel slopes for Reactions 1 and 2, where the subscripts a and c, respectively, represent the anodic and cathodic half reactions. The summation of the current density of each reaction yields the faradaic current density as

\[ i_f = i_M + i_X \]

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The variation of the surface coverage is related to the reaction rates as
\[
\frac{d\bar{y}}{dt} = \frac{b_\text{M} - \bar{y}}{\bar{\nu}F}
\]
where \(\Gamma\) is the maximum surface concentration of the intermediate and \(F\) is the Faraday constant. At steady state, the reaction rates reach constant values, and the surface coverage does not change with time, i.e., \(d\bar{y}/dt = 0\). The steady-state value of \(\bar{y}\) can therefore be calculated from Eq. 3 and 4 as
\[
\bar{y} = \frac{K_M(b_\text{M} + b_\text{M}^\ast)}{K_M(b_\text{M} + b_\text{M}^\ast) + K_X(b_\text{X} + b_\text{X}^\ast)}
\]
Equation 7 indicates that, in the linear regime, the steady-state surface coverage is a function of kinetic parameters only and is not dependent on the surface overpotential. The current density for each reaction, however, is a function of surface overpotential, and therefore the faradaic impedance of the system is the charge-transfer resistance given by
\[
R_t = \frac{\partial\bar{V}}{\partial\bar{y}} = \frac{1}{K_M(1 - \bar{y})(b_\text{M} + b_\text{M}^\ast) + K_X\bar{y}(b_\text{X} + b_\text{X}^\ast)}
\]
As the faradaic impedance is in parallel with the double-layer capacitance, the impedance diagram shows a single capacitive loop in the Nyquist plane.

**Dissolution of iron in sulfuric acid solutions.**—As most of the electrochemical systems do not follow the simple case of linear kinetics, the reaction model presented here is assumed to be in the Tafel regime. The system of interest is the corrosion of a pure iron electrode in 0.5 M sulfuric acid. Bockris and co-workers proposed a reaction model in which two consecutive steps are coupled by an adsorbed intermediate. The anodic dissolution of iron can be described in simplified form as

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + e^-
\]
and

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + e^-
\]
The iron ion oxidizes and forms a monovalent intermediate adsorbed on the electrode surface. This reaction is followed by the oxidation of the intermediate. The ferrous ion is soluble and diffuses away from the electrode. For this work, the system was at a potential such that the system remained in the active dissolution domain.

Under the assumption of Tafel kinetics, the reaction rates for Reactions 9 and 10 can be expressed by
\[
i_1 = K_1(1 - \gamma)\exp[b_1(V - \Phi_0)]
\]
and
\[
i_2 = K_2\gamma\exp[b_2(V - \Phi_0)]
\]
where \(K_1\) and \(K_2\) are the effective rate constants, and \(b_1\) and \(b_2\) are the Tafel slopes for each reaction.

The variation of surface coverage is associated with the two anodic reactions by
\[
\frac{d\bar{y}}{dt} = \frac{i_1 - i_2}{\bar{\nu}F}
\]
When the steady state is achieved, the surface coverage at steady state can be calculated from Eq. 11 and 12 as
\[
\bar{y} = \frac{K_1\exp[b_1(V - \Phi_0)]}{K_1\exp[b_1(V - \Phi_0)] + K_2\exp[b_2(V - \Phi_0)]}
\]
In contrast to the case presented in Eq. 7 for linear kinetics, Eq. 14 shows that the steady-state surface coverage is dependent on the surface overpotential under the assumption of Tafel kinetics.

The impedance is obtained when the system is disturbed by a small perturbation with frequency \(\omega = 2\pi f\). Following the method developed by Epelboin et al., the faradaic impedance \(Z_t\) associated with the coupled reactions can be expressed as
\[
\frac{1}{Z_t} = \frac{1}{R_t} + \frac{A}{j\omega + B}
\]
where \(R_t\) is the charge-transfer resistance, and parameters \(A\) and \(B\) are potential-dependent variables. As the faradaic impedance is in parallel with a double-layer capacitance at the electrode surface, the first term in Eq. 15 gives rise to the high frequency loop in the impedance diagram, and the second term is associated with the low frequency loop, which is related to the formation of an intermediate adsorbed on the electrode surface. Equation 15 provides a general framework for investigation of the appearance of inductive and capacitive low frequency loops for systems with adsorbed intermediates. When the sign of parameter \(A\) is positive, the impedance plot shows a high frequency capacitive loop with a low frequency inductive loop. When \(A\) is negative, it shows high frequency capacitive loop with a low frequency capacitive loop. When \(A\) is equal to zero, the faradaic impedance is equal to the charge-transfer resistance and therefore it shows a single capacitive loop without a low frequency loop in the impedance diagram.

The faradaic impedance associated with the Tafel kinetics can also be expressed by Eq. 15 with the charge-transfer resistance
\[
R_t = \frac{1}{K_1(1 - \bar{y})b_1\exp[b_1(V - \Phi_0)] + K_2\gamma b_2\exp[b_2(V - \Phi_0)]}
\]
and the parameters \(A\) and \(B\) are given by
\[
A = \bar{\nu}F\frac{\partial}{\partial\bar{y}}\left(\frac{d\bar{y}}{dt}\right) = \left[K_2\gamma b_2\exp[b_2(V - \Phi_0)]
\right.

\]
and
\[
B = -\bar{\nu}F\left(\frac{d\bar{y}}{dt}\right) = \frac{K_1\exp[b_1(V - \Phi_0)] + K_2\exp[b_2(V - \Phi_0)]}{\bar{\nu}F}
\]
respectively. According to the values of the kinetic parameters, \(A\) can be positive or negative, but \(B\) is always positive. Substitution of Eq. 14 into Eq. 11 and 12 yields the steady-state polarization curve expressed as
\[
\bar{\eta} = \frac{2K_1\exp[b_1(V - \Phi_0)]K_2\exp[b_2(V - \Phi_0)]}{K_1\exp[b_1(V - \Phi_0)] + K_2\exp[b_2(V - \Phi_0)]}
\]
The faradaic impedance was then calculated from Eq. 15.

In the case of linear kinetics in the previous section, it is easy to verify that \(A = 0\), and the faradaic impedance is only a charge-transfer resistance which is in agreement with Eq. 15.

In a previous study, Wu et al. discussed the dispersion of local impedances for electrochemical reactions involving one adsorbed intermediate. While the global impedance at a given potentiostatic condition may have a specific low frequency feature, e.g., capacitive or inductive, the local impedances show a variation of low frequency features along the electrode surface, which results from the distribution of the potential and corresponds to different values of the local parameters \(A\) and \(B\). The global impedance could be considered to provide an average representation of the electrode surface, and the low frequency feature is determined by the surface average values of \(A\) and \(B\). As the polarization condition changes along
the current-voltage I-V curve, the low frequency loop in the global impedance diagram could change from inductive to capacitive, and vice versa.

Experimental Setup

The disk electrode used in the experiment was a 0.5 cm diameter pure iron electrode embedded in an insulating epoxy resin. The electrolyte solution was a 0.5 M H2SO4 solution prepared with distilled water.

The experimental measurements of LEIS were performed with a bielelectrode that was comprised of two platinum wires sealed in a borosilicate capillary. The configuration and preparation of the bielelectrode were described in earlier papers. The use of a four-bielelectrode that was comprised of two platinum wires sealed in a water-resistance manner. Frateur et al.13 in an experimental perspective. The same notation was confirmed by measuring the impedance using different amplifiers.19,20 The linear response will be used throughout this paper.

Experimental Results

The current–potential curve obtained on a stationary iron electrode in 0.5 M sulfuric acid solution is presented in Fig. 1a. The scan rate was 2 mV/s. The potential was applied to the iron electrode from the open-circuit potential, activating the iron electrode, to a higher potential, passivating the electrode surface. Potentials I and II in Fig. 1b represent the two steady-state conditions for which the impedance measurements were performed. The global impedance responses given in Fig. 2a and b show low frequency loops which are associated with the formation of Fe(II) species adsorbed on the electrode surface, and correspond to different values of surface-average value (A). To facilitate the comparison of results, all frequencies were made dimensionless according to

\[ K = \frac{\omega C_0 R_0}{\kappa} = 4\omega C_0^2 R_e \]

where \( r_0 \) is the electrode radius, \( C_0 \) is the double-layer capacitance, which was assumed to be uniform, \( \kappa \) is the electrolyte conductivity, and \( R_e \) is the electrolyte resistance. The parameters \( C_0 \) and \( R_e \) were determined from the global impedance measurements. The electrolyte resistance \( R_e \) was evaluated from the limiting value of the real part of the impedance in the high frequency range, whereas \( C_0 \) can be easily determined from the characteristic frequency of the first RC time constant, which represents the high frequency capacitive loop corresponding to \( R_e \) in parallel with \( C_0 \). When the potential increases, the feature of the impedance diagram at low frequencies changes from an inductive to a capacitive behavior, implying that \( K \) changes sign.

The experimental local impedance diagrams obtained with a bielelectrode located at different positions on the disk electrode are depicted in Fig. 3. When measurements were performed at the polarization point I, the variations of the local impedance show different reactivity as a function of the probe location over the iron electrode. Such a behavior is attributed to the geometry-induced current and potential distributions.10,13 In Fig. 3a, the low frequency induc-

![Figure 1. The polarization curve for a stationary iron electrode in 0.5 M H2SO4: (a) a scan including both the active and passivated regions and (b) a zoomed portion of the box in (a) showing the potential at which the impedance measurements were performed.](image1)

![Figure 2. Global electrochemical response for a pure iron electrode in 0.5 M H2SO4: (a) global impedance response measured at potential I as indicated in Fig. 1b and (b) global impedance response measured at potential II.](image2)
The local impedance at the center of the disk is presented. The measurement is difficult to perform at a more anodic potential (i.e., at potential II or for larger potentials) because of an increase in the reaction rate leading to an increase in the rate of iron dissolution, especially at electrode edges. There may also be some accumulation of corrosion product species. At low frequencies, the local electrochemical impedance shows an inductive feature which is different from the capacitive behavior shown in the global impedance plot in Fig. 2b, representing a locally positive value of $A$ at the electrode center.

The contribution of the local ohmic impedance can be calculated from the difference of the local and local-interfacial impedance measurements. For the steady-state condition I, the local ohmic impedance is presented in Fig. 4a with the radial position of the probe as parameter. As already observed for blocking electrodes or for simple electron-transfer reactions, this contribution acts as an imped-
Simulations Results

The mathematical development for the calculation of the impedance was described by Wu et al.15 At the electrode surface, the potential perturbation was coupled by the current associated with both the charging of the electrical double layer and the faradaic reactions. The potential in the bulk solution satisfies Laplace’s equation and was solved in cylindrical coordinates.

The experimental polarization curve was first fitted by Eq. 19, allowing the determination of the kinetic parameters $K_1$, $K_2$, $b_1$, and $b_2$. The LEIS results were strongly dependent on these parameters. Then, the kinetic variables were varied to obtain simulations in agreement with both the polarization curve and the global impedances at the two steady-state conditions. The values of kinetic variables and other parameters used in the simulations are given in Table I. The sole purpose of the comparison of experiment and simulations is to verify the prediction made by Wu et al.15 that the ohmic impedance for systems involving adsorbed intermediates may have a complex character at both low and high frequencies. As will be described in the Discussion section, this work was not intended to determine the kinetic constants for the reaction system. Thus, calculated results presented in this section can be used to show a qualitative comparison with the experimental data. The experimental curves can potentially be fitted by other sets of kinetic parameters. The parameters presented in Table I are in agreement with those presented by Epelboin and Keddam.16 The values of $\alpha_1$ and $\alpha_2$ obtained from the values of $b_1$ and $b_2$, respectively, differ from 0.5, consistent with nonelementary step reactions.21

The simulation results for the global impedances corresponding to potentials I and II in the experimental polarization curve are presented in Fig. 7a and b, respectively, and should be compared to experimental electrochemical impedance spectroscopy diagrams presented in Fig. 2a and b. The impedance values for the simulation curves are in agreement with the experimental results, with the exception that the characteristic frequency has a smaller value for steady-state condition II. This can be attributed to the uncertainties in the estimation of the kinetic parameters. The calculated global impedance has a low frequency inductive loop at potential I, corresponding to a positive value of ($\alpha$). The low frequency feature at

Table I. Parameters used in the simulations of iron dissolution in sulfuric acid solution.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Value</th>
<th>Units</th>
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<td>$b_1$</td>
<td>$\alpha_1 F/RT$</td>
<td>38.2</td>
<td>V$^{-1}$</td>
</tr>
<tr>
<td>$b_2$</td>
<td>$\alpha_2 F/RT$</td>
<td>8.05</td>
<td>V$^{-1}$</td>
</tr>
<tr>
<td>$K_1$</td>
<td>Effective rate constant for Reaction 9</td>
<td>$3 \times 10^{11}$</td>
<td>A cm$^{-2}$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>Effective rate constant for Reaction 10</td>
<td>30</td>
<td>A cm$^{-2}$</td>
</tr>
<tr>
<td>$C_b$</td>
<td>Double-layer capacitance</td>
<td>55</td>
<td>µF cm$^{-2}$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Electrolyte conductivity</td>
<td>0.2</td>
<td>S cm$^{-1}$</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Maximum surface coverage by intermediate</td>
<td>$1 \times 10^{-3}$</td>
<td>mole cm$^{-2}$</td>
</tr>
</tbody>
</table>

Figure 5. The imaginary part of the local ohmic impedance as a function of the dimensionless frequency for a pure iron electrode in 0.5 M H$_2$SO$_4$, measured at potential I in Fig. 1b.

Figure 6. Local ohmic impedance for a pure iron electrode in 0.5 M H$_2$SO$_4$ at potential II in Fig. 1b. (a) Nyquist plot for the local ohmic impedances at the center of the electrode. (b) Imaginary part of the local ohmic impedance as a function of dimensionless frequency.
potential II is not very obvious, but a slight capacitive behavior can still be observed in the enlarged region at the low frequency limit, corresponding to a small negative value of $\Delta$.

The calculated local impedance values are shown in Fig. 8 for two different steady-state conditions. In Fig. 8a, the local impedance calculated at potential I shows little differences between electrode center and electrode edge, in contrast to the experimental results in Fig. 3a, especially the inductive loops at low frequencies. The reason for the larger differences in the experimental data could result from the dissolution of iron electrode during the impedance measurements at low frequencies. The iron electrode is recessed more at the edge of the electrode, and, therefore, the impedance data were measured at different heights. The discrepancy of the local impedance among different positions is larger at a higher potentiostatic condition, which is also in good agreement with the above explanation. At potential II, the calculated local impedance at the center of the electrode has a slight inductive loop at low frequencies as shown in the enlarged region, which is in agreement with the experimental result in Fig. 3b. It corresponds to a local positive value of $\Delta$ at the electrode center. The calculated impedance at the electrode edge has a capacitive feature, which corresponds to a local negative value of $\Delta$. Such a behavior is in accordance with the previous work of Wu et al.\textsuperscript{15} that predicted a local variation of $\Delta$ with the electrode radius.

The calculated local ohmic impedances for steady-state condition I are presented in Fig. 9. As compared to Fig. 4, the local ohmic impedances at the center and at the edge of the electrode have similar behaviors. Complex features are evident at low frequencies in both experimental [Fig. 4b and c] and simulation results [Fig. 9b and c]. However, from the dependence of the imaginary part of the local ohmic impedance on the frequency shown in Fig. 10, the complex values at low frequencies are very small as compared to that at high frequencies and are therefore barely evident.

The variation of the imaginary part of the local ohmic impedance with a frequency at potential II is given in Fig. 11. For dimensionless frequencies $10^{-5} < K < 10^{-2}$, small values of the imaginary part are observed. This result demonstrates that the distributions of current and potential are evident at lower frequencies, in which the local ohmic impedances exhibit complex behaviors as the applied potential is increased. For a better qualitative analysis, the experimental results measured at higher potential (potential II) are compared with the calculation by Wu et al.\textsuperscript{15} for the case of $\Delta = 0$. The calculated local ohmic impedance at the electrode center in Fig. 12a is presented in dimensionless format and has similar behavior as compared to that in Fig. 6a. In Fig. 12b, the nonzero values for the imaginary component of the local ohmic impedance at low frequencies are more significant and can no longer be neglected.

**Discussion**

There were two reasons that only a qualitative comparison could be made between experimental and calculated results. The calculated impedance response corresponds to values at the electrode surface, whereas the experimental measurements necessarily are made a small distance above the electrode surface. In addition, the rapid dissolution of the iron electrode caused the distance between the probe and the electrode to change with time. During the course of a cyclic voltammetry measurement, for example, the electrode receded by 2 mm. Impedance measurements at frequencies lower than 0.1 Hz, i.e., $K < 4 \times 10^{-5}$, could not be made because the time

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**Figure 7.** The calculated global impedance corresponding to (a) polarization point I and (b) point II in Fig. 1b. These results are to be compared to the experimental results presented in Fig. 2a and b.

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**Figure 8.** The calculated local impedance corresponding to (a) polarization point I and (b) point II in Fig. 1b. These results are to be compared to the experimental results presented in Fig. 3.
required led to significant electrode recession. In the simulation, the electrode surface is assumed to be smooth, with a position that is independent of time and with an active area unaffected by the deposition of corrosion products. Therefore the simulation cannot give a quantitative comparison to the measured results.

Nevertheless, the qualitative comparison between the experimental and the calculated impedance response provides significant support for the simulation results. The experimental local ohmic impedance exhibits complex values at low frequencies. These complex behaviors are more evident at a higher potential, in agreement with the theoretical calculations. Moreover, the radial dependence of the low frequency response demonstrates that the geometry-induced current and potential distributions influence the impedance response at low frequencies when adsorbed intermediates are involved in the reactions. The calculations are in better agreement with the experimental results at steady-state condition I. At steady-state condition II, the applied potential is more anodic, and the configuration of the iron electrode changed during the course of the experiment. However, these results show a distribution of local impedance caused by the nonuniform distributions of current and potential in agreement with the prediction of the previous study.

Conclusions

The corrosion of iron is considered in this study to comprise two successive charge-transfer steps involving one adsorbed intermediate. The local impedance measured by use of the LEIS technique shows frequency dispersion induced by the disk geometry. The geometry effects are reflected in the local ohmic impedance as having
complex behaviors at both high and low frequencies. The low frequency effect was more significant at the more anodic potential. Using small bielectrode for performing local impedance measurements, it was possible to observe the radial dependence of the iron electrode reactivity.

The comparison between model and experiment was constrained to be qualitative only due to changes of the electrode surface during the course of the experiment. Nevertheless, the qualitative agreement confirms the predicted influences of electrode geometry on the low frequency impedance response for reaction systems involving adsorbed intermediates.

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