Model for corrosion of metals covered with thin electrolyte layers: Pseudo-steady state diffusion of oxygen

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\textbf{A B S T R A C T}

A one-dimensional mathematical model is presented for the free corrosion of a bare metal surface (devoid of any oxide film) under a thin electrolyte layer using mixed potential theory where anodic metal dissolution is controlled by oxygen diffusion through the electrolyte layer and by the oxygen reduction at the metal surface. A pseudo-steady state is considered wherein the oxygen diffusion is at steady state while the metal and hydroxyl ions keep accumulating in the thin electrolyte layer due to a decoupling arising from the assumed Tafel laws for corrosion kinetics. Under free corrosion the oxygen diffusion is shown to depend on a non-linear boundary condition with a non-integer power on oxygen concentration at the metal surface which makes the model non-trivial. Analytical and numerical results for the oxygen concentration at the metal surface, corrosion potential, and corrosion current density are reported which depend on several kinetic, thermodynamic and transport parameters in the system. The model is applied to iron and zinc systems with input data taken from the literature. The experimental utility of the model for gathering thin-film corrosion parameters from a study of the corrosion current and potential as a function of the thickness of the electrolyte layer is discussed. Precipitation and passivity, though not the main object of study in this work, are briefly discussed.

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1. Introduction

Characterizing corrosion in a particular environment simulating the service atmosphere has been an object of study over a century [1,2]. The context of corrosion can range from thin electrolyte layers and droplets covering metals and semiconductors exposed to the daily wet/dry humidity cycles [3–5] to industrial structures in contact with voluminous corrosive environments such as the off-shore structures immersed in the oceans [6]. Though the latter class of the systems have been widely modeled [6] and experimentally studied in the electrochemist’s lab, studies of corrosion under thin electrolyte layers [7–10] and droplets [11–14] are of more recent origin which await more extensive investigations. According to Stratmann et al. [9] the indoor corrosion of the metals and semi-conductors which are part of circuits and electronic equipment, take place under electrolyte layers of varying thickness. In a series of papers [7–9], they developed new techniques using the Kelvin probe to study the corrosion kinetics of metal surfaces covered by very thin electrolyte layers. With a view to understand the experimental results on corrosion under thin electrolyte layers, we embarked upon a theoretical program of which the present work is the first part.

In the case of uniform corrosion, anodic and cathodic sites are distributed randomly over the surface, and are spatially separated over atomic distances. In this situation, the electrode has a “mixed” potential [15] which, like the current density, is macroscopically uniform throughout the metal surface. The metal dissolution reaction (MDR) and the oxygen reduction reaction (ORR) are essentially irreversible [16]. MDR is generally faster than ORR and this along with the very low solubility of oxygen in the solution, leads to a very low concentration of dissolved molecular oxygen, albeit non-zero, at the surface of the corroding metal which effectively determines the corrosion rate of the metal. However, the transport of species is usually left out of consideration in the mixed potential theories of corrosion current and corrosion potential. Hence a simple scheme to predict the surface concentration of oxygen would be a helpful tool for predicting the initial corrosion rates more accurately.

Modeling transport in electrochemical systems dates back to the classical work on binary electrolytes by Nernst [17] who neglected electric migration by assuming a diffusion layer near an electrode where the variation of the concentration was assumed linear. Since then there have been a number of mathematical models of the evolution of the chemical conditions and transport of ions in various electrochemical systems. Most models for corrosion...
in the literature adopt a numerical solution of the coupled partial differential equations [18–23]. Detailed reviews of such modeling efforts in corrosion may be found in Refs. [5,24–26]. Models for corrosion by Pickering and Frankenthal [27] and Galvele [18–20] feature transport of ions both by diffusion and by electrical migration in dilute electrolytes and have found good use to interpret experimental results for systems which resemble an artificial pit and sustain a finite steady current through it. Agarwal et al. [28] modeled the current distribution on an electrode covered by a thin electrolyte layer, where the current is fed from one edge. However, these models cannot represent a freely corroding system with oxygen diffusion in the electrolyte phase and its reduction on the corroding metal surface which leads to zero net current. Song et al. [23] have presented a one-dimensional model for the corrosion of steel under a thin aqueous layer containing both CO2 and O2 incorporating the zero net current density condition. Models like Ref. [23] are very useful in predicting the characteristics of a particular system. Analytic simplification procedures for some corrosion problems, which in the end rely on simple numerical computations, have been developed by Oldham and Mansfeld [29]. A review of such models which present analytical solutions to some basic electrochemical systems may be found in Refs. [5,30–34].

In this paper, we systematically examine the model of uniform corrosion in a dilute system devoid of any oxide film, featuring an MDR with its only counter-reaction being the ORR under steady-state and Tafel conditions. For these conditions, we provide a non-dimensional formalism to predict the corrosion rates of a metal surface based exclusively on the characteristic kinetic, thermodynamic and transport parameters. For certain special cases we also provide explicit analytical solutions for the oxygen concentration at the metal surface (OCMS), corrosion potential and corrosion current density. We also predict the onset of precipitation (of metal hydroxide) in the electrolyte layer. We also point out the interesting origin of non-integer order kinetics on a homogeneous surface under free corrosion conditions. This study is part of the holistic model of atmospheric corrosion our group has developed over the past decade [35] to predict the state of the metal surfaces accurately.

2. Theory

In this section we describe the corroding system, state the model assumptions, develop the model equations and present the solution for the case of pseudo-steady diffusion of oxygen. We report the corrosion current density and corrosion potential as a function of system parameters and also discuss the evolution of ionic concentrations near the surface of the metal and the precipitation of metal hydroxide.

2.1. System

Fig. 1 shows a thin layer of electrolyte (salt solution) settled on the surface of a bare metal. The metal surface is at \( x = 0 \) and the electrolyte layer ends at \( x = L \). The electrolyte layer thickness \( x \) and the coordinate in the direction perpendicular to the metal surface. In the presence of dissolved oxygen, the metal \( M \) readily oxidizes and metal ions \( M^{n+} \) pass into the solution: \( M \rightarrow M^{n+} + ne^- \). The electrons released get captured by the oxygen diffusing through the electrolyte layer and the oxygen gets reduced to \( OH^- \) at the metal surface: \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \). The \( OH^- \) ions thus produced also pass into the electrolyte layer. This is often the situation at hand for a freshly deposited electrolyte layer rich in salt serving as the electrolyte.

![Fig. 1. Corrosion reactions, species transport and currents on a bare metal surface under a thin electrolyte layer of moisture of thickness (L). The grey arrows indicate species movement and the black arrows indicate the ionic currents into the solution. The broken arrow indicates the electronic movement.](image)

2.2. Model

The model is developed under the following assumptions:

(a) The electrolyte layer is assumed to be of constant thickness \( L \) and there is no convection in the layer.

(b) Steady-state diffusion of oxygen through the thin electrolyte layer is considered.

(c) At the metal surface, the only anodic reaction is the ORR and the only cathodic reaction is the ORR which is reasonable in the neutral to alkaline pH ranges [30], although one could include hydrogen evolution in the model if needed.

(d) Free corrosion condition is considered where the metal dissolution current is exactly and locally balanced by the oxygen reduction current. Since there is no current entering or leaving the system, there is no current distribution in the system.

(e) The electrolyte layer is considered well supported by the presence of excess inert ions and there is no electric potential distribution in the system.

(f) In a typical corrosion scenario at the initial stages, the over-potentials for the backward reactions (metal deposition and oxidation of hydroxyl ions) are very low. Additionally the initial metal and hydroxyl ion concentrations are also taken to be very low in our model which allow us to neglect the backward reactions.

(g) Homogeneous reactions in the electrolyte layer such as hydrolysis of metal ions and self-hydrolysis of water are not considered.

2.3. Governing equations

2.3.1. Kinetic models and oxygen transport

We model the MDR as a one-step process and write the Butler–Volmer expression for the current density \( I_{MDR} \) of the MDR as:

\[
I_{MDR} = I_{MDR}^0 \exp \left( \frac{nF(1 - \alpha_{M/M^{n+}})}{RT} \left[ E_{corr} - E_{M/M^{n+}} \right] \right)
\]

(1)

The quantities that appear in the above equation are the exchange current density of the MDR \( I_{MDR}^0 \), the corresponding transfer coefficient \( \alpha_{M/M^{n+}} \), Faraday’s constant \( F \), the gas constant
$R$, the absolute temperature $T$, the potential of the freely corroding system $E_{\text{corr}}$, the standard reduction potential of the MDR $E_{M/Mn^{1+}}$ and number of electrons transferred $n_1$. Note that under imperfect potential conditions $E_{\text{corr}}$ would be replaced by the applied potential $E_{\text{app}}$ in both the MDR and the ORR.

In the ORR, the simultaneous transfer of 4 electrons is less likely. The overall reaction contains several steps and is highly irreversible [16,36]. The interfacial electrochemical processes included in the mechanism have been studied in some detail in the literature for some metals like zinc [37–40] and iron [41]. A direct pathway involving 4 electrons competes with an indirect pathway via $H_2O_2$, where each partial step involves two electrons. In a typical system we consider in this paper, it is either the 2e-pathway or the 4e-pathway that is taken to be present and not both. However, the production, transport and disproportionation of the intermediate $H_2O_2$ are not considered here since they are highly sensitive to the metal under consideration [42]. Since the functional form of ORR kinetics equation derived using Oldham's stoichiokineti equation approach [43] remains unchanged for either pathway, we use a single equation as given below to model the kinetics for either pathway:

$$i_{O_2/\text{OH}^-} = -n_2 \frac{F}{RT} \exp \left( \frac{-n_2 \Delta G_{\text{O}_2/\text{OH}^-}}{RT} \right) \left( \frac{C_{\text{IO}_2/\text{OH}^-}}{C_{\text{O}_2/\text{OH}^-}} \right) \quad (2)$$

where $n_2$ denotes the electrons transferred in the rate determining step of the 2e- and 4e-pathways and is equal to 2 and 4, respectively. $i_{O_2/\text{OH}^-}$ is the current density associated with the corresponding electronic pathway, $p_{O_2/\text{OH}^-}$ is the corresponding exchange current density, $\Delta G_{\text{O}_2/\text{OH}^-}$ is the corresponding transfer coefficient, $C_{\text{IO}_2/\text{OH}^-}$ is the OCMS, and $C_{\text{O}_2/\text{OH}^-}$ refers to the saturated concentration of oxygen in the layer of water which depends on the salinity [44] at the given temperature and pressure.

At the metal surface ($x=0$) the oxygen flux is given by:

$$-D \frac{\partial C}{\partial x} \bigg|_{x=0} = \frac{i_{O_2/\text{OH}^-}}{4F} \quad (3)$$

where $C$ and $D$ are the concentration and the diffusion coefficient of the dissolved oxygen in the electrolyte layer, respectively. At the air–electrolyte interface ($x=L$) dissolved oxygen is assumed to be in equilibrium with the oxygen in atmosphere; $C = C_{\text{atm}}$ as given by Henry's law [45]. In a two- or a three-dimensional system the free corrosion condition would be a non-linear integral condition requiring the anodic and cathodic currents to be equal and opposite [14]. In this one-dimensional system the free corrosion condition simplifies to the equality of anodic and cathodic current densities:

$$i_{M/Mn^{1+}} = -i_{O_2/\text{OH}^-} = i_{\text{corr}} \quad (4)$$

where the convention that the anodic and cathodic current densities are positive and cathodic current densities are negative has been applied. Substituting for $i_{M/Mn^{1+}}$ and $i_{O_2/\text{OH}^-}$ from (1) and (2) in Eq. (4), we can obtain an expression for $E_{\text{corr}}$ which when substituted in Eq. (3) we get:

$$-D \frac{\partial C}{\partial x} \bigg|_{x=0} = -p \frac{C}{x=0} \quad (5)$$

where $\sigma$ and $p$ are groups of system constants given as:

$$\sigma = \frac{1}{(1 + (n_2 \frac{\Delta G_{\text{O}_2/\text{OH}^-}}{RT}))} \quad (6)$$

and

$$p = \left( \frac{1}{C_{\text{sat}}} \right)^{\sigma} \left( \frac{p_{O_2/\text{OH}^-}}{4F} \right) \left( \frac{\sigma}{\text{sat}} \right)^{(1-\sigma)} \exp \left( \frac{F \Delta G_{\text{O}_2/\text{OH}^-} - E_{\text{corr}}}{RT} \right) \quad (7)$$

Since $0 < (a_{O_2/\text{OH}^-}, a_{M/Mn^{1+}}) < 1$, $\sigma$ obeys the inequality $0 < \sigma < 1$. Thus $\sigma$ is a non-integer and the boundary condition (5) resembles a fractional order chemical reaction boundary condition [46] on the OCMS. Immediately after the electrolyte layer deposits over the metal surface, the consumption of oxygen at the metal surface (and the corrosion current density) would be transient and the diffusion of oxygen in the electrolyte layer would be governed by Fick’s law for transient diffusion. This transient situation is described by a one-dimensional parabolic PDE in one variable $C$ ($\sigma$ and $p$ being system constants) and the boundary conditions for this PDE will not involve the concentrations of metal ions and hydroxyls due to the neglect of metal deposition and oxygen generation at the corroding metal surface where metal dissolution and oxygen consumption are the dominant processes. Thus we can solve for the space and time-dependent concentration of the dissolved oxygen independent of other species concentrations. This decoupling holds for the transient as well as the steady state diffusion. Since the electrolyte layer is thin, the steady-state for diffusion of oxygen would be swiftly reached and hence we consider only the steady-state diffusion of oxygen. However, the concentrations of the metal ions and the hydroxyl ions will not be in a steady state as there is a constant and continuous generation of these ions at the corroding metal surface. Thus we can conceive of situation where the oxygen diffusion would be at a steady-state while these ionic concentrations keep increasing which is termed the pseudo-steady state where the diffusion of oxygen is governed by $\frac{\partial^2 C}{\partial x^2} = 0$.

### 2.3.2. Transport of ionic species

The transport of ion $i$ in a well-supported electrolyte is governed by transient Fickian diffusion:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2}, \quad i = 1, 2 \quad (8)$$

where $1 = M^{n_1+}$ and $2 = \text{OH}^-$.

At the metal surface ($x=0$), the ionic fluxes are given by:

$$-D_1 \frac{\partial C_1}{\partial x} \bigg|_{x=0} = - \frac{p_{M^{n_1+}}}{n_1 F} = \frac{i_{\text{corr}}}{n_1 F}, \quad (9)$$

and at the air–electrolyte layer interface ($x=L$), the ionic fluxes are zero.

### 2.3.3. Non-dimensionalization

We introduce the following non-dimensional quantities:
\[
\xi = \frac{x}{L} \\
\tau = \frac{tD}{L^2} \\
\theta = \frac{C_{sat}}{C_{i}} \\
\theta_i = \frac{C_{i}}{C_{sat}} \\
\theta_i^{init} = \frac{C_{i}^{init}}{C_{sat}} \\
\psi = -\frac{D_i (\partial C_{i}/\partial x)}{(DC_{sat}/L)} = -\frac{\partial \theta}{\partial x} \\
\psi_i = -\frac{D_i (\partial C_{i}/\partial x)}{(DC_{sat}/L)} = -\frac{\partial \theta_i}{\partial x} \\
d_i = \frac{D_i}{D} \\
e_{corr} = \frac{F}{RT} \frac{E_{corr}}{L} \\
e_{m/M}^{i+} = \frac{F}{RT} e_{m/M}^{i+} \\
e_{O2/\text{OH}^-}^o = \frac{F}{RT} e_{O2/\text{OH}^-}^o \\
\rho_{corr} = \frac{j_{corr}}{i_{O2/\text{OH}^-}}
\]

Non-dimensional coordinate perpendicular to the metal surface and into the electrolyte layer
Non-dimensional time
Non-dimensional concentration of oxygen in the electrolyte layer
Non-dimensional concentration of ionic species \( i = 1, 2 \) in the electrolyte layer
Non-dimensional initial concentration of ionic species \( i = 1, 2 \) in the electrolyte layer
Non-dimensional flux of oxygen in the electrolyte layer
Non-dimensional flux of ionic species \( i = 1, 2 \)
Non-dimensional diffusion coefficient of species \( i \)
Non-dimensional corrosion potential
Non-dimensional reduction potential of MDR
Non-dimensional reduction potential of ORR
Non-dimensional corrosion current density

We define \( \beta \) as the relative rate of ORR kinetics to the rate of diffusion of oxygen in the electrolyte layer:

\[
\beta = \frac{\rho_{O2/\text{OH}^-}}{i_{lim}}
\]  

(10)

where \( i_{lim} \) is the upper-limit of the corrosion current density given as:

\[
i_{lim} = \frac{4FD\rho_{C_{sat}}}{L}
\]  

(11)

Note that \( i_{lim} \) is the property of the electrolyte layer only and is independent of the interfacial corrosion kinetics. Next we define \( \gamma \) as a measure of the relative electro-catalytic activity of the two reactions namely the MDR and the ORR on the surface of the metal.

\[
\gamma = \frac{\rho_{M/M}^{i+}}{\rho_{O2/\text{OH}^-}}
\]  

(12)

2.4. Solution

2.4.1. Oxygen concentration at the metal surface

The unique possibility of pseudo-steady-state diffusion of oxygen results in a trivial solution for the concentration of oxygen in the thin electrolyte layer \( \theta = 1 - \frac{1}{\alpha_{\text{M/M}^{i+}}} (1 - \xi) \). Substituting this in the boundary condition in Eq. (5) we get:

\[
(1 - \theta|_{\xi=0}) = k'(\theta|_{\xi=0})^\sigma
\]  

(13)

which is a non-linear algebraic equation implicit in \( \theta|_{\xi=0} \) where \( k' \) is the non-dimensional reaction rate constant\(^1\) given by:

\[
k' = \beta y^{1-\sigma} \exp(\alpha_{M/M}^{i+} (e_{O2/\text{OH}^-}^o - e_{\text{M/M}^{i+}}^o))
\]  

(14)

and \( 0 \leq \theta|_{\xi=0} \leq 1 \). We have chosen \( k' \) to distinguish from the dimensional reaction rate constant \( k \) we had used in our earlier work [47] where we analytically solved the two-dimensional oxygen transport to a metal surface in an aerosol droplet. Unlike the present work where the exponent \( \sigma \) on oxygen concentration is less than 1, the earlier work [47] had assumed the oxygen transport to be independent of the other processes and the exponent on oxygen concentration in the surface reaction rate equation was taken to be 1.

It is clear from Eq. (13) that the OCMS \( \theta|_{\xi=0} \) is a function of \( k' \) and \( \sigma \) only, which are functions of the kinetic, thermodynamic and transport parameters of the system. \( \sigma \) depends only on the electron transfer characteristics of the MDR and the ORR and may assume very small values if the ratio \( n_2 \alpha_{O2/\text{OH}^-}/(n_2 (1 - \alpha_{M/M}^{i+})) \) is high. This is possible only when \( \alpha_{M/M}^{i+} \) is close to unity. Although rarely encountered in corrosion systems, it is useful to perceive the case \( \sigma \to 0 \) as a limit, where \( \theta|_{\xi=0} = 1 - k' = 1 - \beta y \).

The other limit, \( \sigma \to 1 \) is representative of those metal surfaces where the transfer coefficient for the oxygen reduction becomes vanishingly small. On some active metal surfaces such a condition may be practically encountered [40,41]. In this case, \( \theta|_{\xi=0, \sigma \to 1} = 1/(1 + k') \) indicating an inverse relation between the OCMS and \( \beta \).

\(^1\) By using \( \sigma \) and \( n_2 \alpha_{O2/\text{OH}^-} \), we still allow for the value of \( n_2 (1 - \alpha_{M/M}^{i+}) \) to be generic but find it more convenient to discuss the results based on the variation of \( \sigma \) and \( n_2 \alpha_{O2/\text{OH}^-} \).
Analytical solutions to Eq. (13) for 3 more special cases $\sigma$ = 1/3, 1/2, and 2/3 are reported in Table 1 along with $\sigma$ = 0 and 1. The reader may note that in many systems the transfer coefficients are usually equal to 1/2. In a system where divalent metal ions are produced through the MDR, i.e. $n_1 = 2$, if the ORR follows a 4e-pathway, i.e. $n_2 = 4$ with transfer coefficients $\alpha_{O_2/OH} = \alpha_{M/OH} = 1/2$, the value of $\sigma = 1/3$. For the same system if the ORR follows a 2e-pathway, $\sigma = 1/2$. Fig. 2 shows the variation of OCMS $\theta_{|z=0}$ with the non-dimensional reaction rate constant $k'$ for $\sigma = (0, 1/3, 1/2, 2/3, and 1)$ where the analytical solutions reported in Table 1 are plotted. Note that, only in the window limited to $10^{-3} < k' < 10^3$ does $\theta_{|z=0}$ vary considerably as a function of $k'$. Fig. 2 depicts two situations: (a) $\theta_{|z=0}$ tends to 1 which corresponds to the charge transfer limiting case where the diffusion of oxygen is much faster than the overall electrochemistry and (b) $\theta_{|z=0}$ tends to zero for values of $k' > 10^4$ where the system is in the diffusion limited regime. Fig. 2 also shows that solutions to all the cases obey the inequality $0 \leq \theta_{|z=0} \leq 1$ and that for the same value of $k'$, higher the value of $\sigma$, higher the OCMS, i.e. $\theta_{|z=0,\sigma_1} > \theta_{|z=0,\sigma_2}$ for $\sigma_1 > \sigma_2$. For the general case of $\sigma \neq (0, 1/3, 1/2, 2/3, and 1)$ numerical solution can be easily obtained by solving Eq. (13) or referring to the graphical solution in Ref. [46].

Levich [48] has discussed the closely related problem of a rotating disc surface in which the diffusion layer is of constant thickness for a given rotation speed thus making the reaction surface uniformly accessible. Based on Frank–Kamenetskii’s treatment [46], Levich also discusses observing fractional order kinetics similar to Eq. (5) on some surfaces and presents the non-linear algebraic equation (13) with a graphical numerical solution (adapted from Ref. [46]) for select cases. Both Kamenetskii and Levich attribute the fractional order reactions to inhomogeneities on the surface which leads to a reduced coverage.

In contrast, we point out that under free corrosion conditions, even on homogenous surfaces non-integer order kinetics may be observed. In our case, the non-integer order is electrochemical in origin. Additionally we report analytical solutions to Eq. (13) for certain cases (see Table 1) which are not reported in Refs. [46,48]. However, we note that the rotating disk surface will provide an excellent setup for measurements pertinent to our model as discussed in Section 3.2.

2.4.2. Profile of oxygen concentration in the electrolyte layer

The profile of oxygen concentration in the electrolyte layer for a pseudo-steady state would be linear. However, since the $\theta_{|z=0}$ is dependent on $k'$ and $\sigma$, the profiles would be different for different values of $k'$ and $\sigma$. For $\sigma = (0, 1/3, 1/2, 2/3, and 1)$, the profile of oxygen in the electrolyte layer can be obtained from Table 1. For the general case $\sigma \neq (0, 1/3, 1/2, 2/3, and 1)$, in Fig. 3 we plot the profiles of oxygen in the electrolyte layer for only those values of $k' = (0.1, 1.0 and 100)$ where there is a significant impact on the value of $\theta_{|z=0}$ and therefore on the concentration profile of oxygen $\theta$ in the electrolyte layer. Fig. 3 shows that in the regime $k' = 0.1$ system encounters charge transfer limitations whereas in the regime for $k' = 100$ the system experiences diffusion limitations. Fig. 3 also shows the case of $k' = 1.0$ where neither the charge-transfer nor the diffusion are limiting but are comparable. Beyond these values of $k'$, the system becomes either fully charge transfer or fully mass transfer controlled and profiles look alike irrespective of the value.
of $\sigma$. For a given value of $k'$, a high value of $\sigma$ leads to a high OCMS and consequently a high concentration of the oxygen at any point $\xi$ in the electrolyte layer.

### 2.4.3. Corrosion potential and corrosion current density

Eq. (4) shows that the expression for $E_{\text{corr}}$ is obtained exclusively from the free-corrosion condition without regards to whether the system is at steady or transient state. Hence, once $\theta_{i=0}$ is known as a function of $k'$ and $\sigma$, analytical or otherwise, $E_{\text{corr}}$ can be calculated for both steady and transient states as:

$$E_{\text{corr}} = \frac{RT}{nF} \left[ \frac{1 - \sigma}{\frac{1}{2} a_{O_2}^{\text{lim}}} - \ln(\theta_{i=0}) \right]$$

$$+ \left[ \sigma E^0_{M/MP+} + (1 - \sigma)E^0_{O_2/\text{OH}^-} - \frac{RT}{nF} \frac{1 - \sigma}{\frac{1}{2} a_{O_2}} \ln y \right]$$

where $i_{\text{corr}}$ is obtained by substituting the expression for $E_{\text{corr}}$ from above into Eqs. (2) and (4):

$$i_{\text{corr}} = (\theta_{i=0})^r \left[ y_{\text{corr}}^{\gamma^{-m}} \exp \left( \frac{F}{RT} \sigma a_{O_2}^{\text{lim}} (E^0_{M/MP+} - E^0_{O_2/\text{OH}^-}) \right) \right]$$

The terms in the square brackets in Eqs. (15) and (16) are the values obtained from the traditional mixed potential theory and rest of the terms may be interpreted as the "thin electrolyte layer corrections" to the mixed potential theory. For the special case of pseudo-steady state, the corrosion current density is related to the OCMS as follows:

$$\theta_{i=0} = 1 - \frac{i_{\text{corr}}}{i_{\text{lim}}}$$

The corrosion potential for the pseudo-steady state can be written as

$$E_{\text{corr}} = E^0_{O_2/\text{OH}^-} + \frac{RT}{nF} \ln \frac{\frac{p_{O_2/\text{OH}^-}}{i_{\text{corr}}} - \frac{p_{O_2/\text{OH}^-}}{i_{\text{lim}}}}$$

### 2.4.4. Precipitation of metal hydroxide

Since $i_{\text{corr}}$ is determined by OCMS and system parameters alone (see Eq. (13)), the fluxes of metal ions and hydroxyl ions at the metal surface (see Eq. (9)) become constants depending only on the system parameters. Thus Eqs. (8) and (9) present two mathematically decoupled systems of linear parabolic PDEs in one variable which can be solved individually. A similar mathematical problem for transient heat conduction in a slab of constant properties with a zero heat flux at one end and non-zero constant heat flux on the other is solved in Carslaw and Jaeger [49]. Since precipitation of metal hydroxide is likely to occur at the metal–electrolyte interface where the concentrations of metal and hydroxyl ions are the highest, we present here only the expression for the non-dimensional species concentration at the metal surface $\theta_{i=0} = C_i^{\text{sat}}/C^{\text{sat}}$.

$$\theta_{i=0} = \psi_{i=0} - \psi_{i=0}^{\lim}$$

where $\psi_{i=0}$ is the corresponding non-dimensional influx of the metal ion $(\psi_{i=0}^{\lim} = i_{\text{corr}}/FDC_{\text{sat}}^{\text{sat}})$ or hydroxyl ion $(\psi_{i=0}^{\lim} = i_{\text{corr}}/FDC_{\text{sat}}^{\text{sat}})$ due to corrosion.

### 3. Results and discussion

In this section we demonstrate how the model can be used to predict the corrosion current density, corrosion potential and the onset of precipitation of metal hydroxide for specific systems based on the inputs from the data in literature.

#### 3.1. Example calculations

Table 2 shows the model predictions for iron and zinc systems based on the list of parameters provided in Table 2. For zinc system, Zhang [50] observed that in solutions where passivation does not occur or there is no oxidizing agent, the corrosion potential of zinc generally lies in the vicinity of its equilibrium value. This is primarily due to the high exchange current density for the dissolution of zinc and relatively low exchange current densities for the cathodic reactions. However, in the presence of dissolved oxygen the corrosion potential shifts from the equilibrium potential of zinc to more cathodic values. We plot $E_{\text{corr}}$ and $i_{\text{corr}}$ vs. $L$ for specific systems like iron and zinc in Fig. 4(a) and (b). Stratmann et al. [9] have experimentally generated similar curves for the rate of oxygen reduction on the thickness of the electrolyte layer on platinum and iron. However, they are not directly comparable to our Fig. 4(a)
and (b) since the curves of Stratmann et al. (Fig. 10(a) in Ref. [9]) do not correspond to a corrosion process but only to the ORR on platinum surface. Similarly, the curves reported for iron–oxygen system in Ref. [9] include passivation which we currently do not address. Fig. 4(c) and (d) shows the corresponding evolution of the ratio of ionic product (IP) to the solubility product (KSP) of zinc and iron hydroxides. When $IP/KSP = 1$, precipitation of metal hydroxide is considered to set in. For an electrolyte layer thickness of 1 mm, the precipitation of metal hydroxide starts almost immediately in the zinc system. However, on iron, the corrosion current density is lower and precipitation of metal hydroxide starts later.

The corrosion current density of zinc and iron systems in Fig. 4(a) and (b) shows almost a linear variation with electrolyte layer thickness. This is because the calculated value of OCMS is very high for both the systems even for an electrolyte layer of thickness 1 mm (see Table 3). For thinner electrolyte layers the value of OCMS would be even higher since diffusion limitations are lower (i.e. the non-dimensional reaction rate $k′$ is small) and both the systems may be operating near the kinetically limited regime. As a result, as Eq. (14) reveals, as the electrolyte layer thickness decreases (i.e. $\beta$ decreases) the function $(1 - \theta_{\text{MDR}})$ also decreases resulting in a partial offset of the effect of electrolyte layer thickness on the corrosion current density. However, it is interesting why both zinc and iron systems which feature widely varying kinetic parameters (see Table 1) would display almost a similar corrosion behavior. Note that, the exchange current density of the MDR for zinc system is 3 orders of magnitude higher than exchange current density of the MDR for iron. One would expect based just on this that zinc would corrode at a rate much higher than iron. However, the zinc surface proves to be a much poorer supporter

### Table 3

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter/variable</th>
<th>Units</th>
<th>Zinc Value</th>
<th>Source</th>
<th>Iron Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Reaction Order</td>
<td>$\eta^o$</td>
<td>–</td>
<td>0.624</td>
<td>(6)</td>
<td>0.478</td>
<td>(6)</td>
</tr>
<tr>
<td>Non-dimensional electrolyte layer thickness</td>
<td>$\beta$</td>
<td>–</td>
<td>$2.1 \times 10^{-10}$</td>
<td>(10)</td>
<td>$2.31 \times 10^{-6}$</td>
<td>(10)</td>
</tr>
<tr>
<td>Ratio of exchange current densities of MDR and ORR</td>
<td>$\gamma$</td>
<td>–</td>
<td>$4.01 \times 10^9$</td>
<td>(12)</td>
<td>$2.12 \times 10^{12}$</td>
<td>(12)</td>
</tr>
<tr>
<td>Non-dimensional reaction rate constant</td>
<td>$k$</td>
<td>–</td>
<td>0.263</td>
<td>(14)</td>
<td>0.108</td>
<td>(14)</td>
</tr>
<tr>
<td>Non-dimensional concentration of oxygen at the metal surface (OCMS)</td>
<td>$\theta_{\text{o}_2}$</td>
<td>–</td>
<td>0.775</td>
<td>(13)</td>
<td>0.898</td>
<td>(13)</td>
</tr>
<tr>
<td>Corrosion potential</td>
<td>$E_{\text{corr}}$ (SHE)</td>
<td>V</td>
<td>0.085</td>
<td>(18)</td>
<td>0.182</td>
<td>(18)</td>
</tr>
<tr>
<td>Corrosion current density</td>
<td>$i_{\text{corr}}$</td>
<td>$\text{A m}^{-2}$</td>
<td>4.58 $\times 10^{-2}$</td>
<td>(16)</td>
<td>2.08 $\times 10^{-2}$</td>
<td>(16)</td>
</tr>
<tr>
<td>Non-dimensional time taken for precipitation</td>
<td>$\tau_{\text{MDR}}$</td>
<td>–</td>
<td>1.3 $\times 10^{-4}$</td>
<td>(19)</td>
<td>0.013</td>
<td>(19)</td>
</tr>
<tr>
<td>Time taken for precipitation</td>
<td>$\tau_{\text{MDR}}$</td>
<td>s</td>
<td>0.059</td>
<td>$\tau_{\text{MDR}}^{1/2}$</td>
<td>5.91</td>
<td>$\tau_{\text{MDR}}^{1/2}$</td>
</tr>
</tbody>
</table>
of ORR since the value of exchange current density of ORR on zinc is 4 orders of magnitude higher than that on iron. Thus the ratio $\gamma$ of exchange current densities of the MDR to the ORR for zinc is almost 7 orders of magnitude higher than for iron. Together with the term $\exp(\sigma M/\sigma_{\text{corr}} - \sigma_{\text{O}_2/\text{OH}^-})$ in Eq. (14) which is once again higher for zinc (since $\sigma_{\text{Zn}^{2+}/\text{Fe}^{2+}} < \sigma_{\text{Fe}^{2+}/\text{Zn}^{2+}}$), one may expect an extremely high value of non-dimensional reaction rate $k'$ and thus a low value of OCMS in zinc system. However, as Eq. (14) reveals, for the same electrolyte layer thickness $L$, the effect of high ratio $\gamma$ of exchange current densities of the MDR to the ORR on non-dimensional reaction rate $k'$ is partially offset by the exponent $(1 - \sigma_{\text{corr}})$ on $\gamma$ and also by the ratio $\beta$ which is directly proportional to the exchange current density of ORR thus eventually leading to comparable values for non-dimensional reaction rate $k'$ and OCMS for both the systems. Thus zinc corrodes faster than iron, although

$$A = \frac{1}{n_1(1 - \sigma_{\text{O}_2/\text{OH}^-})_\text{corr} + n_2 \alpha_{\text{O}_2/\text{OH}^-}^\text{OH}^-} \frac{RT}{F}, \quad B = \frac{n_1(1 - \sigma_{\text{O}_2/\text{OH}^-})_\text{corr} + n_2 \alpha_{\text{O}_2/\text{OH}^-}^\text{OH}^-}{n_1(1 - \sigma_{\text{O}_2/\text{OH}^-})_\text{corr} + n_2 \alpha_{\text{O}_2/\text{OH}^-}^\text{OH}^-}$$

the rates are in the same order of magnitude. The value of corrosion current density calculated in Table 3 for iron agrees well with the value $2.3 \times 10^{-2} A \text{ m}^{-2}$ reported in Ref. [40].

On the other hand, if a metal system supports ORR and MDR at high rates, then one would expect the system to corrode more vigorously. To establish this we conceived of a hypothetical system in which the exchange current density of ORR on the metal surface is two orders of magnitude higher than it is on zinc ($i_{\text{O}_2/\text{OH}^-}^\text{hypothetical} = 4.26 \times 10^{-9} A \text{ m}^{-2}$) with all other system parameters kept unchanged in Table 2 and equal to the zinc system. In this hypothetical system, as Fig. 5 shows, the variation of corrosion current density with thickness is very high and also non-linear. The calculated value of non-dimensional reaction rate $k'$ and OCMS for the hypothetical system are approximately 4.664 and 0.07 which puts the system near a mass transfer limited regime. Since corrosion potential shows a logarithmic dependence on OCMS (see Eq. (15)), the variation of corrosion potential with the OCMS is much less pronounced than the variation of corrosion current density with the OCMS which shows a power-law dependence (see Eq. (16)).

Thus under the given model assumptions, the value of OCMS which eventually determines the corrosion current density is dependent only on the system parameters that characterize the competition between kinetics and diffusion. In our calculations we have used some typical values of exchange current density reported in the literature. However, Frankel and Stratmann [51] point out the difficulties in obtaining the exchange current density values for ORR on active metals and more experimental research is required. In the following section we explain how the model could be useful for determining the system parameters.

3.2. Experimental utility of the model

The central object in the model is the OCMS $\theta_{\text{Ecorr}}$ which is a function of $k'$ and $\sigma$. There are two ways of experimentally measuring OCMS: (i) by having a micro-oxygen sensor at the metal–electrolyte interface and (ii) by relating OCMS to the experimentally accessible corrosion current density $i_{\text{corr}}$ by Eq. (17). One method of experimentally measuring the corrosion current density $i_{\text{corr}}$ is by weight-loss. However, in the case of metal covered by an electrolyte layer, it will not be possible to find the weight-loss of the metal alone. Nevertheless, the weight-gain in the “metal + thin electrolyte layer” due to the oxygen intake can be measured in a quartz crystal micro-balance as a function of time and thereby the corrosion current density $i_{\text{corr}}$ may be obtained. Stratmann et al. have adopted a slightly different approach using a differential pressure chamber [7].

Having outlined the possible experimental methods of obtaining the OCMS, we proceed to relate the numerical master-curves in Fig. 2 to the experimental data. First note that (see Eq. (14)) $k' = LK$ and $L = \ln L + \ln K$ where $K$ is a composite system parameter. Now, plot $(1 - (i_{\text{corr}}/i_{\text{lim}}))$ vs. $\ln L$ to obtain a curve similar to the one of the master-curves except for a shift in $\ln L$ along the abscissa. Thus one can obtain $k'$ and $\sigma$ from the experimental data just by juxtaposing the experimental curves on the master-curves.

Eqs. (15) and (17) show that the corrosion potential $E_{\text{corr}}$ is linearly related to $\ln(1 - (i_{\text{corr}}/i_{\text{lim}}))$, i.e.:

$$E_{\text{corr}} = A \ln \left(1 - \frac{i_{\text{corr}}}{i_{\text{lim}}}\right) + B \quad (20)$$

where

$$E_{\text{corr}} = \frac{RT}{n_1 \alpha_{\text{O}_2/\text{OH}^-}^\text{OH}^-} \ln \left(1 - \frac{i_{\text{corr}}}{i_{\text{lim}}}\right) + E_{\text{O}_2/\text{OH}^-}$$

Hence, by plotting $E_{\text{corr}}$ vs. $\ln(1 - (i_{\text{corr}}/i_{\text{lim}}))$, we will obtain a straight line giving the thin electrolyte layer constants $A$ and $B$. Eq. (20) can be used to characterize corrosion in all thin electrolyte layer systems that operate under the conditions assumed in this model. Another equation for thin-electrolyte layer corrosion comes from rearranging Eq. (18) as follows:

$$E_{\text{corr}} = \frac{RT}{n_1 \alpha_{\text{O}_2/\text{OH}^-}^\text{OH}^-} \ln \left(1 - \frac{i_{\text{corr}}}{i_{\text{lim}}}\right) + E_{\text{O}_2/\text{OH}^-} + \frac{RT}{n_2 \alpha_{\text{O}_2/\text{OH}^-}^\text{OH}^-} \ln i_{\text{lim}} \quad (22)$$

Using this equation one can obtain $\alpha_{\text{O}_2/\text{OH}^-}$ and $i_{\text{lim}}$ by plotting $E_{\text{corr}}$ vs. $\ln(1/(1 - i_{\text{corr}}))$. This, together with $k'$ and $\sigma$ obtained aforesaid to the complete knowledge of the kinetic parameters: $\alpha_{\text{O}_2/\text{OH}^-}$, $i_{\text{lim}}$, $\alpha_{\text{O}_2/\text{OH}^-}$, $\alpha_{\text{M/M}^+}$, $\alpha_{\text{M/M}^+}$, $n_1$, and $n_2$ of corrosion. In any experimental setup, the thickness $L$ of the electrolyte layer needs to be varied through the experiment. One way of varying $L$ is to control the ambient temperature and humidity so that very slow evaporation takes place in the electrolyte layer and at each thickness the electrolyte layer measurement of $E_{\text{corr}}$ and $i_{\text{corr}}$ may be made. Another convenient way is to use a rotating disc surface where the diffusion layer thickness (which is equivalent to thin electrolyte layer thickness) can be controlled hydrodynamically [48].
4. Conclusions

In this paper, a one-dimensional mathematical model is presented for the free corrosion of a bare metal surface devoid of any oxide film under a thin electrolyte layer. The model presented uses mixed potential theory and features a system where the metal dissolution is the only anodic reaction and oxygen reduction is the only cathodic reaction. Under steady oxygen diffusion and Tafel conditions, the model predicts the corrosion current density and corrosion potential as a function of kinetic, thermodynamic, and mass transport parameters. Multiple oxygen reduction pathways are considered but are treated as though they are mutually exclusive. Non-integer-order kinetics of oxygen arising on a freely corroding homogenous metal surface is explained. Corrections to the traditional mixed potential theory are presented accounting for the mass transfer limitations in thin electrolyte layers. Non-dimensional analytical expressions for the oxygen concentration at the metal surface, corrosion potential, and corrosion current density are reported where applicable. It was shown how the model parameters like transfer coefficients, exchange current densities and number of electrons transferred in the metal dissolution reaction and the oxygen reduction reaction can be obtained by experimentally studying the corrosion current and potential as a function of the thickness of the electrolyte layer. The onset of precipitation of metal hydroxide was predicted.

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References