Mathematical model for cathodic delamination using a porosity–pH relationship

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Abstract

A mathematical model was developed to simulate the transient propagation of the cathodic delamination on a coated metal. The model employed porosity and the polarization kinetics at the metal-coating interface that were assumed to be dependent on the local pH. The simulations provided qualitative agreement with published experimental results for a zinc coated system characterized by extremely rapid cathodic delamination. The mathematical model described in this work provides a foundation on which more sophisticated models can be constructed.

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1. Introduction

Cosmetic corrosion at the metal/paint-coating interface is a major problem for automotive and building applications, particularly when ecological surface treatments and coating systems are required to replace the very efficient but polluting systems involving Cr6+ or Ni2+ ions. Recent progress in the Scanning Kelvin Probe experimental technique has made possible the measurement of the spatial distribution of potential at the buried metal-coating

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interface during the cathodic delamination of a coated surface [1–6]. These experimental findings have been interpreted in terms of qualitative mechanisms which attribute the cathodic delamination process to electrochemical differences between the bare metal surface of a defect and the metal-coating interface beneath the delaminated coating coupled with diffusion and migration phenomena. In principle, such models should be useful in optimizing the metal-coating properties so as to engineer new products with enhanced anticorrosion properties. In practice, the models proposed to date remain essentially qualitative, and it has proven difficult to verify that they actually do predict the observed potential and pH variations. Therefore, a more quantitative approach is necessary.

A mathematical model of the cathodic delamination process was developed for a micron-scale thick section of coating that is immediately adjacent to the metal surface and with the adhesive bonds between the coating and metal being partially broken. The cathodic delamination process is influenced by heterogeneous reactions at the metal-coating interface, homogeneous reactions, and transport of species within the partially disbonded coating section. In the development of the model, an effort was made to identify physical properties that could be independently measured. These included physico-chemical parameters that accounted for the surface area available for electrochemical activity at the metal-coating interface, the electrochemical reactivity of the metal-coating interface, and the porosity of the coating adjacent to the metal. Experimental results for the cathodic delamination of coated zinc was reported by Furbeth and Stratmann and [4–6] these were analyzed to obtain estimates for the physico-chemical parameters as functions of position. The present work is intended to serve as a foundation for development of refined models for delamination of coatings on metals.

2. Model development

Furbeth and Stratmann reported that the cathodic delamination process on a coated zinc substrate with a coating defect was the result of a galvanic couple made possible by the high permeability of the coating to oxygen [4–6]. Cathodic reactions at the metal-coating interface were balanced by anodic reactions at the bare metal exposed by the defect. The schematic representation given in Fig. 1 is consistent with the physical descriptions provided by Furbeth and Stratmann [4–6] and designates regions that distinguish the cathodic delamination system. The coating defect shown represents an uncoated section of metal which may be the result of a scratch in the coating. Adjacent to the defect is the detached region in which the coating is completely detached from the metal. Electrochemical reactions can occur at the exposed metal surface in this region as well as deposition of corrosion products. Furthest from the detached region is the intact region that is representative of the coating in pristine condition without there being any damage to the adhesive bonding between the coating and the metal.

Experimental transient potential profiles associated with the metal-coating interface indicate that there is a propagation of the cathodic delamination into the intact region [6–8]. This propagation occurs through a process in which the adhesive bonds attaching the coating to the metal are progressively degraded until the coating detaches [4]. The bonds between the coating and the metal may be attacked by hydroxide ions or by free radicals associated with oxygen reduction reactions.

Thus, the intact region is separated from the detached region by a zone where there is the weakened coating attachment due to the partially degraded bonds at the metal-coating interface.
interface. Furbeth and Stratmann reported that the coating immediately adjacent to the metal surface consists of a highly oxidized polymer gel within the zone between the detached and intact regions [4]. Based on the reported transient potential distributions this zone can be divided into delaminated and front regions (see Fig. 1). The delaminated region represents a location where the delamination process has occurred and the front region represents a location where the delamination process is ongoing. The process by which the detached region grows is therefore accomplished by two moving regional interfaces, one being the interface between the detached and delaminated regions and the other between the front and intact regions.

The delaminated, front and intact regions may be characterized by changes in porosity as shown in Fig. 1. Evidently, the porosity in the detached and defect regions must be equal to unity. The smallest porosity is seen in the intact region, and the porosity is somewhat larger in the delaminated region due to the bonds between the coating and the metal being partially broken. The representation of porosity shown in Fig. 1 is necessarily qualitative, but it reflects the idea that the porosity must somehow make a transition from the value associated with electrolyte ($\varepsilon = 1$) in the detached region to the value associated with the intact region ($\varepsilon = \varepsilon_{\infty}$). The experimental results of Furbeth and Stratmann suggest that there is a non-unity porosity within the delaminated region and that the porosity associated with the front region can be defined in terms of the transition from the porosity of the delaminated region to the porosity of the intact coating.

The model development presented here is restricted to the delaminated, front and intact regions shown in Fig. 1. Due to the difference in porosity of the regions, one modeling approach would be to treat the regions separately and to account for the motion of inter-regional boundaries explicitly. The alternative approach employed was to model a domain encompassing all the regions with the porosity distribution addressed by an expression that related the local porosity at a given position with the local pH. This approach allowed simulation of the growth of the regions within a fixed domain encompassing the delaminated, front and intact regions. The inter-regional delaminated-front and front-intact boundaries were not fixed during the simulation. The motion of inter-regional boundaries can therefore be seen to be a consequence of the contributing
phenomena. The model accounted for transport within the regions undergoing cathodic delamination, the relationship between porosity and physical properties, and the relationship between the rates of electrochemical reactions and physical properties.

2.1. Transport processes

In dilute electrochemical systems the flux of a species \( i \) is given by

\[
N_i = -z_i u_i c_i F \nabla \Phi - D_i \nabla c_i + c_i v
\]

where \( u_i \) is the mobility, \( D_i \) is the diffusion coefficient, \( z_i \) is the charge number, \( c_i \) is the concentration, \( \Phi \) is the solution potential, \( v \) is the local velocity of the electrolyte, and \( F \) is Faraday’s constant [9]. The terms on the right-hand side of Eq. (1) represent, respectively, migration, diffusion, and convection contributions to the flux.

Furbeth and Stratmann reported that the diffusion coefficients of species in the regions undergoing cathodic delamination were two orders of magnitude smaller than in an aqueous medium [4–6]. The diffusion coefficient of a species in a porous environment \( D_i^* \) can be related to the porosity of the environment by [10]

\[
D_i^* = \varepsilon^{1.5} D_i
\]

where \( \varepsilon \) is the porosity of the environment. The flux of species in a porous environment \( N_i^* \) was therefore given by

\[
N_i^* = \varepsilon^{1.5} (-z_i D_i c_i \nabla \phi - D_i \nabla c_i) = \varepsilon^{1.5} N_i
\]

where diffusion coefficients and mobility values were related by the Nernst–Einstein equation \( D_i = u_i R_g T \), \( R_g \) is the molar gas constant, \( T \) is the temperature, and \( \phi \) is the dimensionless potential \( \phi = (\Phi F) / (R_g T) \). Convection, \( c_i v \) in Eq. (1), was neglected. The governing equations developed in this work are written in a more compact form using the dimensionless potential instead of the dimensional potential.

Conservation of a species in a porous environment can be expressed as

\[
\frac{\partial (\varepsilon c_i)}{\partial t} = -\nabla \cdot (\varepsilon^{1.5} N_i) + R_i
\]

where the term on the left-hand side represents the rate of change of concentration with time \( t \) (accumulation) and the terms on the right-hand side represent the net input due to the flux \( N_i \) and the net rate of production by homogeneous reactions \( R_i \), respectively.

2.2. Dependence of porosity on pH

Under the assumption that the bond degradation can be attributed to attack by hydroxide ions, a relationship between porosity and pH is proposed in this section. Furbeth and Stratmann reported that, during the cathodic delamination process, the coating at the metal-coating interface undergoing delamination degrades to a gel-type medium and the adhesive bond between the coating and the metal is weakened [4]. The cathodic delamination process has been linked to the presence of \( \text{OH}^- \) ions generated by the cathodic oxygen reduction reaction [11,12].

Experimental results revealed that in the delaminated and front regions the concentrations of the two major species, \( \text{Na}^+ \) and \( \text{OH}^- \), were approximately equal [4]. Therefore,
the distribution of $c_{\text{OH}^-}$ can be assumed to be similar to that observed for $c_{\text{Na}^+}$. The adhesive strength between the coating and the metal was measured as a function of position by the de-adhesion test [4]. Comparison of experimental $c_{\text{OH}^-}$ and adhesive strength distributions indicated that at a high pH the adhesive strength was low and that at a low pH the adhesive strength was high. This observation is consistent with the experimental observation that the $\text{OH}^-$ ion was linked to the degradation of the coating and the weakening of the adhesion between the metal and the coating.

As indicated in Eq. (2), the transport of species in the delaminated and front regions is influenced by the porosity of the gel-type medium. Since the adhesion strength between coating and metal and the degradation of the coating are both related to pH, the porosity of the gel-medium was also assumed to be related to the local pH within the delamination zone.

The experimental results of Furbeth and Stratmann [4] were used to guide development of an appropriate relationship between porosity and pH. Their results indicated that the adhesive strength increased monotonically with position. Therefore, the interfacial porosity was assumed to decrease monotonically with position. This assumption was consistent with the reasoning that coating degradation was associated with increased porosity. Following Furbeth and Stratmann [4], an assumed spatial distribution for $\varepsilon$ is given in Fig. 2a. In the delaminated region, $\varepsilon$ was assumed to vary non-linearly with position from values of $\varepsilon_1$ to $\varepsilon_2$. The $\varepsilon$-distribution in the front region was non-linear with $\varepsilon$ decreasing from $\varepsilon_2$ to $\varepsilon_3$. The porosity was assigned a uniform value of $\varepsilon_3$ in the intact region.

The relationship between $\varepsilon$ and pH was constructed by coupling the distributions shown in Fig. 2a and the pH-distribution reported by Furbeth and Stratmann [4]. The resulting $\varepsilon$–pH distribution is shown in Fig. 2b. An expression for the $\varepsilon$–pH relationship was obtained by fitting an equation of the form

$$
\varepsilon = \frac{b_{\varepsilon,1}}{1 + \exp(b_{\varepsilon,2}(\text{pH} - b_{\varepsilon,3}))} + \frac{b_{\varepsilon,4}}{1 + \exp(b_{\varepsilon,5}(\text{pH} - b_{\varepsilon,6}))} + b_{\varepsilon,7}
$$

(5)

to the plot in Fig. 2b where $b_{\varepsilon,1-7}$ were fitting parameters. The fitting parameters associated with the assumed $\varepsilon$–pH distribution shown in Fig. 2b are given in Table 1. The porosity was assumed to reach the value given by Eq. (5) instantaneously; thus the $\varepsilon$–pH

![Fig. 2. Calculated values of the interfacial porosity (a) as a function of position and (b) as a function of pH along the metal-coating interface at the initial time.](image-url)
relationship represented an equilibrium condition between $\varepsilon$ and pH. While the form of Eq. (5) was chosen to provide a good description of experimental profiles, a simpler version using only four parameters yielded calculation results similar to those reported here.

The phenomena of bond-breakage and coating degradation involve chemical reactions. When the time constants for these phenomena are large compared to the time constants for the processes of diffusion and migration, the assumption that the equilibrium value of $\varepsilon$ is attained instantaneously is invalid. A more appropriate, non-equilibrium relationship between $\varepsilon$ and pH was considered

$$\frac{\partial \varepsilon}{\partial t} = -k_{\text{neq}} (\varepsilon - \varepsilon_{\text{eq}})$$

where the equilibrium porosity $\varepsilon_{\text{eq}}$ was given by Eq. (5) and $k_{\text{neq}}$ was a rate constant for the bond-breakage and coating degradation phenomena. In the limit that $k_{\text{neq}} \to \infty$ the value of $\varepsilon$ attains its equilibrated value $\varepsilon = \varepsilon_{\text{eq}}$. In the limit that $k_{\text{neq}} \to 0$ then $\frac{\varepsilon}{\partial t} \approx 0$ and the value of the local porosity is unchanged.

### 2.3. Dependence of polarization kinetics on pH

The rates of heterogeneous reactions are known to be strongly influenced by pH-dependent changes at the metal surface. Expressions for the polarization kinetics at the metal-coating interface were based on expressions applicable to a bare metal surface. The behavior of the reversible reaction involving zinc is described by activation polarization. Only the forward zinc dissolution reaction

$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e$$

was considered because the backward reaction, involving the deposition of zinc, is negligible in the delaminated, front and intact regions. In an aqueous medium with a bare zinc surface, the current density due to zinc dissolution $i_{\text{Zn}}$ can be obtained using the Tafel expression

$$i_{\text{Zn}} = i_{0,\text{Zn}} 10^{(V - E_{\text{Zn}}^0)/\beta_{\text{Zn}}}$$

where $\beta_{\text{Zn}}$ is the Tafel slope, $E_{\text{Zn}}^0$ is the equilibrium potential, and $i_{0,\text{Zn}}$ is the exchange current density for the zinc dissolution reaction, respectively. The potential $V$ is defined as

$$V = E - \Phi$$

### Table 1

<table>
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<th>$k$</th>
<th>$b_{\varepsilon,k}$</th>
<th>$b_{\text{wO,k}}$</th>
<th>$b_{\text{wA,k}}$</th>
<th>$b_{\text{wZn,k}}$</th>
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<tr>
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<td>-4</td>
<td>-7</td>
</tr>
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<td>10.5</td>
</tr>
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<td>0.0001</td>
<td>$1 \times 10^{-12}$</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>$1 \times 10^{-6}$</td>
<td>-</td>
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</tr>
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</table>
where $E$ is the metal potential and $\Phi$ the potential of the medium adjacent to the metal surface. The current density due to zinc dissolution reaction at the zinc-coating interface $i_{\text{Zn}}^{\text{coat}}$ was calculated using

$$i_{\text{Zn}}^{\text{coat}} = w_{\text{O}_2} w_{\text{Zn}} i_{0, \text{Zn}} 10^{(V-E_{E^{0,\text{Zn}}})/\beta_{\text{Zn}}}$$  \(10\)

where $w_{\text{A}}$ and $w_{\text{Zn}}$ were weighting parameters. The surface area parameter $w_{\text{A}}$ represented the surface area available for the reaction where

$$w_{\text{A}} = \frac{\text{available area for electrochemical reaction}}{\text{area of surface}}$$  \(11\)

The exchange current density for an electrochemical reaction is dependent on the nature of the surface of the metal. Experimental observations indicated that the anodic metal dissolution reaction at a metal-coating interface is inhibited or poisoned [1,4]. At a metal-coating interface the exchange current would be very different from that of an electrolyte-metal interface. The poisoning parameter $w_{\text{Zn}}$ represented the influence of surface on the exchange current density where

$$w_{\text{Zn}} = \frac{i_{0, \text{Zn}}^{\text{coat}}}{i_{0, \text{Zn}}}$$  \(12\)

and $i_{0, \text{Zn}}^{\text{coat}}$ was the exchange current density for zinc dissolution at a metal-coating interface.

The oxygen reduction reaction was assumed to follow

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$$  \(13\)

and be mass-transfer-limited at the metal-coating interface. The current density due to oxygen reduction on the metal-coating interface $i_{\text{O}_2}^{\text{coat}}$ was calculated using

$$i_{\text{O}_2}^{\text{coat}} = -w_{\text{A}} w_{\text{O}_2} i_{\text{lim}, \text{O}_2}^{\text{coat}}$$  \(14\)

where $i_{\text{lim}, \text{O}_2}^{\text{coat}}$ was the mass-transfer-limited current density for oxygen reduction at the metal-coating interface, and $w_{\text{O}_2}$ was a weighting parameter. The blocking parameter $w_{\text{O}_2}$ addressed the reduction in the transport of oxygen due to the presence of a porous salt film. The value of $i_{\text{lim}, \text{O}_2}^{\text{coat}}$ at any given position along metal surface (see Fig. 1) was calculated using

$$i_{\text{lim}, \text{O}_2}^{\text{coat}} = -nFD_{\text{O}_2} c_{\text{O}_2} \infty \frac{\varepsilon^{1.5} g_c^{1.5} \varepsilon_c^{1.5}}{\gamma^{1.5} g_c^{1.5}}$$  \(15\)

where $g_m$ and $\varepsilon$ are the thickness and porosity, respectively, of the locally degraded coating, and $g_c$ and $\varepsilon_c$ are the thickness and porosity, respectively, of the intact coating. Eq. (15) accounts for the effective resistance to transport of two diffusion barriers in series.

The polarization parameters $w_{\text{A}}$, $w_{\text{Zn}}$, and $w_{\text{O}_2}$ were used in the calculation of the current densities. These parameters were assumed to be functions of pH and the construction of relationships for these parameters and pH were performed in a manner similar to the construction of the $E$–pH relationship. The relationships for these parameters are shown in Fig. 3.

In the plots shown in Fig. 3, positions associated with pH values <8.7, between 8.7 and 11, and >11 were located in the intact, front, and delaminated regions, respectively. The values of $w_{\text{A}}$ and $w_{\text{Zn}}$ increased monotonically in the front region. This change was based on the assumption that the smallest and largest values of the surface area and poisoning
parameters were associated with positions in the intact and delaminated regions, respectively. The value of $w_{O_2}$ was the largest in the front region and decreased towards the intact and delaminated regions. This was based on the assumption that salt films were absent in the front region.

Expressions for the relationships shown in Fig. 3 were obtained by fitting by inspection equations of the form

$$w_A = \frac{b_{wA,1}}{1 + \exp(b_{wA,2}(pH - b_{wA,3}))} + \frac{b_{wA,4}}{1 + \exp(b_{wA,5}(pH - b_{wA,6}))} + b_{wA,7} \quad (16)$$

for the surface area parameter,

$$w_{O_2} = \left( \frac{b_{wO_2,1} \exp(-b_{wO_2,2}(pH - b_{wO_2,3}))}{1 + b_{wO_2,1} \exp(-b_{wO_2,2}(pH - b_{wO_2,3})) + b_{wO_2,7}} \right) \cdot \left( \frac{1}{1/b_{wO_2,4} + \exp(-b_{wO_2,5}(pH - b_{wO_2,6})) + b_{wO_2,8}} \right) \quad (17)$$

Fig. 3. Graphical representations of polarization parameters as functions of pH. (a) Surface area available for reaction $w_A$, (b) blocking parameter for oxygen reduction $w_{O_2}$, and (c) poisoning parameter for zinc dissolution $w_{Zn}$. 
for the blocking parameter, and
\[
W_{\text{Zn}} = \frac{b_{w_{\text{Zn}}1}}{1 + \exp(b_{w_{\text{Zn}}2}(pH - b_{w_{\text{Zn}}3}))} + \frac{b_{w_{\text{Zn}}4}}{1 + \exp(b_{w_{\text{Zn}}5}(pH - b_{w_{\text{Zn}}6}))} + b_{w_{\text{Zn}}7}
\]  
(18)
for the poisoning parameter. In Eqs. (16)–(18), \(b_{w_{\text{A}1-7}}, b_{w_{\text{O}21-8}}\), and \(b_{w_{\text{Zn}1-7}}\) were fitting parameters. The fitting parameters associated with the assumed distributions shown in Fig. 3 are given in Table 1.

3. Numerical method

The solution method included representing the delaminated, front and intact regions as a one-dimensional domain with two boundaries. There were no boundaries specified between these regions. The two boundaries were located at the detached-delaminated regional interface and an external boundary at the end of the intact region. The approach taken here was similar to that employed by Walton et al. [13] and Sharland [14] to model corrosion in crevices. The ionic species considered in the model were \(\text{Na}^+, \text{Cl}^-\), \(\text{OH}^-\), and \(\text{Zn}^{2+}\). The details of the numerical method are presented by Allahar [15].

Eq. (4) was rewritten for a one-dimensional domain as
\[
\frac{\partial (\varepsilon c_i)}{\partial t} = -\varepsilon^{1.5} \frac{\partial N_i}{\partial x} - N_i \frac{\partial \varepsilon^{1.5}}{\partial x} + S_i
\]  
(19)
where \(S_i\) is the rate of production of the species due to heterogeneous reactions. Homogeneous reactions were not considered; thus \(R_i\) was omitted in Eq. (19).

The conservation equations for species \(\text{Na}^+\) and \(\text{Cl}^-\), which did not participate in heterogeneous reactions, were obtained by assigning \(S_{\text{Na}^+} = 0\), and \(S_{\text{Cl}^-} = 0\). The conservation equations for \(\text{Zn}^{2+}\) and \(\text{OH}^-\) were formulated using
\[
S_{\text{Zn}^{2+}} = \frac{i_{\text{coat}}^{\text{Zn}}}{2F}
\]  
(20)
and
\[
S_{\text{OH}^-} = \frac{i_{\text{coat}}^{\text{O}_2}}{-F}
\]  
(21)
where \(i_{\text{Zn}}^{\text{coat}}\) and \(i_{\text{O}_2}^{\text{coat}}\) were given by Eqs. (10) and (14), respectively.

The domain was assumed to be electrically neutral [9], i.e.
\[
\sum_i z_i c_i = 0
\]  
(22)
The constitutive relationship for the \(\varepsilon-\text{pH}\) relationship was given by Eq. (5) under the assumption that the porosity and pH attained equilibrium instantaneously.

The governing equation for \(c_i\)
\[
\frac{\partial (\varepsilon c_i)}{\partial t} = z_i D_i \left( c_i \varepsilon^{1.5} \frac{\partial^2 \phi}{\partial x^2} + \varepsilon^{1.5} \frac{\partial c_i}{\partial x} \frac{\partial \phi}{\partial x} + 1.5 c_i \varepsilon^{0.5} \frac{\partial \phi}{\partial x} \frac{\partial \varepsilon}{\partial x} \right)
\]
\[
+ D_i \left( \varepsilon^{1.5} \frac{\partial^2 c_i}{\partial x^2} + 3 \varepsilon^{0.5} \frac{\partial c_i}{\partial x} \frac{\partial \varepsilon}{\partial x} + 1.5 \varepsilon^{0.5} c_i \frac{\partial^2 \varepsilon}{\partial x^2} + 0.75 \varepsilon^{0.5} \frac{\partial \varepsilon}{\partial x} \frac{\partial \phi}{\partial x} \right) + S_i
\]
(23)
was obtained by introducing the one-dimensional form of Eq. (1) for stagnant environments into Eq. (19). The system of governing equations consisted of equations of the form of
Eq. (23) for each specie, electroneutrality, Eq. (22), and the porosity–pH relationship equation (5). The system of governing equations was discretized at each node in the domain using approximations for the derivatives. The first order temporal derivative was used where terms of the order \( (\Delta t) \) and higher was neglected in the temporal derivative. The spatial derivatives for a non-boundary node used the central finite difference approximation and the spatial derivative for the external boundary node used the backward difference approximation. Terms of the order \( (\Delta x)^2 \) and higher were neglected in the spatial derivatives.

The detached-delaminated boundary represented the beginning of the delaminated region (see Fig. 1) and was assigned a position \( x = 0 \). The conditions at this boundary were fixed at \( c_i = c_{i,0}, \Phi = \Phi_0, \) and \( \varepsilon = \varepsilon_0 \). The external boundary represented the end of the intact region far from the delaminated region. A no-flux boundary condition was used for the species at this boundary. The initial conditions used are described in a subsequent section. This approach allowed treatment of a moving boundary problem without explicit numerical treatment of the inter-regional boundaries.

The governing equations for \( c_i \) and \( \phi \) in the domain were discretized in time and space and cast into the matrix form

\[
K \cdot C^{n+1} = R
\]

where \( C^{n+1} \) was the solution vector containing the values of \( c_i, \phi, \) and \( \varepsilon \) at the time step \( n + 1 \). The coefficient matrix \( K \) was a function of \( C^{n+1} \) and the load vector \( R \) was a function of \( C^n \) the vector containing the values of \( c_i, \phi, \) and \( \varepsilon \) at time step \( n \). An iterative algorithm employing Newton’s method was used to solve the system of coupled, non-linear, partial differential equations [16]. The details of this procedure are given by Allahar [15]. The algorithm was used for the solution of the \( C^{n+1} \) at each time step with a convergence criterion of 0.01%.

4. Simulation results

The model was used to simulate the evolution of the electrochemistry of a coating section undergoing cathodic delamination with assumed initial conditions. The initial conditions, simulated results, and a discussion of these results are presented in this section.

The geometric parameters used in the model included a coating thickness \( g_c = 50 \mu m \), a gel-medium thickness \( g_m = 5 \mu m \), and a net length of 0.4 cm for the delaminated, front and intact regions. The initial lengths of these regions were 0.1, 0.05, and 0.25 cm, respectively. The grid size for the numerical method was 10 \( \mu m \), and the time step was 0.1 s. The potential of the metal was chosen as \( E = -1 \) V (SCE) to be consistent with the metal being under a cathodic potential. The potential \( \Phi \) reported was with respect to the potential at the defect boundary.

The diffusion coefficient values assigned for the defect and detached regions (with \( \varepsilon = 1 \)) were \( D_{Na^+} = 1.3341 \times 10^{-5} \) cm\(^2\)/s, \( D_{Cl^-} = 2.0344 \times 10^{-5} \) cm\(^2\)/s, \( D_{OH^-} = 5.2458 \times 10^{-5} \) cm\(^2\)/s, \( D_{Zn^{2+}} = 0.71231 \times 10^{-5} \) cm\(^2\)/s, and \( D_{O_2} = 1.9000 \times 10^{-5} \) cm\(^2\)/s [9]. The concentration of dissolved oxygen at the surface of the coating was \( 1.26 \times 10^{-3} \) M [9].

4.1. Initial distributions

The objective of this work was to explore the propagation phase of the delamination process. Thus, an initial condition was established which reflected a system after the
delamination process had begun. The detached-delaminated boundary at \( x = 0 \) is reported to be highly alkaline with pH values as high as 13 to 14 reported in the literature [11]. The value for \( c_{\text{Na}^+} \) at position \( x = 0 \) was set to \( c_{\text{Na}^+,0} = 10^{-1} \) M such that, under the assumption that \( c_{\text{OH}^-} \approx c_{\text{Na}^+}, \) the pH at that position would be equal to 12. The values of \( c_{\text{Na}^+} \) and \( c_{\text{Cl}^-} \) were then used to calculate the initial concentration distributions shown in Fig. 4a. There was a monotonic decrease with position in the value of \( c_i \) for all the species except \( \text{Zn}^{2+} \) which was used to maintain electroneutrality in the intact region.

The initial distributions for \( c_i \) were used to calculate the initial potential distribution that is shown in Fig. 4b. The value of potential increased with position in all the regions. In the delaminated region (\( x = 0 \) to \( x = 0.1 \) cm at \( t = 0 \)) the potential gradient was small as compared to the gradient in the front region (\( x = 0.1 \) to \( x = 0.15 \) cm at \( t = 0 \)). In the intact region (\( x = 0.15 \) to \( x = 0.4 \) cm at \( t = 0 \)) the potential was approximately uniform. The variation of potential with position for the calculated initial distribution was consistent with experimentally observed potential distributions. This consistency demonstrated that the assumptions used in deriving the initial distributions for \( c_i, e, \) and the polarization parameters were reasonable for the propagation phase of the cathodic delamination process.

4.2. Potential distributions

The distributions calculated for the interfacial potential \( V \) are shown in Fig. 5a with elapsed time as a parameter. The initial distribution for \( V \) included discontinuities caused by assumptions needed to create the initial distributions. These discontinuities were reduced significantly after 10 s (0.167 min) of elapsed time. The shape of the distribution of \( V \) remained similar to the 10 s distribution throughout the remainder of the simulation. This result agrees with experimental observations reported by Furbeth and Stratmann [6]. The maintenance of the shape indicated that the phenomena considered in the model could sustain the profile of \( V \) while the delamination front propagated along the metal-coating interface into the intact region.

The potential in the intact region was observed to increase by 40 mV with time over the duration of the simulation. This result was inconsistent with the reported results of Furbeth and Stratmann for the cathodic delamination associated with zinc [6]. The reason
for this increase in potential for the intact region may be propagation of error in the time steps or use of time-independent boundary conditions at \( x = 0 \). Relaxation of these assumptions may lead to better agreement between the simulated and experimental potential results in the intact region.

Following the approach of Leng and Stratmann [2], the potential distributions were differentiated with respect to position to yield distributions of \( \frac{dV}{dx} \) as shown in Fig. 5b with elapsed time as a parameter. The position \( x_{\text{del}} \) was associated with a peak of a \( \frac{dV}{dx} \) distribution and represented the point of inflexion for the \( V \) distribution located in the front region. The value of \( x_{\text{del}} \) increased with time indicating that the front propagated along the metal-coating interface. The rate of this propagation is discussed in a subsequent section.

The peak height corresponded to the value of \( \frac{dV}{dx} \) at the peak position \( x_{\text{del}} \) and decreased with time for the simulated results. The trend of decreasing peak height with time was consistent with the experimental results reported for the cathodic delamination of coated iron [2]. The explanation given by Leng and Stratmann to account for this trend was that, with time, there was a more gradual change in the conditions across the front region [2]. The simulated results presented below supported this explanation as the differences between the values of the dependent variables \( c_i, \Phi, \) and \( \varepsilon \) in the delaminated and intact regions were reduced during the simulation. The width of the \( \frac{dV}{dx} \) distribution increased with time as seen in Fig. 5. This result was not consistent with the experimental results on iron [2].

4.3. Concentration distributions

The distribution for pH is shown in Fig. 6a with elapsed time as a parameter. The pH in the intact region approached a uniform value that was independent of time. The shape of the distribution remained similar to the shape of the 10 s distribution over the simulation. The phenomena considered in the model were able sustain the profile of pH while the delamination front propagated along the metal-coating interface.

The calculated results showed that the pH at any position within the delaminated region increased with time and the pH in the intact region remained unchanged. The increase in pH can be attributed to the electrochemical production of OH\(^-\) and the flux...
of OH\(^{-}\), \(N_{OH^{-}}\), from the detached regions into the regions under cathodic delamination. The production of OH\(^{-}\) by oxygen reduction along the metal-coating interface can be seen in the distribution of the absolute value of \(i_{O_2}^\text{coat}\) along the metal-coating interface (see Fig. 7a). There was an increase in the electrochemical reactivity at the metal-coating interface as the delamination front propagated into the intact region.

The distribution of \(N_{OH^{-}}\) is shown in Fig. 7b with elapsed time as a parameter. For a given distribution, the value of \(N_{OH^{-}}\) decreased with position in the front region. The value of \(N_{OH^{-}}\) was negligible for positions in the intact region when compared to values in the other regions. The value of \(N_{OH^{-}}\) for a position in the delaminated region decreased with time and for positions in the front region \(N_{OH^{-}}\) increased slightly with time.

The change in pH per unit time was largest for the positions in the front region immediately adjacent to the intact region. This can be attributed to the flux of OH\(^{-}\) towards the intact region that was driven by concentration gradients (see Fig. 7b). Fig. 7b suggests that the propagation of the delamination process involved a decreasing trend for the flux of OH\(^{-}\) in the delaminated region and an increasing trend for positions in the intact region.

Fig. 6. Calculated distributions along the metal-coating interface with elapsed time in minutes as a parameter.
(a) pH and (b) \(c_{Na^+}\).

Fig. 7. Calculated distributions along the metal-coating interface with elapsed time in minutes as a parameter.
(a) Oxygen reduction current density and (b) hydroxide ion flux.
The change in pH with position across the regions became more gradual with time. This supported the explanation given by Leng and Stratmann for the decreasing \( \frac{dV}{dx} \) peak height trend that was observed experimentally for coated iron surfaces \(^2\).

The calculated distributions for \( c_{Na^+} \) are shown in Fig. 6 with elapsed time as a parameter. The trends associated with the \( c_{Na^+} \) distributions were consistent with the trends of the pH distributions. During the course of the simulation the change of \( c_{Na^+} \) with position across the delaminated and front regions became more gradual as the delamination process propagated into the intact region. The increase in the value of \( c_{Na^+} \) was approximately equal to the increase observed for \( COH^- \) at any given position in the delaminated or front regions.

The increase in the value of \( COH^- \) at any position was attributed to the production of \( COH^- \) ions by the oxygen reduction reaction and the flux of \( OH^- \) towards the intact region. The zinc dissolution reaction was considered to be poisoned at the metal-coating interface. Therefore, to satisfy electroneutrality a flux of \( Na^+ \) into the delaminated and front regions was needed. This flux included the migration of \( Na^+ \) facilitated by the positive electric filed \( \frac{dV}{dx} \) and the diffusion of \( Na^+ \) due to the negative concentration gradient of \( Na^+ \). The distribution of the flux of \( Na^+ \) is shown in Fig. 8a with elapsed time as a parameter. A positive value for \( Na^+ \) indicated a net transport of \( Na^+ \) into the delaminated and front regions. For a given distribution the value of \( Na^+ \) decreased with position as the intact region was approached. Although the delaminated/front boundary was not clearly identifiable in the distributions of \( V \), it was observed that the value of \( Na^+ \) at any position <0.1 cm decreased with time. Thus the value of \( Na^+ \) in the delaminated region reduced with time while the value of \( Na^+ \) at any position in the front region increased with time.

The changes in the values of \( Na^+ \) and \( OH^- \) over the 30 min simulation can be seen in Fig. 8b. In this figure the values of \( Na^+ \) and \( OH^- \) as functions of position are shown at 10 s and 30 min elapsed times. After 10 s the value of \( Na^+ \) was greater than \( OH^- \) for positions <0.1 cm. The values of \( Na^+ \) and \( OH^- \) were approximately equal for positions >0.1 cm. During the 30 min simulation, for a position <0.125 cm the decrease in \( OH^- \) was larger than the decrease associated with \( Na^+ \). Whereas, for a position >0.125 cm and <0.26 cm, the increase associated with \( Na^+ \) was larger than the increase associated with \( OH^- \). This result demonstrates that there was a net flux of positive ions into the delaminated, front, and intact regions from the detached region.

![Fig. 8. Calculated distributions of the flux along the metal-coating interface with elapsed time in minutes as a parameter. (a) Na\(^+\) and (b) Na\(^+\) and OH\(^-\).](image-url)
4.4. Interfacial porosity distributions

The calculated porosity distribution is shown in Fig. 9a with elapsed time as a parameter. The shape of the interfacial porosity distribution was maintained throughout the simulation. As the delamination front propagated into the intact region, the interfacial porosity increased to satisfy the equilibrium $\varepsilon$–pH relationship. The increase in the value of $\varepsilon$ with time at any position in the front region was reflected by increased flux of species in these regions (see Figs. 8a and 7b).

The calculated distribution of the interfacial porosity gradient along the metal-coating interface is shown in Fig. 9b with elapsed time as a parameter. The peak associated with a given distribution corresponded to the front of the interfacial porosity. The velocity of the interfacial porosity front was associated with the degradation of the coating and the breakage of the adhesive bonds between the metal and the coating. Thus, the velocity of the interfacial porosity front represents the true delamination rate.

4.5. Front velocities

The instantaneous front velocities, calculated from the time-dependent position of the maxima given in Figs. 5b and 9b, are presented in Fig. 10. The rate initially is very large but exponentially decreases to a constant value, indicated in Fig. 10 by the dotted lines. The rate of front propagation based on the potential front was found to be 2.154 mm/h; whereas, the rate of front propagation based on the porosity front was found to be 1.781 mm/h. These values can be compared to the rate of propagation of about 0.8 mm/hr reported by Furbeth and Stratmann for iron [6].

4.6. Polarization parameters

The polarization parameters $w_{O_2}$, $w_A$ and $w_{Zn}$ were assumed to be pH-dependent and expressions for these dependencies were developed. The distributions for $w_{O_2}$, $w_A$ and $w_{Zn}$ are shown in Fig. 11 with elapsed time as a parameter. The shape of the distribution for a given parameter was maintained throughout the simulation because the shape of the

![Fig. 9. Calculated distributions along the metal-coating interface with elapsed time in minutes as a parameter. (a) Porosity and (b) gradient of porosity.](image-url)
pH-distribution was also maintained throughout the simulation. The delaminated, front, and intact regions can be identified in the distributions for $w_{O_2}$. The delaminated and front regions grew in length with time.

Fig. 10. Instantaneous front velocities, calculated from the time-dependent position of the maxima given in Figs. 5a and 9b. The dotted lines correspond to the limiting values obtained by regression of an exponential decay model.

Fig. 11. Calculated distributions of polarization parameters along the metal-coating interface with elapsed time as a parameter. (a) Surface coverage parameter $w_A$, (b) blocking parameter $w_{O_2}$, and (c) poisoning parameter $w_{Zn}$. 

4.7. Influence of non-equilibrium porosity pH relationship

To explore the role of finite rates of bond breakage, the equilibrium relationship between porosity and pH, given as Eq. (5) was replaced by Eq. (6). The resulting distributions of interfacial potential are shown in Fig. 12a and b for $k_{\text{neq}} = 0.1 \text{ s}^{-1}$ and $k_{\text{neq}} = 0.001 \text{ s}^{-1}$, respectively. The corresponding distributions of interfacial potential gradient $dV/dx$ are shown in Fig. 13a and b. As shown in Fig. 13a and b, the changes in potential progress as a moving front, much as was seen in Fig. 5a for an equilibrium pH–porosity relationship. The potential front velocity taken from Fig. 13a ($k_{\text{neq}} = 0.1 \text{ s}^{-1}$) and extrapolated to long times was 2.5 mm/h, slightly larger than the value calculated for the equilibrium pH–porosity relationship. A result based on equilibrium porosity–pH relationship was expected to provide an upper bound for the more realistic case where the rate of bond breakage limits the process of delamination. The unexpected result is attributed here to propagation of numerical errors. More recent work is dedicated to improving the numerical algorithm. The potential front velocity taken from Fig. 13b ($k_{\text{neq}} = 0.001 \text{ s}^{-1}$) and extrapolated to long times was 2.1 mm/h.

![Fig. 12. Calculated distribution of potential along the metal-coating interface with elapsed time as a parameter. (a) $k_{\text{neq}} = 0.1 \text{ s}^{-1}$ and (b) $k_{\text{neq}} = 0.001 \text{ s}^{-1}$.]

![Fig. 13. Calculated distribution of potential gradient $dV/dx$ along the metal-coating interface with elapsed time as a parameter. (a) $k_{\text{neq}} = 0.1 \text{ s}^{-1}$ and (b) $k_{\text{neq}} = 0.001 \text{ s}^{-1}$.]
The corresponding distributions of porosity are shown in Fig. 14a and b. The appearance of a moving front evident in Fig. 14a for $k_{\text{neq}} = 0.1 \, \text{s}^{-1}$ is less apparent in Fig. 14b for $k_{\text{neq}} = 0.001 \, \text{s}^{-1}$. As seen in the corresponding distributions of porosity gradient $d\varepsilon/dx$ (Fig. 15a and b), the lower value for $k_{\text{neq}}$ results in a gradual increase in porosity in the region of increased pH. Thus, the potential front suggested in Figs. 12b and 13b corresponds to the boundary of a region in which bond-breakage is taking place, but does not correspond to the position of a delamination front.

The potential front correlates more closely to the distributions of pH shown in Fig. 16a and b. A pH front velocity, calculated using the protocol established for the potential front, agrees well with the potential front velocity. A value of 2.4 mm/h was obtained for ($k_{\text{neq}} = 0.1 \, \text{s}^{-1}$) which is close to the value of 2.5 mm/h based on the calculated potential. A value of 2.1 mm/h was obtained for ($k_{\text{neq}} = 0.001 \, \text{s}^{-1}$) which is identical to that based on calculated potential. The decreased value of pH front velocity seen for $k_{\text{neq}} = 0.001 \, \text{s}^{-1}$ can be attributed to the lower value for diffusivity in the region of reduced porosity.

Fig. 14. Calculated distribution of porosity along the metal-coating interface with elapsed time as a parameter. (a) $k_{\text{neq}} = 0.1 \, \text{s}^{-1}$ and (b) $k_{\text{neq}} = 0.001 \, \text{s}^{-1}$.

Fig. 15. Calculated distribution of porosity gradient $d\varepsilon/dx$ along the metal-coating interface with elapsed time as a parameter. (a) $k_{\text{neq}} = 0.1 \, \text{s}^{-1}$ and (b) $k_{\text{neq}} = 0.001 \, \text{s}^{-1}$.
5. Discussion

The mathematical approach presented in this work is well suited for the analysis of cathodic delamination. The development presented here was based on the assumption that the delamination is caused by breakage of bonds between the coating and the metal. A kinetic relationship was established which could account for the irreversible increase in local porosity associated with bond breakage. While the formalism presented here was based on hydroxide ions as the causative agent, the framework presented could account as well for the proposed role of OH\(^-\) free radicals.

The simulations are in qualitative agreement with recent experiments on the cathodic delamination of coated metals which have used the Scanning Kelvin Probe to measure the potential distribution at the buried metal-coating interface\(^1\)–\(^8\). The interfacial potential results have shown that there is a propagation of a front during the cathodic delamination of a coated metal. The experiments have also shown that there exists large differences in interfacial potential and concentrations between the delaminated and intact regions.

The propagation of the front during the cathodic delamination of coated zinc was simulated by the model. This result supported the hypotheses that the interfacial porosity and interfacial polarization kinetics contributed to the front propagation. The simulated distributions for the dependent variables, fluxes of species, and polarization parameters were reconciled to the propagation of the front into the intact region. The flux distributions of Na\(^+\) and OH\(^-\) demonstrated that the net transport of the positively charged Na\(^+\) ion was in response to the production of the negatively charged OH\(^-\) ion at the interface of the front.

The pH-dependent interfacial porosity represented a novel approach at implicitly accounting for the breakage of adhesive bonds between the coating and the metal. The mathematical model presented is the first model that simulates the propagation of the front during cathodic delamination. In this model only the conditions in the regions undergoing cathodic delamination were simulated. The galvanic couple between the defect and detached regions and these regions was not accurately accounted for as the conditions at the detached-delaminated boundary were fixed. The coupling of this model to a model for the defect and detached regions is the basis of future work.

Fig. 16. Calculated distribution of pH along the metal-coating interface with elapsed time as a parameter. (a) \(k_{\text{eq}} = 0.1\) s\(^{-1}\) and (b) \(k_{\text{eq}} = 0.001\) s\(^{-1}\).
6. Conclusions

The qualitative agreement between the simulated and experimental results for the cathodic delamination process on zinc in the delaminated, front and intact regions supported the assumption that the porosity and polarization kinetics can be treated as functions of pH. The use of porosity to represent the bond-breaking process occurring during the cathodic delamination process provides a mathematical framework for the development of advanced models.

The analysis of the simulated results demonstrated the strength of the model at understanding the coupled electrochemical processes that occur during cathodic delamination. This analysis together with the concepts of pH-dependent porosity and polarization kinetics can be used to improve the existing mechanistic model for cathodic delamination process on zinc.

The simulated results obtained from the model were in qualitative agreement with those reported by Furbeth and Stratmann for coated zinc [4–6]. This agreement suggests that the physics included in the mathematical model represented, in part, the phenomena contributing to the cathodic delamination process. Simulated results for potential, concentrations, and physico-chemical parameters were used to demonstrate the performance of the model at simulating the cathodic delamination process.

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