Application of a submerged impinging jet for corrosion studies: development of models for the impedance response

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Abstract

A model was established for the impedance response associated with convective diffusion to a disk electrode subjected to a submerged impinging jet. The model accounted for a finite Schmidt number by employing a series expansion in terms of $Sc^{-1/3}$. The model was incorporated into a quantitative analysis of impedance data for the corrosion of a steel disk in brine saturated with CO$_2$. This work showed that the impedance response was influenced by diffusion through a stagnant layer as well as through a convective region. The Schmidt number obtained was very large, suggesting that the thick layer, observed by in situ video microscopy, is a colloidal gel. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: CO$_2$ corrosion; Steel; Impinging jet; Impedance spectroscopy; Colloidal gel

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>hydrodynamic constant for the impinging jet, $s^{-1}$</td>
</tr>
<tr>
<td>$c_i$</td>
<td>concentration of species $i$, mol/cm$^3$</td>
</tr>
<tr>
<td>$c_{i,0}$</td>
<td>concentration of species $i$ on the electrode surface, mol/cm$^3$</td>
</tr>
<tr>
<td>$c_{i,c}$</td>
<td>bulk concentration of species $i$, mol/cm$^3$</td>
</tr>
<tr>
<td>$c_d$</td>
<td>double layer capacitance, F/cm$^2$</td>
</tr>
<tr>
<td>$D_i$</td>
<td>diffusion coefficient of species $i$, cm$^2$/s</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant, 96 487 C/equiv</td>
</tr>
<tr>
<td>$i_f$</td>
<td>Faradic current density, A/cm$^2$</td>
</tr>
<tr>
<td>$i_0$</td>
<td>exchange current density, A/cm$^2$</td>
</tr>
<tr>
<td>$j$</td>
<td>imaginary number, $\sqrt{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate constant (e.g. see Eqs. (13), (16)–(18), and (22))</td>
</tr>
<tr>
<td>$K_i$</td>
<td>dimensionless frequency (see Eq. (6))</td>
</tr>
<tr>
<td>$n$</td>
<td>number of electrons transferred for a given electrochemical reaction</td>
</tr>
</tbody>
</table>

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universal gas constant, $R = 8.3143 \text{ J/mol/K}$

electrolyte resistance, $R_e \Omega \text{ cm}^2$

effective lumped kinetic resistance, Eq. (40), $R_{eff} \Omega \text{ cm}^2$

kinetic resistance for oxygen reduction, Eq. (28), $R_{t,O_2} \Omega \text{ cm}^2$

radial coordinate, cm

radius of disk, cm

Schmidt number, $Sc = \mu / \rho D_o$, dimensionless

temperature, K

time, s

potential of the metal referenced to the potential of the solution, V

radial velocity component, cm/s

axial velocity component, cm/s

impedance, $Z \Omega \text{ cm}^2$

Warburg impedance for the reduction of oxygen, Eq. (27), $Z_{D,O_2} \Omega \text{ cm}^2$

$k$-th term for the expansion of the Warburg impedance, Eq. (12), $Z_k \Omega \text{ cm}^2$

axial distance from disk, cm

apparent transfer coefficient

characteristic length for mass transfer (see Eq. (7))

dimensionless axial position scaled to the characteristic length for fluid flow

dimensionless position variable $\eta = z \sqrt{a/v}$

dimensionless concentration variable $\tilde{\eta}_i = \tilde{c}_i / \tilde{c}_{i,0}$

dimensionless concentration variable following the series expansion Eq. (8)

viscosity, g cm/s

kinematic viscosity, cm$^2$/s

dimensionless axial position scaled to the characteristic length for mass transfer

density, g/cm$^3$

shear stress, N/cm$^2$ (see Eq. (4))

parameter defined in Eq. (1) and given as an expansion in $\eta$ in Eq. (3) for regions close to the disk surface

frequency of perturbation, s$^{-1}$

rotation speed, s$^{-1}$

superscript denoting oscillating variable

superscript denoting steady-state variable

1. Introduction

Interpretation of impedance data for electrochemical systems that are influenced by flow requires both experimental systems that can be easily modeled and models that account correctly for reaction kinetics and convective diffusion. The submerged impinging jet can be designed to provide uniform mass transfer to a disk electrode and, being stationary, is well suited for visual observation. The purpose of the present work is to provide a framework for interpretation of impedance data taken with a submerged impinging jet. The example system studied is corrosion of steel in brine containing dissolved CO$_2$.

The corrosion of steel in brines containing dissolved CO$_2$ gas is a topic of considerable interest with practical applications and substantial economic impact in the oil and gas industry. Examples include flow-enhanced corrosion in oil/gas production piping networks, tube heat exchangers, and condensers. Metals subjected to large fluid velocities can corrode at very large rates. Steel pipelines containing high-temperature brine with high CO$_2$ content and in the absence of oxygen are also subject to enhanced corrosion [1]. This phenomenon is...
sometimes attributed to erosion–corrosion associated with localized breakdown or removal of protective layers [2,3].

There exists a considerable body of literature on corrosion in CO₂ environments. Newton and Hausler [4] provide a compendium of early work, including a discussion on the dissociation of CO₂ [5] and early mechanistic studies [6–8]. Linter and Burstein provide a summary of proposed mechanisms for CO₂-influenced corrosion in oxygen-free environments [9]. Several authors have proposed that the cathodic reaction controls the rate of corrosion in CO₂ solutions at temperatures below 60 °C, where the corrosion rate increases with the partial pressure of the gas [10,11]. This is consistent with the observation by many researchers that the cathodic evolution of hydrogen is accelerated by dissolved CO₂. Others suggest that the role of CO₂ is to increase the rate of the anodic reaction by facilitated formation of a complex ion such as FeHCO₃⁺ [9]. The rate of corrosion is said to be controlled by diffusion of the complex ion away from the metal surface. Carbon dioxide is found to cause an enhanced rate of general corrosion and localized corrosion, sometimes as pitting corrosion, and the kind of corrosion caused by dissolved CO₂ varies considerably with environmental conditions. In addition, because CO₂ is an acid which first associates to give carboxylic acid and can then dissociate further into bicarbonate and carbonate ions, these mechanisms are influenced by the resulting acidic pH. The buffering action of these carbon-containing species may also play an important role [9]. The effects of dissolved carbon dioxide on the corrosion of steel are therefore the subject of considerable controversy [9,12].

It is clear, in any case, that the corrosion of steel in CO₂ environments is greatly influenced by deposition of films on the surface. The films formed on steel in brines saturated with CO₂ have a complex chemical structure. The cathodic and anodic reactions provide a chemical environment which promotes the formation of iron carbonate (FeCO₃), but the corrosion behavior strongly depends on the fluid velocity as well as on the physicochemical and electrochemical properties of the different developed corrosion layers, which can be modified as a function of time [13]. The corrosion resistance of carbon steel in waters containing high concentrations of calcareous salts is determined by the properties of the layers (corrosion products, calcium and magnesium carbonate and/or sulfate) formed at the metal surface. The formation of precipitates in some systems may be facilitated by a local increase in pH at the metal surface due to oxygen reduction [14,15]. An additional complication is that preferential dissolution can isolate phases, e.g. cementite (Fe₃C), which can enhance corrosion through galvanic coupling [12]. In addition to the role of inclusions, the composition of the steel has a significant influence on corrosion in CO₂ environments [16–18].

There is considerable interest in assessing the influence of fluid velocity on corrosion. At elevated temperatures, generally above 60 °C, steel is subject to shear-induced erosion–corrosion in brines saturated with CO₂. A considerable effort has been expended on both multi-phase [1,19–25] and single-phase flow studies [26,27]. The correspondence between experiments conducted in different flow geometries is only qualitative if the flow is not well characterized as is the case, for example, for the rotating cage [28,29]. In well-defined flows, correlation has been made on the basis of mass transfer correlations or shear stress [2,30–34].

Much of what is known about corrosion of steel in brines containing dissolved CO₂ was obtained from surface analysis and potentiodynamic experiments. For this system, impedance spectroscopy has been used primarily to establish relative measures of surface reactivity. Altoe et al., for example, used impedance spectroscopy to identify qualitative characteristics of the influence of single-phase flow on corrosion [35]. Chen et al. used an electrical circuit analogue to obtain qualitative assessments of the role played by mass transfer [21,23]. Guo and Tomoe also used an electrical circuit analogue to obtain an interpretation of impedance measurements [36]. Kinsella et al. [37] and Tan et al. [38] used electrochemical impedance spectroscopy and surface characterization techniques to study carbon dioxide corrosion product scales. In all cases, the models used to interpret the impedance results were approximate in that they did not account correctly for mass transfer under flow conditions.

The objective of the present work was to develop a mathematical framework within which impedance spectroscopy could be used to obtain physically meaningful kinetic and transport parameters. An essential feature of this development was use of a flow geometry which could be interpreted in terms of a one-dimensional model for mass transfer. Convective mass transfer is not uniform for flow past electrodes, such as seen in coupon experiments or within the wall-jet region of an impinging jet electrode [39,40]. The geometry chosen for this work was a submerged impinging jet with the electrode dimension chosen to lie completely within the stagnation region of the jet.

### 2. Experimental technique

An axisymmetric impinging jet system was chosen for this study, which allowed use of in situ video microscopy, impedance spectroscopy, and monitoring of corrosion potential. The system geometry was chosen such that the entire disk surface lay within the stagnation region. Within the stagnation region, the axial...
velocity is independent of radial position and convective
diffusion to the disk is uniform, much as is seen for
the rotating disk electrode [32,41,42].
Because the mass transfer rate is uniform for an
electrode that lies entirely within the stagnation region,
differential mass transfer cells are not established. The
impinging jet system can therefore be used in single-
phase flow to isolate the influence of the hydrodynamic
shear stress. Removal of protective layers by hydrody-
namic shear may be observed if the shear stress outside
a certain critical radius is sufficiently large. Since shear
stress is a function of both radial position and jet
velocity, the critical radius corresponding to the critical
shear stress would be a function of jet velocity for fixed
geometry. Details of the experimental apparatus and a
schematic of the impinging jet cell have been presented
previously [3,43,44].

The working electrode was a disk of pipeline-grade
SLX52 steel (0.6 × 10−2 m diameter) embedded in an
insulating epoxy surface. The surface was polished us-
ing 800 grit SiC-paper followed by 1 μm alumina,
cleaned in ethanol, and rinsed with deionized water.
The nominal chemical composition of the steel is given
in Table 1.

The brine was prepared using ion-exchanged water
and reagent-grade chemicals. The chemical composition
of the brine solution used is given in Table 2. The
composition of the brine used for this study simulated
that found in the Prudhoe Bay oil
fields [45], with the
exception that a residual level of dissolved oxygen was
present, as discussed below.

The reference electrode was saturated calomel (SCE),
and potential measurements were performed using an
EG&G PAR 273 potentiostat/galvanostat. Electro-
chemical impedance measurements were made using the
same potentiostat interfaced with a Solartron Instru-
ments 1254 frequency response analyzer. The experi-
ments were controlled using programs written in-house
in the LabView language. Impedance measurements
were carried out in the frequency range of 5 kHz–0.05
Hz under galvanostatic modulation, used to ensure that
the system remained at a net current equal to zero. The
variable-amplitude galvanostatically modulated (VAG)
protocol [44,46] was used with a target sinusoidal signal
amplitude of 5 × 10−3 V. As compared to fixed-ampli-
tude galvanostatic or potentiostatic modulation, the
VAG algorithm was previously shown to provide a less
invasive measurement of the impedance of freely cor-
rodning systems [44,46]. Video microscopy images were
obtained under computer control using a Sony Model
XC-003 3CCD Color Video Camera Module.

For the experiments described here, the temperature
was controlled at a value of 30 or 60 °C. The solution
was deaerated by purging with 99.5% CO2 at a partial
pressure of 1 atm for at least 12 h before the experi-
ments. Under the assumption that the only impurity
was air, the dissolved oxygen content of the brine was
estimated to be at least 30 ppb at 60 °C and 40 ppb at
30 °C. The sparging continued during the electrochem-
ical measurements in such a manner that bubbles were
not entrained in the jet flow. The pH and the electrolyte
resistance were observed to be stable as reported in
Table 3.

3. Summary of experimental results

The experimental results presented by Cardoso and
Orazem [47–49] are summarized briefly here to provide
a context for the modeling effort. For these experi-
ments, the system was held at a jet velocity of 3.3 m/s
for a period of 24 h. The resulting corrosion potential is
presented as a function of time in Fig. 1 for experi-
ments conducted at 30 and at 60 °C. The corrosion
potential reached a relatively stable value within the
first few hours of the experiment, but the polarization
impedance, given in Fig. 2, required a longer time to
reach a steady value. The error bars in Fig. 2 corre-
spond to the 1σ-confidence interval obtained by the
regression procedure for data found to be consistent.

Table 1
Nominal chemical composition of the steel used in this study

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>C</th>
<th>Fe</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>0.040</td>
<td>0.090</td>
<td>98.487</td>
<td>1.070</td>
<td>0.007</td>
<td>0.009</td>
<td>0.250</td>
<td>0.047</td>
</tr>
</tbody>
</table>

Table 2
Chemical composition of the brine used in this study

<table>
<thead>
<tr>
<th>Species</th>
<th>HCO3−</th>
<th>SO42−</th>
<th>Cl−</th>
<th>Na+</th>
<th>Ca2+</th>
<th>Mg2+</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/l</td>
<td>200</td>
<td>1150</td>
<td>14 000</td>
<td>8775</td>
<td>278</td>
<td>643</td>
</tr>
</tbody>
</table>

Table 3
Chemical characteristics of the brine used in this study

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>5.4</td>
<td>0.039</td>
</tr>
<tr>
<td>60</td>
<td>5.5</td>
<td>0.055</td>
</tr>
</tbody>
</table>
with the Kramers–Kronig relations. The polarization impedance was obtained using the measurement model, as presented by Orazem et al. [50]. The change in impedance behavior was associated with formation of surface films, as shown in successive video microscopy images, collected in situ and presented in Fig. 3. At short times (Fig. 3(a)) a black and uniform surface is seen. Fig. 3(c) and (e) shows the evolution of the corrosion product layers, and Fig. 3(e) shows a thick reddish-brown layer, probably a mixture of iron oxyhydroxides, seen after reaching steady state.

After a steady impedance value was obtained, a systematic study was undertaken to examine the potential influence of large fluid velocities. The velocity was changed in such a way as to isolate the role of velocity from possible time-dependent trending. The protocol for the adjustment of flow velocity is presented in Fig. 4. The methods described by Orazem et al. [50] were used to determine the polarization impedance of data collected as a function of jet velocity. The impedance response showed no particular trend when plotted as a function of time; whereas the response as a function of jet velocity fell into three clear zones of behavior, as shown in Fig. 5. It is interesting to note that very similar behavior was seen in the experiments conducted at 30 and at 60 °C. Even though the values of the impedance at 30 °C were 2.7 times larger than the impedance at 60 °C, normalization by the extrapolated zero-velocity value caused the curves to superimpose, showing the same regions of behavior.

The polarization impedance decreased with jet velocity at low jet velocities (Region I), suggesting the coupled influence of convective diffusion and diffusion through a stagnant layer. At higher jet velocities (Region II), the polarization impedance was observed to be independent of jet velocity. At still higher jet velocities (Region III), mechanical removal of protective layers was observed by in situ video microscopy, during which time the polarization impedance dropped sharply (see Fig. 6). Very similar behavior was seen in the experiments conducted at 30 °C. In subsequent plots, thin vertical lines are provided as reference to the three zones of behavior.

4. Theoretical development

The theoretical development is presented here in the context of the convective diffusion impedance of the impinging jet, the reaction mechanism, and diffusion impedance of a stagnant inner layer.

4.1. Convective diffusion for the impinging jet

The fluid flow within the region of the electrode is well defined [51–55]. The submerged impinging jet geometry can be made to give uniform mass-transfer rates across a disk electrode within the stagnation region. The stagnation region is defined to be the region surrounding the stagnation point in which the axial velocity, given by

$$v_z = -\sqrt{a\phi(\eta)} \quad (1)$$

is independent of radial position, and the radial velocity is given by

$$v_r = \frac{ar}{2} \frac{d\phi(\eta)}{d\eta} \quad (2)$$

where $a$ is the hydrodynamic constant which is a function only of geometry and fluid velocity, $r$ and $z$ are the radial and axial positions, respectively, $\nu$ is the kinematic viscosity, and $\phi$ is the stream function which is given in terms of dimensionless axial position $\eta = z\sqrt{a}/\nu$ as [55]

$$\phi(\eta) = 1.352\eta^2 - \frac{1}{3}\eta^3 + 7.2888 \times 10^{-3}\eta^6 + \cdots \quad (3)$$

Esteban et al. used ring electrodes to find that the stagnation region extends to a radial distance roughly equal to the inside radius of the nozzle [32].

Within the stagnation region, the surface shear stress $\tau_{rz}$ is given by
\[ \tau_z = -1.312 r (\mu \rho)^{1/2} a^{3/2} \]  \hspace{1cm} (4)

where \( \mu \) and \( \rho \) are the viscosity and density of the fluid, respectively. The hydrodynamic constant \( a \) can be determined experimentally using ring or disk electrodes at the mass-transfer-limited condition and is proportional to the jet velocity.

The uniform appearance of the surface films in Fig. 3 supports the assumption that a one-dimensional model for mass transfer can be employed. Thus, the equation governing mass transfer in the frequency domain is given by

\[ \frac{d^2 \tilde{\theta}}{d \xi^2} + \left( \frac{\beta^2}{1.352^2} - \frac{3}{1.352^2} \right) \frac{d \tilde{\theta}}{d \xi} - j K \tilde{\theta} = 0 \]  \hspace{1cm} (5)

Fig. 3. Video micrographs obtained in function of time for the coupon of steel in brine (60 °C and nozzle jet velocity of 3.3 m/s). (a) and (b) 0.25 h; (c) and (d) 1 h; and (c) and (d) 24 h after immersion of the electrode.

Fig. 4. The experimental protocol showing how the jet velocity and hydrodynamic constant were selected after the 24 h stabilization period.
Fig. 5. Polarization impedance as a function of hydrodynamic constant.

where

\[ K_i = \frac{\omega_i}{a} \left( \frac{9}{(1.352)^2} \right)^{1/3} \frac{1}{Sc^{1/3}} = 1.70123 \frac{\omega Sc^{1/3}}{a} \]  

represents a dimensionless frequency, \( \xi = z/\delta_i \), is a dimensionless position where

\[ \delta_i = \left( \frac{3}{1.352} \right)^{1/3} \frac{1}{Sc^{1/3}} \frac{1}{a} = 1.180 \frac{1}{Sc^{1/3}} \frac{1}{a} \]

is a characteristic distance for transport of species \( i \).

Following Tribollet and Newman [56], the concentration term could be expressed as a series expansion in \( Sc^{-1/3} \) as

\[ \hat{\delta}_i = \hat{\delta}_{i,0} + \frac{\delta_{i,1}}{Sc^{1/3}} + \frac{\delta_{i,2}}{Sc^{2/3}} + \cdots \]  

where \( \hat{\delta}_{i,k} \) represents the solution to

\[ \frac{d^2 \hat{\delta}_{i,0}}{d\xi^2} + 3\xi^2 \frac{d\hat{\delta}_{i,0}}{d\xi} - jK_i \xi \hat{\delta}_{i,0} = 0 \]  

and

\[ \frac{d^2 \hat{\delta}_{i,1}}{d\xi^2} + 3\xi^2 \frac{d\hat{\delta}_{i,1}}{d\xi} - jK_i \xi \hat{\delta}_{i,1} = \left( \frac{3}{(1.352)^2} \right)^{1/3} \xi^3 \frac{d\hat{\delta}_{i,0}}{d\xi} \]  

The Warburg impedance can be tabulated directly as a function of Schmidt number as

\[ \frac{1}{\hat{\delta}(0)} = Z_0 + \frac{Z_1}{Sc^{1/3}} + \frac{Z_2}{Sc^{2/3}} + \cdots \]

4.2. Reaction mechanism

The anodic reaction was presumed to be corrosion of steel, expressed as

\[ \text{Anodic reaction} \]

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Tabulated values of \( Z_0, Z_1, \) and \( Z_2 \) were found as a function of \( pSc^{1/3} \) where \( p \) is the frequency made dimensionless by the hydrodynamic constant, \( p = \omega/a \).

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where \( \hat{\delta}_{i,k} \) represents the solution to

\[ \frac{d^2 \hat{\delta}_{i,0}}{d\xi^2} + 3\xi^2 \frac{d\hat{\delta}_{i,0}}{d\xi} - jK_i \xi \hat{\delta}_{i,0} = 0 \]  

and

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\[ \frac{1}{\hat{\delta}(0)} = Z_0 + \frac{Z_1}{Sc^{1/3}} + \frac{Z_2}{Sc^{2/3}} + \cdots \]

Tabulated values of \( Z_0, Z_1, \) and \( Z_2 \) were found as a function of \( pSc^{1/3} \) where \( p \) is the frequency made dimensionless by the hydrodynamic constant, \( p = \omega/a \).
The corresponding steady-state current density is given by

$$i_{F_2} = n_{F_2}Fk_{F_2} \exp\left(\frac{2\Delta F}{RT}(V - V_{F_2})\right)$$  \hspace{1cm} (14)

The oscillating variable can be expressed as

$$i_{F_2} = n_{F_2}Fk_{F_2} \exp\left(\frac{2\Delta F}{RT}(V - V_{F_2})\right)$$  \hspace{1cm} (15)

The cathodic production of H$_2$ was assumed to follow

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^-$$  \hspace{1cm} (16)

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-}$$  \hspace{1cm} (17)

and

$$2H^+ + 2e^- \rightarrow H_2$$  \hspace{1cm} (18)

The corresponding steady-state current densities were given as

$$i_{H_2CO_3} = n_{H_2CO_3}Fk_{H_2CO_3} \bar{c}_{H_2CO_3}(0) \exp\left(\frac{2\Delta F}{RT}(V - V_{H_2CO_3})\right)$$  \hspace{1cm} (19)

$$i_{HCO_3^-} = n_{HCO_3^-}Fk_{HCO_3} \bar{c}_{HCO_3}(0) \exp\left(\frac{2\Delta F}{RT}(V - V_{HCO_3^-})\right)$$  \hspace{1cm} (20)

and

$$i_{H^+} = n_{H^+}k_{H^+} \bar{c}_{H^+}(0) \exp\left(\frac{2\Delta F}{RT}(V - V_{H^+})\right)$$  \hspace{1cm} (21)

respectively. The trace amounts of oxygen present in the system were assumed to react according to

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$  \hspace{1cm} (22)

The corresponding steady-state current density is given by

$$i_{O_2} = -n_{O_2}Fk_{O_2} \bar{c}_{O_2}(0) \exp\left(-\frac{\Delta F}{RT}(V - V_{O_2})\right)$$  \hspace{1cm} (23)

which can be linearized and expressed in terms of the charge transfer resistance to obtain an expression for the oscillating current density given by

$$i_{O_2} = n_{O_2}k_{O_2} \bar{c}_{O_2}(0) \exp\left(-\frac{\Delta F}{RT}(V - V_{O_2})\right)$$  \hspace{1cm} (24)

Also, the flux of oxygen to the electrode surface is

$$i_{O_2} = -n_{O_2}Fk_{O_2} \frac{\partial \bar{c}_{O_2}}{\partial y}$$  \hspace{1cm} \bigg|_{y = 0}$$  \hspace{1cm} (25)

where \(\bar{c}(0)\) is the dimensionless oscillating flux at the surface. Combination of Eqs. (24) and (25) yields

$$\bar{i}_{O_2} = \frac{\bar{V}}{R_{c, O_2} + k_{O_2} \bar{c}_{O_2}(0)} \exp\left(-\frac{\Delta F}{RT}(V - V_{O_2})\right)$$  \hspace{1cm} (26)

where the diffusion impedance is given by

$$Z_{D, O_2} = n_{O_2}F^2D_{O_2} \bar{c}_{O_2}(0) \frac{1}{n_{O_2}Fk_{O_2} \bar{c}_{O_2}(0)} \exp\left(-\frac{\Delta F}{RT}(V - V_{O_2})\right)$$  \hspace{1cm} (27)

and

$$R_{c, O_2} = \left(\frac{Fk_{O_2} \bar{c}_{O_2}(0) \Delta F}{RT}ight)^{-1}$$  \hspace{1cm} (28)

All other reactions were assumed to be unaffected by mass transfer. Thus,

$$\bar{i}_{H_2} = n_{H_2}k_{H_2} \frac{2\Delta F}{RT} \exp\left(-\frac{\Delta F}{RT}(V - V_{H_2})\right)$$  \hspace{1cm} (29)

and

$$\bar{i}_{HCO_3^-} = n_{HCO_3^-}k_{HCO_3} \frac{2\Delta F}{RT} \exp\left(-\frac{\Delta F}{RT}(V - V_{HCO_3^-})\right)$$  \hspace{1cm} (30)

where

$$R_{c, H_2} = \left(\frac{Fk_{H_2} \bar{c}_{H_2}(0) \Delta F}{RT}ight)^{-1}$$  \hspace{1cm} (31)

and

$$R_{c, HCO_3^-} = \left(\frac{Fk_{HCO_3} \bar{c}_{HCO_3}(0) \Delta F}{RT}ight)^{-1}$$  \hspace{1cm} (32)

The reaction mechanism considered here is preliminary in that mass transfer and homogeneous reactions of dissociated products of CO$_2$ were not considered.
4.3. Cell impedance

Under the assumptions that the Faradaic currents associated with individual reactions can be summed to yield the net Faradaic current $i_f$ and that the total current density is equal to the sum of Faradaic and charging current densities, i.e.

$$i = i_f + C_d \frac{dV}{dt}$$

then

$$\dot{i} = \dot{i}_f + j\omega C_d \dot{V}$$

The cell potential can be expressed as the sum of an ohmic contribution to the electrode potential as

$$U = V + iR_e$$

Following Eq. (37), the oscillating cell potential is given by

$$\ddot{U} = \ddot{V} = iR_e + \dot{V}$$

The impedance is therefore given by

$$\frac{U}{i} = Z(\omega) = R_e + \left( \frac{1}{R_{ef}} + \frac{1}{R_{i,\text{Fe}} + Z_{D,\text{O}_2}(\omega)} + j\omega C_d \right)^{-1}$$

where

$$\frac{1}{R_{ef}} = \frac{1}{R_{i,\text{Fe}}} + \frac{1}{R_{i,\text{H}^+} + \frac{1}{R_{i,\text{HCO}_3}} + \frac{1}{R_{i,\text{H}_2\text{CO}_3}}}$$

The form of Eq. (39) is not sensitive to the species assumed to be affected by mass-transfer, but the value of the Schmidt number obtained by regression may give allow identification of the species if the respective diffusivities are known. For example, the framework presented here could be used for the case where diffusion of corrosion products away from the surface plays a significant role. While Eq. (39) can be expressed by a series–parallel combination of electrical circuit elements, the advantage of the development is that the model parameters are explicit impedance response measures in terms of specific proposed kinetic and transport processes.

4.4. Coupled convective and stagnant diffusion impedance

The images presented in Figs. 3 and 6 showed that a thick layer of reddish brown precipitate, consistent with a $\text{Fe}_2\text{O}_3 \times x\text{H}_2\text{O}$ film, was present over a black layer. Thus, convective diffusion associated with the impinging jet was assumed to be coupled with diffusion through a stagnant layer, as shown in Fig. 7. Following Deslouis et al. [57] the net diffusion impedance could be expressed as being composed of a contribution from an outer, convective, term and an inner, stagnant, term as

$$z_d = \frac{z_{d,o} + D_{k,o} \delta_{k,o} z_{d,i}}{D_{k,i} + D_{k,o} \delta_{k,o}}$$

where

$$z_{d,i} = \frac{j\omega \delta_i^2}{D_{k,i}}$$

and $z_{d,o} = -1/\delta_0(0)$. The diffusion impedance given in Eq. (39) can be expressed as

$$z_{d,o_2} = z_{d,0}\left(-\frac{1}{\delta_0(0)}\right)$$

where $z_{d,0}$ is a constant and $z_d$ is a function of the time constant $\tau_r = \delta_i^2 D_{k,i}$, the ratio $D_{k,b} \delta_{k,b} D_{k,c} \delta_{k,c}$, and $Sc$. 

5. Results and discussion

The model described by Eq. (39) was regressed to the impedance data collected by Cardoso and Orazem at steady state after the films had grown for a period of 24 h [47–49]. The nonlinear complex regression was weighted by the error structure determined from replicated measurements following the method of Agarwal et al. [58–60]. The standard deviation of the experiments was roughly proportional to the modulus of the measurement, and the magnitude of the standard deviations ranged from 0.1 to 0.3% of the modulus. The data were found to be consistent with the Kramers–Kronig relations except at the largest fluid velocities tested for which mechanical removal of surface films was observed.
Model parameters were retained only if the 95.4% confidence interval for the parameter estimate, obtained by linearization about the trial solution, did not include zero. The six model parameters obtained by regression included $R_{\text{eff}}$, which included the influence of both corrosion and cathodic reactions, $C_d$, $\tau_\gamma$ and $\tau_c$. The confidence interval for $R_{\text{eff}}$ included zero for all regressions; therefore, $R_{\text{O}_2}$ was excluded from the process model.

The regression of the process model to typical impedance data is presented in Fig. 8. The weighted regression statistic

$$J = \frac{\sum_k (Z_{r,k} - \hat{Z}_{r,k})^2 + \sum_k (Z_{j,k} - \hat{Z}_{j,k})^2}{2\sum_k \sigma_k^2}$$

was, on average, equal to 3; whereas, the corresponding value for the regression to the measurement model was 1.3. The process model did not describe adequately high-frequency behavior that was found to be consistent with the Kramers–Kronig relations, yet was nevertheless attributed to instrument artifact. The regression statistic is shown in Fig. 9 for the process model and the measurement model. The fit was worse for both the process and measurement models at higher jet velocities where nonstationary effects were evident at low frequencies.

The most surprising result of the regression analysis was that the apparent Schmidt number was much larger than the expected value of 1000, ranging between $7 \times 10^6$ and $8 \times 10^7$ (see Fig. 10). The Schmidt number decreased dramatically when the outer layer was partially removed by hydrodynamic forces (Region III). The large Schmidt number obtained after the surface films were removed entirely by the highest jet velocities (given by the $\triangle$) suggests that the outer layer began re-forming rapidly when the jet was returned to a lower velocity.

The large Schmidt number could be explained by the gel-like behavior of the outer reddish-brown layer. An empirical relationship for the viscosity of a colloidal gel is given as a function of particle volume fraction by

$$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_{\text{max}}}\right)^{-[\gamma] \phi_{\text{max}}}$$

where, under large shear rates, $\eta = 2.71$ and $\phi_{\text{max}} = 0.708$ [61]. Under the assumption that

$$D_i = D_{i,0}(1 - \phi)^{1.5}$$

and that the density is a weighted sum of contributions from particles with a density of 2.8 g/cm$^3$ and solvent with a density of 1 g/cm$^3$, the expected Schmidt number for the colloidal gel can be given as a function of particle volume fraction $\phi$ as shown in Fig. 11. Thin horizontal lines indicate the range of Schmidt number obtained by regression to the impedance data in Regions I–III. The vertical line corresponds to the maximum particle volume fraction. The suggestion that the thick outer layer is in fact a viscous colloidal gel is supported by micrographs (Fig. 3(e)) showing that, under the influence of large jet velocities, the film was capable of spreading over the insulating region surrounding the coupon.

The resulting function $(1 - \phi / \phi_{\text{max}})$, presented in Fig. 12 as a function of hydrodynamic constant, shows that...
the particle volume fraction is very close to its maximum packing value $\phi_{\text{max}}$ except at the large jet velocity where the gel was partially removed by hydrodynamic forces. While the data are insufficient to establish a clear trend, the results suggest that, as reported in the literature for general colloidal gel behavior [61], the layer may become compacted with increased velocity in Region I. There is also a suggestion that the layer became somewhat less compacted with increased velocity in Region II. The layer is certainly much less compacted in Region III. The corresponding kinematic viscosity, shown in Fig. 13, shows that the large $\text{Sc}$ is due primarily to the large value of kinematic viscosity, which reaches a value of 100 cm$^2$/s in Regions I and II, but decreases to a value near 0.04 cm$^2$/s when the film is partially removed.

The characteristic length for diffusion in the outer region, calculated from Eq. (7), is presented in Fig. 14. The characteristic length was a smooth function of hydrodynamic constant and showed no particular discontinuity at the transition regions identified in Fig. 5. The thickness of the inner layer, in contrast, shows a marked discontinuity at the transition regions identified in Fig. 5 as seen in Fig. 15. The porosity of the inner film, obtained under the assumption that Eq. (46) applies, is presented in Fig. 16.
6. Conclusions

The analysis presented here must be considered to be preliminary. The equations relating diffusivity and viscosity to particle volume fraction are empirical, and the model for hydrodynamics assumed a uniform viscosity. Nevertheless, the regression of the process model to the impedance data provided useful results. The most important is that the outer layer has the properties of a colloidal gel. A corresponding result was obtained previously by electrohydrodynamic impedance spectroscopy for corrosion of iron in sulfuric acid [62]. As discussed by Barcia et al. [62] the presence of a layer with a different viscosity necessitates development of a refined model for the hydrodynamics. Barcia et al. [62] developed such a model under the assumption that the region of increased viscosity tracked with the ferrous iron concentration. In the present case, concurrent in situ video microscopy confirmed the presence of a colloidal gel, suggesting that a layered-viscosity model may be more appropriate.

The use of polarization impedance values alone provides misleading interpretation of the role of velocity on the impedance results. The properties of the inner film track very well with the transitions between regions identified by the polarization impedance plot given as Fig. 5, suggesting that the inner film is dependent on jet velocity. The thinning of the outer layer, which begins in region II, may be connected to a corresponding thinning of the inner compact layer.

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References


Fig. 16. Porosity of the inner diffusion layer as a function of hydrodynamic constant. The triangle indicates the value obtained after the surface films were removed entirely by the highest jet velocities.


[48] J.C. Cardoso Filho, M.E. Orazem, Application of a submerged impinging jet to investigate the influence of temperature, dissolved CO2, and fluid velocity on corrosion


