An extended finite-element model coupled with level set method for analysis of growth of corrosion pits in metallic structures

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Mass balance between metal and electrolytic solution, separated by a moving interface, in stable pit growth results in a set of governing equations which are solved for concentration field and interface position (pit boundary evolution). The interface experiences a jump discontinuity in metal concentration. The extended finite-element model (XFEM) handles this jump discontinuity by using discontinuous-derivative enrichment formulation, eliminating the requirement of using front conforming mesh and re-meshing after each time step as in the conventional finite-element method. However, prior interface location is required so as to solve the governing equations for concentration field for which a numerical technique, the level set method, is used for tracking the interface explicitly and updating it over time. The level set method is chosen as it is independent of shape and location of the interface. Thus, a combined XFEM and level set method is developed in this paper. Numerical analysis for pitting corrosion of stainless steel 304 is presented. The above proposed model is validated by comparing the numerical results with experimental results, exact solutions and some other approximate solutions. An empirical model for pitting potential is also derived based on the finite-element results. Studies show that pitting profile depends on factors such as ion concentration, solution pH and temperature to a large extent. Studying the individual and combined effects of these factors on pitting potential is worth knowing, as pitting potential directly influences corrosion rate.
1. Introduction

Stable pit growth is the third stage of pitting corrosion, the first two being breakdown of the passive layer [1] and metastable pit growth [2]. Owing to breakdown of the passive layer, rapid dissolution occurs within the pit, i.e. the metal undergoes oxidation. While anodic oxidation of the metal takes place within the pit, cathodic reduction takes place on the remaining surface of the metal. As the cathodic area is large compared with the anodic area, current flows to the extremely small anodic region, increasing the current density and potential difference between anodic and cathodic regions. Owing to these reasons, pitting corrosion is considered as an electrochemical and self-stimulating process [3,4]. Rapid dissolution of the metal results in accumulation of excess positive charge within the pit. To maintain the electro-neutrality, the anionic species such as chloride ions migrate to the pit to form a metal chloride solution. Thus, the pit is enriched with an acidic metal chloride solution that acts as a driving force for further pitting corrosion. Formation of a salt layer on the pit surface is enforced owing to the increase in ionic concentration within the pit solution that reaches supersaturation conditions [5,6]. The ionic concentration of the salt layer is known as the saturation concentration, as a notion of chemical equilibrium [7,8] between anodic and cathodic reactions. The movement of the dissolved metal ions in the pit governs the movement of the electrode boundary of the pit, making it a diffusion-controlled process. In simple words, pitting corrosion is a process that accelerates with time and is autocatalytic in nature. Metal composition, nature of electrolytic solution and potential difference are the important factors that can affect the pit growth rate. The mass-transport characteristics of the pit influence pit growth kinetics through the pit electrolyte concentration. Ionic flux in the pit solution is driven by Fick’s law of diffusion [9]. This problem requires a detailed mass balance formulation between the metal and the electrolytic solution that can model a sharp moving electrode boundary [10]. Stable pitting corrosion of the metal is a diffusion-controlled dissolution process with a moving boundary. Such a problem is known as the classic Stefan problem [11].

Stable pits grow at potential, which is much higher than repassivation potential, and is known as the pitting potential. Pitting corrosion is a complex phenomenon and is influenced by many different parameters, including the environment, metal composition, potential, velocity, temperature and surface condition. Temperature is the most primary factor that governs pitting corrosion, because most of the materials are corrosion resistant at temperatures below a certain value [12]. The next important factor is the environment to which the metal is exposed, which means pitting corrosion is directly related to the aggressive nature of the ions present in the environment. Halide ions are considered to be the most aggressive anions owing to their high reactivity nature. And the metal composition is also responsible for pitting corrosion [13]. Studying the combined effect of these parameters on pitting potential is worth investigating for quantifying pitting corrosion.

The most conventional numerical way to solve such problems is by the moving mesh method. The moving mesh method requires a front-conforming mesh, i.e. the generated mesh has to be aligned with the discontinuity or the current interface location and also has to be updated at every time step. Although it produces accurate results, applying this method for complex geometries becomes iterative and redundant. Another major drawback is handling nonlinearities and post-processing requires more effort. For pit growth problems, the interface evolves with time making the moving mesh methods inefficient. In re-meshing techniques, as the pit or the crack grows, a new mesh has to be generated at every time step. The nodal shape functions and all the finite-element matrices have to be calculated for every time step, making it a repetitive process. For a dynamic analysis, the new mesh has to updated with the history of the field variables. The process of mapping variables from the old mesh to the new mesh may also result in loss of accuracy. The extended finite-element method is an extension of the conventional finite-element method [14,15], in which the discontinuities can be embedded to standard finite-element approximation using enrichment functions. The enriched basis is formed by the combination of the nodal shape functions associated with the mesh and the product of nodal shape functions with discontinuous functions. The enrichment functions are constructed using signed distance functions that describe
concentration gradients across the interface. The enrichment is only confined to the local domain of interest. This method eliminates the necessity for re-meshing, front-conforming mesh and can be used effectively for modelling complex geometries that are independent of mesh. All these properties provide this method with a striking advantage over the standard finite-element method for modelling arbitrary discontinuities. The level set method [16,17] is an attractive numerical technique to track the moving interface as it is independent of shape and contour of the moving interface. It uses the signed distance function to represent the interface and updates it over time retaining the interface as the signed distance function all the time. This property is taken as an advantage to identify the enriched nodes and compute enriched matrices in the extended finite-element model (XFEM). The coupling of the level set method with XFEM is very effective for solving moving interface problems such as growth (pit, biofilm), phase change, crack growth problems [18–21].

From the reviewed literature, it is quite clear that a robust numerical model for solving Galvanic pitting corrosion problem is currently not available. The main objective of this paper is to develop an extended finite-element model (FEM) for obtaining a pitting profile on an element subjected to environmental parameters such as ion concentration, temperature, pH, etc. The developed model will use the level set approximation to determine the metal electrolyte boundary. Both one- and two-dimensional XFEM models are developed. The developed XFEM models are used to derive empirical formulae for pitting potential as a function of temperature, pH and concentration. Such formulae will be very useful to designers. The paper is organized as follows: §2 briefly describes the governing equations of the pit growth model. The extended finite-element formulation along with the overview of the coupling with the level set method is presented in §3. Section 4 details the level set methodology for tracking and updating the interface position. The summary of the complete procedure is given as an algorithm in §5. Empirical models for pitting potential variation are developed in §6. Validation of the proposed model, by comparing the numerical results with exact, experimental results and some approximate solutions, is presented in §7.

2. Governing model

Consider the domain \( \Omega \) (figure 1) comprising two subdomains, namely solid metal domain \( \Omega_{\text{solid}} \) and pit or electrolytic solution domain \( \Omega_{\text{pit}} \). Let the concentration field in \( \Omega \) be \( c(x, t) \). Pit solution domain \( \Omega_{\text{pit}} \) remains a subset of \( \Omega \) at all times and is bounded by \( \Gamma_{\text{pit}}(t) = \Pi_{\text{lacy}} \cup \Gamma_{\text{int}}(t) \), which is assumed to remain regular at all times. The boundary \( \Pi_{\text{lacy}} \), known as lacy cover, is the fixed boundary of the pit. The boundary \( \Gamma_{\text{int}}(t) \), known as the interface between solid metal and pit solution, is the moving boundary of the pit with normal velocity \( v_{\text{outward}} \) and interface ionic flux \( \vec{J} \).

Subdomain \( \Omega_{\text{solid}} \) contains solid metal \( P \), whose apparent mass density \( \rho_{\text{solid}} \) and average molar mass \( \bar{M}_{\text{solid}} \) are used to define the ion concentration \( c_{\text{solid}} \) by the equation \( c_{\text{solid}} = \rho_{\text{solid}}/\bar{M}_{\text{solid}} \). \( \Gamma_{\text{solid},c} \) is the Dirichlet boundary for concentration, on which a constant value \( c_{\text{solid}} \) is prescribed. It is a function of time and at a distance of \( d_s \) away from the interface \( \Gamma_{\text{int}} \) (in the direction of evolution) at any particular time. The Neumann boundary for concentration is prescribed on \( \Gamma_{\text{solid},\vec{J}} \).

As the solid metal \( P \) undergoes oxidation (\( P \rightarrow P^{2+} + e^- \)), excess positive charge accumulates in the pit solution, which is neutralized by migrated chloride ions, and leads to an increase in the overall ionic concentration until chemical equilibrium between solid metal and electrolytic solution is achieved. This results in the formation of the salt film at the interface \( \Gamma_{\text{int}}(t) \), also known as the dissolution phenomenon. Constant saturation concentration \( c_{\text{sat}} \) and concentration \( c_{\text{solid}} \) are observed on the electrolytic side \( \Gamma_{\text{int}}^- \) and solid side \( \Gamma_{\text{int}}^+ \) of the interface, respectively. This leads to a jump discontinuity of magnitude \( (c_{\text{solid}} - c_{\text{sat}}) \) at the interface \( \Gamma_{\text{int}} \). Diffusion behaviour of the dissolved metal ions governs the movement of the interface \( \Gamma_{\text{int}}(t) \).
Figure 1. Domain representation $\Omega = \Omega_{\text{solid}} \cup \Omega_{\text{pit}}$.

Subdomain $\Omega_{\text{pit}}$ is the pit or electrolytic solution containing dissolved metal ions. The ion concentration field falls in the range of $0 \leq c \leq c_{\text{sat}}$ due to the fact that the dissolved metal ions reach the saturation concentration $c_{\text{sat}}$ at the electrolytic side of the interface $\Gamma_{\text{int}}$. The basic relation for conductive ion transport is Fick’s law, which states that the driving force of the transport of the solute is the concentration gradient. Fick’s law of diffusion is mathematically represented as $J = -D \nabla c$, where $J$ is the ionic flux, $D$ is the effective diffusion coefficient. $D$ depends on temperature and is governed by the Einstein relation $D / D_0 = T / T_0$, where $D_0$ is the diffusion coefficient measured at room temperature $T_0 = (273.20 + 25) \, \text{K}$. Bulk solution is the domain outside the pit, in which the concentration field is taken as zero.

The governing equations for domain $\Omega$ are derived by using the mass conservation law. As no metal ions are formed within $\Omega$, we equate the temporal material derivative of the overall mass in $\Omega$ to zero:

$$\frac{dM}{dt} = \frac{dM_{\text{solid}}}{dt} + \frac{dM_{\text{pit}}}{dt} = 0,$$  

(2.1)

where $M_{\text{solid}}$ and $M_{\text{pit}}$ are total mass quantities in the $\Omega_{\text{solid}}$ and $\Omega_{\text{pit}}$, respectively. The detailed explanation of the derivation is given in [22] and repeated here. Substituting the expressions for $M_{\text{solid}}$ and $M_{\text{pit}}$, equation (2.1) results in the following equation

$$\int_{\Omega_{\text{pit}}} \left[ \frac{\partial c}{\partial t} - \nabla \cdot (D \nabla c) \right] \, d\Omega + \int_{\Gamma_{\text{int}}} (D \nabla c) \cdot n - (c_{\text{solid}} - c_{\text{sat}}) v \, d\Gamma = 0.$$  

(2.2)

Equation (2.2) holds for any subdomain $\Omega_{\text{pit}}$ and for any surface of discontinuity $\Gamma_{\text{int}}(t)$. Therefore, the governing partial differential equation for mass balance expressed by the local continuity equation in the pit solution $\Omega_{\text{pit}}$ is given by

$$\frac{\partial c}{\partial t} - \nabla \cdot (D \nabla c) = 0,$$  

(2.3)

and the jump or Rankine–Hoginiot condition across interface $\Gamma_{\text{int}}(t)$ is given by

$$\bar{J} = -(D \nabla c)|_{\Gamma_{\text{int}}} \cdot n = (c_{\text{solid}} - c_{\text{sat}}) v.$$  

(2.4)

The boundary conditions for the pit solution $\Omega_{\text{pit}}$ are

$$c = 0 \quad \text{on } \Pi_{\text{lacy},c}$$  

(2.5)

and

$$- D \nabla c \cdot n = 0 \quad \text{on } \Pi_{\text{lacy},J},$$  

(2.6)

where $\Pi_{\text{lacy},c}$ denotes the Dirichlet boundary for the concentration and $\Pi_{\text{lacy},J}$ denotes the Neumann boundary for the ionic flux normal, meeting the requirements $\Pi_{\text{lacy}} = \Pi_{\text{lacy},c} \cup \Pi_{\text{lacy},J}$.
Table 1. Summary.

<table>
<thead>
<tr>
<th>domain</th>
<th>description</th>
<th>governing equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk solution</td>
<td>outside the pit</td>
<td>( c = 0 )</td>
</tr>
</tbody>
</table>
| pit solution \( \Omega_{\text{pit}} \) | contains dissolved metal ions and are driven by Fick’s law of diffusion | \( 0 \leq c \leq c_{\text{sat}} \)  
\[
\frac{\partial c}{\partial t}(x, t) - \nabla \cdot (D \nabla c(x, t)) = 0 
\]  
\( \forall x \in \Omega_{\text{pit}} \)  
B.C: on \( \Pi_{lacy} \Rightarrow c = 0 \)  
on \( \Pi_{lacy} \Rightarrow J \cdot n = 0 \)  
I.C: in \( \Omega_{\text{pit}} \Rightarrow c = 0 @ t = 0 \) |
| interface \( \Gamma_{\text{int}} \) | across which ionic concentration exhibits jump discontinuity of magnitude \( (c_{\text{solid}} - c_{\text{sat}}) \) | \[
[-D \nabla c(x, t)] \cdot n(x, t) - (c_{\text{solid}} - c_{\text{sat}}) v = 0 
\]  
\( \forall x \in \Gamma_{\text{int}} \)  
Int.C: on \( \Gamma_{\text{sat}} \Rightarrow c = c_{\text{sat}} \) |
| solid metal \( \Omega_{\text{solid}} \) | contains solid metal \( P \) and undergoes oxidation | \( c = c_{\text{solid}} = \frac{\rho_{\text{solid}}}{M_{\text{solid}}} \) |

and \( \Pi_{lacy,c} \cap \Pi_{lacy,J} = 0 \) along the interface \( \Gamma_{\text{int}}(t) \). These are the boundary conditions applicable on fixed boundary of the pit. The initial condition for the pit solution \( \Omega_{\text{pit}} \) is

\[
@ t = 0 : c = 0 \quad \text{in} \quad \Omega_{\text{pit}}. 
\]  
(2.7)

The interface concentration condition along the electrolytic side of the interface \( \Gamma_{\text{int}}(t) \) is

\[
c = c_{\text{sat}} \quad \text{on} \quad \Gamma_{\text{int}}^{-}. 
\]  
(2.8)

For the solid metal domain \( \Omega_{\text{solid}} \)

\[
c = c_{\text{solid}} = \frac{\rho_{\text{solid}}}{M_{\text{solid}}} \quad \text{on} \quad \Gamma_{\text{solid,c}} 
\]  
(2.9)

and

\[
-D \nabla c \cdot n = 0 \quad \text{on} \quad \Gamma_{\text{solid,J}}. 
\]  
(2.10)

The set of governing equations (2.3) and (2.4), along with condition equations (2.5)–(2.10), is solved simultaneously for the concentration profile within the pit and interface location or the moving boundary of the pit. Table 1 summarizes the complete model description and governing equations of the individual subdomains.

3. Extended finite-element model formulation

The set of governing equations (2.3) and (2.4), with boundary conditions, is the strong form of the problem, which represent a set of equilibrium equations. The weak form is a variational statement of the problem which is an alternate statement of equilibrium. The aim of the weak form is to convert the governing PDE of the problem into a set of ODEs for the temporal-dependent problem and algebraic equation for a static problem. This is carried out by assuming the variation of the dependent variable (in the present case, it is concentration) through the use of some basis functions. By this, the problem can be relaxed such that instead of finding an exact solution everywhere (which is often very difficult in most cases), we are finding a solution that satisfies the strong form of the governing PDE is an approximate sense over the domain.

The method of weighted residual (MWR) is used here to obtain the weak form. When a solution is assumed over a domain for the dependent variable, the assumed solution will never satisfy the governing equations exactly, leaving behind certain residues. The objective of the MWR is to force this residual to zero in some average sense over the domain. The test function \( w \) consists
of weight functions equal to the number of unknowns in $c$. This results in a set of $m$ algebraic equations for the unknowns in $c$. The exact solution satisfies each and every weight. Multiplying the equation (2.3) with a test function $w$ and integrating by parts, we obtain

$$\int_{\Omega} w \left[ \frac{\partial c}{\partial t} - \nabla \cdot (D \nabla c) \right] \, d\Omega = 0 \quad (3.1)$$

and

$$\int_{\Omega} w \frac{\partial c}{\partial t} \, d\Omega + \int_{\Omega} \nabla w \cdot (D \nabla c) \, d\Omega = \int_{\Pi_{lacy,c}} w(D\nabla c) \cdot \mathbf{n} \, d\Gamma + \int_{\Pi_{lacy,J}} w(D\nabla c) \cdot \mathbf{n} \, d\Gamma + \int_{\Gamma_{solid,c}} w(D\nabla c) \cdot \mathbf{n} \, d\Gamma + \int_{\Gamma_{solid,J}} w(D\nabla c) \cdot \mathbf{n} \, d\Gamma \quad (3.2)$$

The boundary condition equation (2.6) can be used for part $\Pi_{lacy,J}$. The test function $w$ is chosen such that it satisfies the homogeneous boundary conditions wherever the actual solution satisfies Dirichlet boundary conditions (equation (2.5)), thus we can set $w$ to zero on $\Pi_{lacy,c}$. Equation (2.9) acts as Dirichlet boundary condition for part $\Gamma_{solid,c}$ and flux on Neumann boundary $\Gamma_{solid,J}$ is considered as zero (equation (2.10)). The test function $w$ is piecewise continuously differentiable and vanishes on the Dirichlet boundary of the domain. The form of equation (2.3) can be written as

$$\int_{\Omega} w \frac{\partial c}{\partial t} \, d\Omega + \int_{\Omega} \nabla w \cdot (D \nabla c) \, d\Omega = 0. \quad (3.3)$$

The time derivative of $c$ follows the $\theta$-family of approximation:

$$\Delta t [\theta \dot{c}_{n+1} + (1 - \theta) \dot{c}_n] = \dot{c}_{n+1} - \dot{c}_n \quad \text{for } 0 \leq \theta \leq 1, \quad (3.4)$$

where $n$ is the current time step. For $\theta = 0$, the scheme is known as explicit Euler with forward difference approximation and for $\theta = 1$, it is known as implicit Euler with backward difference approximation. $\theta = \frac{1}{2}$ yields the Crank–Nicolson scheme. The clear disadvantage of choosing $\theta = 0$ as time step must be restricted in order to achieve a stable solution. Choosing $\theta = 1$, equation (3.4) yields

$$\dot{c}_{n+1} = \frac{\dot{c}_{n+1} - \dot{c}_n}{\Delta t} \Rightarrow \dot{c}^n = \frac{\dot{c}_n - \dot{c}_{n-1}}{\Delta t}. \quad (3.5)$$

Using the $\theta$-method and replacing the time derivative of $c$ with backward difference approximation equation (3.5), equation (3.3) can be written in the following form

$$\frac{1}{\Delta t} \int_{\Omega} w^n (c^n - c^{n-1}) \, d\Omega + \int_{\Omega} \nabla w^n \cdot (D \nabla c)^n \, d\Omega = 0. \quad (3.6)$$

A solution of the strong form will also satisfy the weak form, but not vice versa. The finite element method is used to compute the approximate solution. The concentration gradient is discontinuous at the interface $\Gamma_{int}$. This discontinuity in the concentration gradient is embedded into finite-element approximation using enrichment functions. We define the enrichment function $\psi_i(x,t)$ as

$$\psi_i(x,t) = (|\phi(x,t)| - |\phi(x_i,t)|), \quad (3.7)$$

where $\phi(x,t)$ is the signed distance function, which defines the location of the interface by taking the value zero along the interface. It is also known as the level set function and its variation is explained in detail in the next section. Such enrichment functions are known as ramp functions.
and are used to incorporate strong discontinuities in gradient of a function in the domain. The physical domain $\Omega$ is divided into finite elements and is approximated as

$$c(x, t) = \sum_{i \in M_{\text{std}}} N_i(x) C_i(t) + \sum_{j \in M_{\text{enr}}} N_j(x, t) \psi_j(x, t) a_j(t). \tag{3.8}$$

The matrix form of equation (3.8) can be written as

$$c(x, t) = N(x, t) C(t), \tag{3.9}$$

where

$$N(x, t) = [N_1 N_2 \ldots N_m N_1 \psi_1 N_2 \psi_2 \ldots N_{m_e} \psi_{m_e}] = [N_{\text{std}} N_{\text{enr}}] \tag{3.10}$$

and

$$C(t) = [C_1 C_2 \ldots C_m a_1 a_2 \ldots a_{m_e}]^T = [C_{\text{std}} A_{\text{enr}}], \tag{3.11}$$

where $N_i(x)$ are the standard finite-element shape functions, $C_i$ are nodal degrees of freedom (unknown concentrations to solve for), $M_{\text{std}}$ contains the set of all nodes with total number of nodes $m$, $\psi_j(x, t)$ are enriched functions, $a_j$ are nodal enrichment degrees of freedom, $M_{\text{enr}}$ contains the set of enriched nodes with total number of enriched nodes $m_e$ and satisfying the condition $M_e \subset M$. $N_{\text{std}}$ contains the standard finite-element shape functions and $N_{\text{enr}}$ contains the enriched shape functions. Similarly, $C_{\text{std}}$ is the vector of concentration degree of freedom and $A_{\text{enr}}$ is the additional degree of freedom added to the system. The fully enriched element is defined as an element crossed by the interface and its corresponding nodes are known as enriched nodes. Elements adjacent to the fully enriched element are known as partially enriched elements; they act as blending elements between fully enriched and standard finite elements. The enrichment is applicable only to the enriched elements and thus adding additional degrees of freedom to the elements. In the case of two-node linear element, standard finite element has two degrees of freedom, whereas the fully enriched element has four degrees of freedom and the partially enriched element has three degrees of freedom [14,23]. Figure 2 shows the XFEM mesh defining the enriched nodes. Considering a fully enriched element with enriched nodes $a$ and $b$, where $a, b \subset M_{\text{enr}}$, the enriched shape functions $N_a \psi_a$ and $N_b \psi_b$ take the value zero at both enriched nodes $a$ and $b$, and also are discontinuous at the interface, whereas the summation $N_a \psi_a + N_b \psi_b$ becomes linear between the interface and enriched nodes.

In Galerkin’s formulation, the test function $w(x, t)$ is approximated in a similar way to $c(x, t)$. Weighting functions taken in the approximation of the test function $w$ are the same as basis functions.
functions taken in the approximate solution of \( c \). The approximation for concentration field equation (3.9) is substituted in the weak form equation (3.6) and yields the following discretized form

\[
\frac{1}{\Delta t} M^n C^n + K^n C^n = \frac{1}{\Delta t} M^{n-1} C^{n-1},
\] (3.12)

where \( M, K \) are mass and stiffness matrices, respectively. \( C \) is the nodal concentration vector. They follow the standard definition as in the conventional finite-element method. The simplified form of mass matrix \( M \) is

\[
M^n = \int_{\Omega} (N^n)^T N^n \, d\Omega = \begin{bmatrix} M^n_{s-s} & M^n_{s-e} \\ M^n_{e-s} & M^n_{e-e} \end{bmatrix}
\]

\[
= \begin{bmatrix} \int_{\Omega} N_{\text{std}} N_{\text{std}} \, d\Omega & \int_{\Omega} N_{\text{std}} N_{\text{enr}} \, d\Omega \\ \int_{\Omega} N_{\text{enr}} N_{\text{std}} \, d\Omega & \int_{\Omega} N_{\text{enr}} N_{\text{enr}} \, d\Omega \end{bmatrix}.
\] (3.13)

In a similar way, \( M^{n-1} \) can be expanded. The stiffness matrix \( K \) is defined as

\[
K^n = \int_{\Omega} \nabla(N^n)^T \mathbf{D} \nabla N^n \, d\Omega = \begin{bmatrix} K^n_{s-s} & K^n_{s-e} \\ K^n_{e-s} & K^n_{e-e} \end{bmatrix}
\]

\[
= \begin{bmatrix} \int_{\Omega} \nabla N_{\text{std}} \nabla N_{\text{std}} \, d\Omega & \int_{\Omega} \nabla N_{\text{std}} \nabla N_{\text{enr}} \, d\Omega \\ \int_{\Omega} \nabla N_{\text{enr}} \nabla N_{\text{std}} \, d\Omega & \int_{\Omega} \nabla N_{\text{enr}} \nabla N_{\text{enr}} \, d\Omega \end{bmatrix}.
\] (3.14)

The interface Dirichlet boundary condition, i.e. interface concentration \( c = c_{\text{sat}} \) (equation (2.8)), must also be imposed to the above finite-element equation (3.12), which is done by adding the following equality constraint,

\[
\lambda = c - c_{\text{sat}} = 0 \quad \text{on } \Gamma_{\text{int}}^{-}.
\] (3.15)

This method of imposing the interface concentration condition on the enriched field through the above constraint equation is known as the penalty method [24,25], in which the quadratic terms of constraints multiplied by a penalty parameter \( \beta \) are introduced in the finite-element energy equation. The enriched energy equation contains the term \( \int_{\Gamma_{\text{int}}^{-}} \beta \lambda^T \lambda \, d\Gamma \) signifying the constraint contribution. This relaxes the constrained problem to the unconstrained problem. As the signed distance function \( \phi(x_{\Gamma_{\text{int}}^{-}}, t) = 0 \) along the interface \( \Gamma_{\text{int}}^{-} \), the concentration field along the interface can be written as (from equations (3.7) and (3.8))

\[
c = \sum_{i \in M} N_i C_i - \sum_{j \in M_e} N_j |\phi_j| a_j \quad \text{along } \Gamma_{\text{int}}^{-}.
\] (3.16)

Substituting the expression (3.16) in equation (3.15), we obtain

\[
\lambda = \sum_{i \in M} N_i C_i - \sum_{j \in M_e} N_j |\phi_j| a_j - c_{\text{sat}}
\] (3.17)

and

\[
\lambda = N|_{\text{int}} C - c_{\text{sat}}.
\] (3.18)

where \( N|_{\text{int}} = [N_1 N_2 \ldots N_m - N_1 |\phi_1| - N_2 |\phi_2| \ldots - N_{m_e} |\phi_{m_e}|] \).
Figure 3. Subelement division of enriched elements: plus, standard finite; asterisks, sublinear; solid line, subtriangles; slash, subquadrilateral.

The penalty terms, penalty stiffness matrix and penalty force vector, computed along the interface, are the additional contributions to the finite-element equation. The global penalty matrices are mostly populated with zeros as they are calculated only along the interface, i.e. they contain only enriched degrees of freedom. The penalty stiffness matrix is given by

\[ K_p^n = \beta \int_{\Gamma_{int}} (N^n)^T N^n \, d\Gamma \]  

and the penalty force vector is given by

\[ F_p^n = \beta \int_{\Gamma_{int}} (N^n)^T c_{sat} \, d\Gamma. \]  

Adding the above two expressions to the global finite-element equation (3.12):

\[ \frac{1}{\Delta t} M^n C^n + K^n C^n + K_p^n C^n = \frac{1}{\Delta t} M^{n-1} C^{n-1} + F_p^n. \]  

Standard Gauss quadrature cannot be applied while computing coefficient matrices in equation (3.21). As the enriched elements contain the discontinuity, the standard Gauss quadrature produces inadequate integration of the elemental matrices. For accurate and correct integration, the enriched element has to be divided into subelements with boundaries coinciding with the interface (discontinuity). Division can be of two types: subpolygons or subtriangles. While computing the elemental matrices, the integration loop over the element is replaced by a loop over the subelements. The subelements are integrated individually using the standard Gauss quadrature rule. Division of the fully enriched element into subelements increases accuracy and is purely intended for integration purposes; therefore, the shape of subelements does not matter. Figure 3 shows subelemental division for an enriched element. In the case of a two-node linear fully enriched element, the element is divided into two sublinear elements with two Gauss quadrature points each.

The next aspect in the modelling is the determination of the moving interface, which is obtained using the level set method. An extended finite-element mesh is used to solve the concentration field, whereas the finite difference grid is used to update the level set function. Taking the initial interface location, interface concentration condition and boundary conditions as inputs, XFEM constructs the signed distance function and computes the concentration field in the domain. The level set engine constructs the extended velocities, taking the signed distance function and concentration field as inputs from XFEM. The level set function is updated over time using the computed extended velocities, and the new interface location is obtained from the updated level set function. The XFEM engine takes the new interface location as input to solve for concentration field for the following time step. The advantage of using XFEM is that the entire finite-element mesh need not be re-meshed at every time step. Only in the vicinity of the interface, the matrices are reconstructed, i.e. for every time step, enriched elements are identified using the level set function, and the corresponding matrices are recalculated. XFEM mesh consists
of line elements in the case of a one-dimensional problem and triangular elements in the case of a two-dimensional problem. The set mesh is a finite difference grid composed of line elements in the case of a one-dimensional problem and square elements in the case of a two-dimensional problem. The new interface location is mapped onto the XFEM mesh using bilinear interpolation.

4. Level set method

The level set method is a numerical technique used for analysing and tracking moving interfaces. The interface can be evolved by representing it with isocontours of a level set function \( \phi \). Without the knowledge of the exact location [26,27] of the interface, it can be moved implicitly by updating the level set function \( \phi \). At all times, the interface is represented as its zero level:

\[
\Gamma_{\text{int}} = \{ x : \phi(x,t) = 0 \}.
\]

We initialize the level set function \( \phi \) as a signed distance function,

\[
\phi(x,t) = \min_{x_{\Gamma_{\text{int}}} \in \Gamma_{\text{int}}} \| x - x_{\Gamma_{\text{int}}} \| \text{sign}(n \cdot (x - x_{\Gamma_{\text{int}}})) \), (4.1)
\]

where \( \phi \) follows (figure 4):

\[
\phi(x,t) = \begin{cases} 
> 0, & x \in \Omega_{\text{solid}} \\
0, & x \in \Gamma_{\text{int}} \\
< 0, & x \in \Omega_{\text{pit}}.
\end{cases}
\]

The level set function evolves in time according to the advection equation,

\[
\frac{D\phi}{Dt} = \frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \frac{\partial \phi}{\partial t} + V_{\text{nor}} \| \nabla \phi \| = 0, (4.2)
\]

where \( D/Dt \) is the total time derivative which enforces the condition that \( \phi \) remains constant on the interface, \( \mathbf{V} \) is the flow velocity field and \( V_{\text{nor}} \) is the scalar velocity field (also known as speed function or extension velocity). \( V_{\text{nor}} \) is defined as the dot product of the flow velocity \( \mathbf{V} \) and surface normal \( \mathbf{n} \):

\[
V_{\text{nor}} = \mathbf{V} \cdot \mathbf{n} = \mathbf{V} \cdot \frac{\nabla \phi}{\| \nabla \phi \|}. (4.3)
\]

From this, one sees that it is sufficient to evolve the level set function with the normal component of the advection velocity \( \mathbf{V} \). Prior to \( \phi \) update, scalar velocity field \( V_{\text{nor}} \) must be constructed on the domain \( \Omega_{\text{pit}} \). Solving equation (4.2) through level set method involves three steps, namely

- constructing scalar velocity field \( V_{\text{nor}} \);
- time updation; and
- reinitialization of \( \phi \).

(a) Construction of scalar velocity field \( V_{\text{nor}} \)

As the normal velocity \( v \) at the interface \( \Gamma_{\text{int}} \) can be computed directly from equation (2.4) and acts as a boundary condition while constructing \( V_{\text{nor}} \) on the domain \( \Omega \). The level set equation along the interface \( \Gamma_{\text{int}} \) can be written as

\[
\frac{\partial \phi}{\partial t} + v \| \nabla \phi \| = 0. (4.4)
\]
Before we construct $V_{\text{nor}}$, we need to compute $V = \{V^1, V^2, V^3, V^4\}$ on the whole domain. The expanded discretized form of equation (4.3) is

$$V_{\text{nor},i,j} = \frac{1}{2} \left[ V_{i,j}^1 \left( \frac{\phi_x}{\|\nabla \phi\|} \right)_{i,j} + V_{i,j}^2 \left( \frac{\phi_y}{\|\nabla \phi\|} \right)_{i,j} + V_{i,j}^3 \left( \frac{\phi_\eta}{\|\nabla \phi\|} \right)_{i,j} + V_{i,j}^4 \left( \frac{\phi_\zeta}{\|\nabla \phi\|} \right)_{i,j} \right],$$

where $V^1, V^2, V^3$ and $V^4$ are components of flow velocity $\mathbf{V}$ along the four coordinate directions $x, y, \eta$ and $\zeta$. Figure 4 shows the finite difference grid composed of square elements. The domain is discretized in only two dimensions. $x, y$ are standard Cartesian coordinates and $\eta, \zeta$ are 45° rotated coordinates. This is carried out to cut down the grid orientation effects and also due to the fact that the sign of flow velocity components drives the discretization of spatial first derivatives of $\phi$.

Along the interface $\Gamma_{\text{int}}$, the flow velocity $\mathbf{V}_{i,j} = \{V^1, V^2, V^3, V^4\}_{i,j}$ is computed using Rankine–Hugoniot jump condition or equation (2.4):

$$V_{i,j}^1 = -\frac{D}{(c_{\text{solid}} - c_{\text{sat}})} \left( \frac{\partial c}{\partial x} \right)_{i,j},$$

$$V_{i,j}^2 = -\frac{D}{(c_{\text{solid}} - c_{\text{sat}})} \left( \frac{\partial c}{\partial y} \right)_{i,j},$$

$$V_{i,j}^3 = -\frac{D}{(c_{\text{solid}} - c_{\text{sat}})} \left( \frac{\partial c}{\partial \eta} \right)_{i,j}$$

and

$$V_{i,j}^4 = -\frac{D}{(c_{\text{solid}} - c_{\text{sat}})} \left( \frac{\partial c}{\partial \zeta} \right)_{i,j}.$$

Away from the interface $\Gamma_{\text{int}}$, the flow velocity $\mathbf{V}_{i,j} = \{V^1, V^2, V^3, V^4\}_{i,j}$ is computed using the following discretizations [28]:

$$V_{i,j}^1 = -\frac{D}{(c_{\text{solid}} - c_{\text{sat}})} \frac{S_{i,j}(\phi_x)((C_{i+2,j} - C_{i+1,j}) - (C_{i-1,j} - C_{i-2,j}))}{h_x},$$

$$V_{i,j}^2 = -\frac{D}{(c_{\text{solid}} - c_{\text{sat}})} \frac{S_{i,j}(\phi_y)((C_{i,j+2} - C_{i,j+1}) - (C_{i-1,j} - C_{i-2,j}))}{h_y},$$

$$V_{i,j}^3 = -\frac{D}{(c_{\text{solid}} - c_{\text{sat}})} \frac{S_{i,j}(\phi_\eta)((C_{i+2,j+2} - C_{i+1,j+1}) - (C_{i-1,j-1} - C_{i-2,j-2}))}{\sqrt{h_x^2 + h_y^2}},$$

$$V_{i,j}^4 = -\frac{D}{(c_{\text{solid}} - c_{\text{sat}})} \frac{S_{i,j}(\phi_\zeta)((C_{i+2,j+2} - C_{i+1,j+1}) - (C_{i-1,j-1} - C_{i-2,j-2}))}{\sqrt{h_x^2 + h_y^2}}.$$
and
\[
V_{ij}^k = -\frac{D}{(c_{\text{solid}} - c_{\text{sat}})} \frac{S_{ij}(\phi_t)(c_{i+2,j-2} - c_{i+1,j-1}) - (c_{i-1,j+1} - c_{i-2,j+2})}{(\sqrt{h_x^2 + h_y^2})},
\]

(4.13)

where \(h_x\) and \(h_y\) are grid spacing in the \(x\)- and \(y\)-directions, respectively. The sign function \(S\) is defined as +1 for \(\phi > 0\) (solid metal region), −1 for \(\phi < 0\) (pit solution region) and 0 for \(\phi = 0\) (along the interface). It is used to ensure that jumps are consistently computed in the domain.

Once \(\phi\) and \(V\) are defined at every grid point, one needs to evaluate the spatial first derivative of \(\phi\) in equation (4.5). For explanation only one dimension is considered; it can be easily extended for other dimensions with relative ease. Movement of \(\phi\) values is driven by the sign of \(V^1\). If \(V^1 > 0\), it means the values of \(\phi\) are moving from left to right and if \(V^1 < 0\), it means the values of \(\phi\) are moving from right of left. From the method of characteristics, it is well known that \(D_x^-\) should be approximated for \(\phi_x\) when \(V^1 > 0\). Similarly, \(D_x^+\) should be approximated for \(\phi_x\) when \(V^1 < 0\). This method of approximating spatial first derivatives \(V\phi\) depending on the sign of flow velocity \(V\) is known as up-winding. However, simple finite difference methods will fail to conserve the level set shape over the period of time steps. For this reason, higher-order finite difference methods have to be used. The approximations for spatial first derivatives of \(\phi\) can be performed more accurately using a second-order scheme called the essentially non-oscillatory (ENO) scheme. The ENO scheme [29–32] provides better numerical approximations for \(V\phi\) by extending first-order accurate up-winding differencing to higher-order spatial accuracy and it is defined as

\[
(\phi_x)_{ij} = \begin{cases} 
D_x^- \phi_{i,j} + \frac{h_x}{2} \minmod(D_x^- D_x^+ \phi_{i,j}, D_x^- D_x^+ \phi_{i-1,j}), & \text{if } V_{ij}^1 > 0 \\
D_x^+ \phi_{i,j} - \frac{h_x}{2} \minmod(D_x^- D_x^+ \phi_{i,j}, D_x^- D_x^+ \phi_{i+1,j}), & \text{if } V_{ij}^1 < 0,
\end{cases}
\]

(4.14)

where \(D_x^-, D_x^+\) are backward and forward finite difference operators in the \(x\)-direction, respectively. Similarly, approximations for \((\phi_y)_{ij}, (\phi_n)_{ij}\) and \((\phi_t)_{ij}\) can be computed. The \(\minmod\) function in equation (4.14) is defined as

\[
\minmod(a, b) = \begin{cases} 
a, & \text{if } |a| < |b| \text{ and } ab > 0 \\
b, & \text{if } |a| > |b| \text{ and } ab > 0 \\
0, & \text{if } ab \leq 0.
\end{cases}
\]

The process of constructing the scalar velocity field \(V_{\text{nor}}\), which is a continuous extension of \(v\) off \(\Gamma_{\text{int}}\) onto the domain \(\Omega\), is completed by plugging the values of flow velocity field \(V = \{V^1, V^2, V^3, V^4\}\) computed from equations (4.6)–(4.13) and spatial first derivatives \(V\phi\) computed from equation (4.14) into equation (4.5). The above scheme for constructing extended velocities is equivalent to the method in which the orthogonality property of extended velocity with signed distance function is used [26,33,34]. Fast marching methods [35,36] can also adapted for constructing extended velocities, in which reinitialization of the level set function is not required. However, the advantage of the above-explained method of constructing extended velocities can sometimes result in numerical difficulties, which can be avoided while updating the level set function using certain techniques.

(b) Time updation

As the level set equation (4.2) is classified as hyperbolic PDE, choosing a non-total variation diminishing (TVD) scheme for time discretization may provide oscillatory results. TVD schemes are discretization techniques used for solving hyperbolic partial differential equations. Thus, higher-order TVD–Runge–Kutta schemes [37] for time discretization combined with an ENO scheme for spatial discretization provides a stable and non-oscillatory result. The level set
equation (4.2) is integrated in time with a three-step third-order TVD–Runge–Kutta (TVD-RK3) scheme,

\[
\begin{align*}
\phi^{(1)} &= \phi^n + \Delta t L(\phi^n), \\
\phi^{(2)} &= \frac{3}{4} \phi^n + \frac{1}{4} \phi^{(1)} + \frac{1}{4} \Delta t L(\phi^{(1)}), \\
\phi^{n+1} &= \frac{1}{3} \phi^n + \frac{2}{3} \phi^{(2)} + \frac{2}{3} \Delta t L(\phi^{(2)})
\end{align*}
\]  

(4.15)

where \( n \) denotes the current time step, the superscript (.) denotes the Runge–Kutta step. The operator \( L(\phi) \) denotes the numerical approximation of the term \( V_n \| \nabla \phi \| \) in equation (4.2). The new interface’s location \( I_{n+1}^{\text{int}} \) is now equal to the zero level set of \( \phi^{n+1} \). For stability, the time step \( \Delta t \) is required to satisfy CFL condition:

\[
\Delta t \left( \frac{\max |V|}{\min \{|h_x, |h_y|, \ldots\}} \right) \leq \frac{1}{2}.
\]  

(4.16)

(c) Reinitialization of \( \phi \)

The updated level set function, i.e. \( \phi^{n+1} \), is no longer an exact signed distance function. We require \( \phi \) to be a signed distance function throughout the computational time; this ensures the level set function to be well behaved near the interface. Thus, \( \phi \) needs to be reinitialized to be an exact signed distance function from the interface after every time step \([27]\). This is done by evolving the following partial differential equation to steady state

\[
\phi_t + S(\phi_0)(\| \nabla \phi \| - 1) = 0,
\]  

(4.17)

where \( \phi_0 \) is the updated level set function, \( \phi(x,0) = \phi_0 \), \( S \) is the sign function defined by

\[ S_\epsilon(\phi_0) = \frac{\phi_0}{\sqrt{\phi_0^2 + \epsilon^2}} \]

and

\[ \| \nabla \phi \|_{ij} \simeq H_G(D_x^+, D_x^-, D_y^+, D_y^- \phi_{ij}), \]  

(4.18)

where \( D_x^+, D_x^-, D_y^+, D_y^- \) are approximated using the second-order ENO scheme and \( H_G \) is the Gudonov Hamilton \([38]\) given by

\[
H_G(a,b,c,d) = \begin{cases} 
\sqrt{\max((a-)^2, (b^+)^2) + \max((c-)^2, (d^+)^2)}, & \text{if } S(\phi_0) \geq 0 \\
\sqrt{\max((a^+)^2, (b^-)^2) + \max((c^+)^2, (d^-)^2)}, & \text{if } S(\phi_0) < 0.
\end{cases}
\]

Equation (4.17) is evolved in time to steady state using TVD-RK3 method.

5. Algorithm

Here, we provide the complete algorithm for the XFEM-level set coupled solution procedure. Steps (i–iii) use XFEM and steps (iv–ix) use FDG. Given the initial conditions and initial interface location \( I_{n+1}^{\text{int}} \) at \( t = t^n \), we perform the following functions

(i) Construct the signed distance function \( \phi^n \) and define the enrichment function \( \psi^n \).

(ii) Identify the set of enriched nodes \( M_e \) and build global matrices \( K^n, M^n, K_p^n \) and \( F_p^n \) by applying boundary conditions and enforcing interface concentration using penalty method.

(iii) Using direct time integration, solve for the concentration field \( C^n \) in the domain \( \Omega_p^{int} \).

(iv) Initialize the level set function \( \phi^n \) on the domain \( \Omega \), a signed distance function from the interface location \( I_{n+1}^{\text{int}} \) (from \( n+1 \) time step, it is known as reinitialization step).

(v) Compute the interface normal velocity \( v^n \) from the jump condition.
(vi) Construct scalar velocity field \( V^n_{\text{nor}} \) on domain \( \Omega_{\text{pit}} \), which is a continuous extension of \( v^n_{\text{off}} \) off \( \Gamma_{\text{int}} \). Here, spatial first derivatives of \( \phi^n \) are calculated using the second-order ENO scheme.

(vii) Update the level set equation \( \phi_t + V_{\text{nor}}|\nabla \phi| = 0 \), using the third-order TVD–Runge–Kutta method.

(viii) The new interface location \( \Gamma_{\text{int}}^{n+1} \) is equal to the zero level set of \( \phi^{n+1} \).

(ix) Go to step 1 and repeat the process until the final time step is achieved.

6. Pitting potential

In general, pitting starts at a certain critical potential value, known as the pitting potential \( E_p \). Determination of the pitting potential is most important as it is directly related to the intensity of the pitting. Numerous attempts have been made to understand the behaviour of the pitting potential. However, the nature of pitting potential is uncertain for many reasons. Ionic concentration, especially \( \text{Cl}^- \) concentration, largely effects the initiation of pitting. In classical pitting, breakdown of the passive film occurs owing to \( \text{Cl}^- \) penetration. Several experiments have been performed to investigate the behaviour of the pitting potential with respect to ionic concentration. It is believed that a linear relation exists between the pitting potential and ionic concentration. Temperature and pH value variation with pitting potential has also been studied to a large extent. The critical pitting temperature [12] is defined as the lowest temperature at which pitting starts. At higher temperatures, the pitting potential decreases with increasing temperature and chloride concentration. It is well known that the pitting potential decreases with increase in temperature. But, this relation is true only in certain ranges of temperature. It has also been observed that the pitting potential increases with increase in pH value.

Hence, ion concentration, temperature and pH value are the three variables which influence the pitting potential \( E_p \) value to a large extent. Even though studies are performed using various solutions under various environmental conditions, most of the experiments involved observing the effects individually. Therefore, the combined effect of all three variables on the pitting potential is worth knowing. Hence, in this paper, we develop an empirical model for the pitting potential \( E_p \) in terms of all three variables. The FE solution for the concentration field in the pit acts as an input for determining the pitting potential \( E_p \) values within the pit. Nernst’s equation can be used to determine the pitting potential \( E_p \) value. Therefore, pitting potential \( E_p \) values from Nernst’s equation and concentration values \( C \) from FE solution can be used to propose an empirical model for pitting potential \( E_p \) and study its variation on temperature and pH.

(a) Proposed empirical models

From previous works [39,40], it has been observed that the pitting potential follows the relation

\[
E_p = a + bX,
\]

where \( X \) can stand for any of the three variables, namely ion concentration \( c \), temperature \( T \) and pH value, and \( a, b \) are constants. The variable \( X \) can have different variation for different variables. Most work reported based on experiments has measured each of these variations individually. To the authors’ best knowledge, no work is reported in the literature that takes into account all three variables taken together on the values of \( E_p \). From studies regarding individual effects, it is well known that \( E_p \) varies with the logarithm of concentration \( c \), is inversely proportional to temperature and directly proportional to pH. Hence, taking into account all the observations, two empirical models are proposed for pitting potential \( E_p \) taking ionic concentration, temperature and pH value into consideration together, which are given by model 1:

\[
E_{p1} = a_1 + b_1T + c_1(T \log c) + d_1(pH \log c). \tag{6.2}
\]

model 2:

\[
E_{p2} = a_2 + b_2pH + c_2(T \log c) + d_2(pH \log c), \tag{6.3}
\]
where $a, b, c$ and $d$ are known as model parameters. Such mathematical models have already been proposed in [41], in which pitting potential $E_p$ values are experimentally determined. In the above proposed models given in equations (6.2) and (6.3), pitting potential $E_p$ values are computed using Nernst’s equation.

(b) Nernst’s equation

Nernst’s equation is used to calculate equilibrium potentials $E_p$ with the aid of standard potentials

$$E_p = E_0 + \frac{2.3RT}{nF} \ln c,$$

where $E_p$ is the equilibrium potential, $E_0$ is the standard potential, $n$ is the number of transmitted electrons, $c$ is the ionic concentration, $F$ is the Faraday constant and $R$ is the universal gas constant. The standard potentials are tabulated in the literature for standard conditions (metals immersed in a solution of its metal ions with the concentration $c = 1 \text{ mol l}^{-1}$). Plugging the ionic concentrations $c$ obtained from FE solution, pitting potentials $E_p$ can be calculated in the pit using Nernst’s equation.

(c) Least-square approximation

Model parameters $(a, b, c, d)$ in model 1 and model 2 are determined using least-squares approximation. Concentrations from FE solution, pitting potentials from Nernst’s equation, different temperatures assumed in finite-element analysis and solution pH form the discrete data for the empirical models. Discrete data are $(E_{p_i}, T_i, (T \log c_i), (pH \log c_i))$ for $i = 1, 2, \ldots N$ for model 1. Error $Er$ associated with equation (6.2) is defined as

$$Er_1(a, b, c, d) = \sum_{i=0}^{N} [E_{p_i} - (a_1 + b_1 T_i + c_1 (T \log c_i) + d_1 (pH \log c_i))]^2.$$

The main idea behind the least-square methods is to find the values of model parameters that minimize the error, i.e. model parameters are found such that the following conditions are satisfied.

$$\frac{\partial Er_1}{\partial a_1} = 0, \quad \frac{\partial Er_1}{\partial b_1} = 0, \quad \frac{\partial Er_1}{\partial c_1} = 0 \quad \text{and} \quad \frac{\partial Er_1}{\partial d_1} = 0.$$

This yields a linear system of equations in model parameters, which can solved easily. A similar procedure is also followed for determining the model parameters $(a_2, b_2, c_2, d_2)$ for model 2. A model with close relevance to experimental results is chosen to study the variation of pitting potential $E_p$, within the pit, with respect to variables: ionic concentration $C$, temperature $T$ and pH value.

7. Results and discussion

Numerical results for the proposed pitting corrosion model are now presented. The input values for this model are solid metal concentration $c_{\text{solid}}$, saturation concentration of the dissolved metal ions $c_{\text{sat}}$ and effective diffusion coefficient $D$. $c_{\text{solid}}$ can be determined analytically knowing the density and molar mass of the solid metal alloy components, whereas $c_{\text{sat}}$ is determined experimentally. It depends on the electrolytic solution composition, solid metal and environmental conditions. The diffusion coefficient $D$ is also determined experimentally.

The example of stainless steel 304 is considered for analysing the pitting corrosion model. Stainless steel 304 consists of 71.70% of Fe, 17.90% of Cr and 10.40% of Ni as mass fractions. It has the following material properties: density $\rho = 7920 \text{ kg m}^{-3}$ [42], valence $z = 2.19$ and average molar mass $M = 55.39 \text{ g mol}^{-1}$ [43]. For stainless steel 304, $c_{\text{solid}} = 143.0 \text{ mol l}^{-1}$ [44–46]. $c_{\text{sat}}$ for stainless steel 304 has been determined by in situ energy dispersive X-ray analysis, in a 0.5 M HCl + 0.5 M NaCl solution [46,47], from which $c_{\text{sat}} = 5.1 \text{ mol l}^{-1}$ is taken. $D_0 = 0.85 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$
at room temperature 25°C for stainless steel 304, which was determined from rotating disc electrode experiments [48,49].

(a) One-dimensional analysis

Numerical results for one-dimensional stable pitting corrosion are presented here. The domain $\Omega$ of length 0.001 m with unit cross-sectional area is considered. The computational domain is discretized into 100 finite-elements. A two node element with one degree of freedom per node is considered for one-dimensional formulation. This structured mesh consists of $m = 101$ nodes. The interface is crossed by only one element with $m_e = 2$ enriched nodes. Thus introducing two additional degrees of freedom to the system. Total number of degrees of freedom is 103. The mesh consists of 97 standard, two partially enriched and one fully enriched elements. The initial condition is $c(x,0) = 0 \text{ mol l}^{-1}$ at time $t = 0 \text{ s}$. The Dirichlet boundary condition for concentration ($\Pi_lacy,c$) is $c(0,t) = 0 \text{ mol l}^{-1}$ at $x = 0 \text{ m}$. The interface concentration condition is $c(x_{int},t) = c_{sat} = 5.1 \text{ mol l}^{-1}$ at $x = x_{int}$. The initial interface location is given by the exact solution at time $t = 0.5 \text{ s}$. The Dirichlet boundary $\Gamma_{solid,c}$ for concentration is assumed to be at 5 µm away from the interface location $x_{int}$ towards the solid metal side and $c_{solid} = 143 \text{ mol l}^{-1}$ is prescribed on it. Lagrange interpolation function formulation with linear polynomial is used for approximating the concentration field within the finite-element, resulting in linear shape functions. Figure 5 describes the one-dimensional pitting problem.

The signed distance function $\phi(x, t)$ for the one-dimensional case is defined as

$$\phi(x, t) = \pm |x - x_{int}|,$$

where $\Gamma_{int}$ is the interface location and the $+$ sign is taken for $\Omega_{solid}$ and the $-$ sign for $\Omega_{pit}$. The enrichment functions are computed using the above-signed distance function and added to the concentration approximation along with the standard finite-element approximation. Only the enriched finite-elemental matrices are computed for every time step as the new interface location is updated from the level set engine. For computing stiffness and mass matrices over the enriched element, it is divided into two sublinear line elements and integration is done on both sides of the interface. However, as standard finite-elements do not contain discontinuity, integration is performed on the entire element at once. The assembled set of ordinary differential equations are solved for concentration field $c(x, t)$ using direct time integration, as explained in §3. The level set function is discretized by finite difference grid and consists of 200 line elements (i.e. 201 grid points). Figure 6 shows the level set finite difference grid for a one-dimensional problem. Here, pit depth is defined as the length of pit solution domain $\Omega_{pit}$, i.e. from $x = 0$ to $x = x_{int}$. The level set function $\phi$ is constructed such that $\phi = 0$ at $x = x_{int}$ and while constructing the scalar velocity field the boundary condition considered is $V_{nor} = v$ at $x = x_{int}$.

Figure 7 depicts the pit depth evolution with time for a one-dimensional case. Numerical results are compared with exact solutions and experimental results. Experimental data are obtained from the study of one-dimensional pit growth kinetics using pencil electrode
Figure 6. One-dimensional level set grid.

Figure 7. One-dimensional pit depth evolution: (a,b) comparison of numerical results with experimental data for 15°C and 25°C, respectively; (c) pit depth versus time for different temperatures.

experiments [42,44]: 50 μm diameter 304 SS wire with one end exposed to 1 M NaCl electrolytic solution and applied potential 600 mV (SCE) was used in pencil electrode experiments. Pit depth, current density response with time and potential dependence on pit growth were measured in the artificial pit formed. Experimental results for pit depth evolution in time at temperatures 15°C and 25°C are taken for verifying the proposed numerical model. The results are in good agreement. Pit depth varies parabolically with time. Analytical solution for the one-dimensional problem exists and can be obtained from the similarity solution [10]. It is solved, using a similarity variable, for pit depth evolution with time and concentration profile. Temperature dependence on the diffusion coefficient is well recorded in [46]. Figure 7 also shows the variation of pit depth with time at various temperatures. It is observed that the pit grows faster at higher temperatures, i.e. as the temperature increases the diffusion coefficient increases and the pit growth rate increases. The level set method predicted the interface motion successfully with relative error of less than 1%. It is also observed that the pit depth follows parabolic law with time. Concentration
profiles in the domain at 25°C at different times are shown in figure 8 and is compared with the exact solution. The jump in the concentration at the interface is well captured by the enriched approximation for jump discontinuity. These concentration profiles evolve with time, reaching saturation concentration at the interface and solid metal ion concentration beyond the interface. From Faraday’s second law, electric current can be determined. It states that total electric charge passed through the electrode is directly proportional to the mass dissolved per time instant. Shape and velocity of the interface can be predicted by the direction of the electrons leaving the solid metal domain. For the proposed model, it can written as $i = \nu_{\text{solid}} zF$, where $i$ is the electric current density and Faraday constant $F = 96485 \text{ cmol}^{-1}$. The variation of current density with time is shown in figure 9 at different temperatures. Experimental results from [42,44] for current density at 15°C are taken for comparing the numerical results. Electric current density

Figure 8. One-dimensional concentration profiles in the domain at 25°C at different times: markers, circles, crosses indicate the exact solution, and lines (one-dashed, double-dashed) indicate the XFEM solution for the concentration distribution in the domain.

Figure 9. One-dimensional current density variation: (a) comparison of numerical and experimental results at 15°C and (b) current density variation with time at different temperatures.
decreases monotonically with time, i.e. current density decreases with the square root of time. Stable pitting corrosion is characterized by decreasing current density with time [9], and this point is validated from the plot of current density and time. Laycock & Newman [46] detail the experimental procedure for understanding the temperature effects on pit growth, in which experiments were carried out using 50 \(\mu\)m diameter 302 SS wire in 1 M NaCl solution at different temperatures. The experiments were carried at an applied potential of 500 mV for the initial 300 s and 200 mV for the remaining time. Figure 10 compares the numerical and experimental results of inverse electric current density versus pit depth. Linear variation is observed in these plots.

(b) Two-dimensional analysis

For two-dimensional implementation, the domain \(\Omega\) is a slab of dimensions 0.005 x 0.001 m with unit thickness. Figure 11 shows the two-dimensional domain, and numerical analysis is performed for half the region by taking the centreline \(S - S\) as an adiabatic boundary. Figure 12 shows the two-dimensional XFEM mesh and two-dimensional-level set grid. The computational domain is discretized into 400 finite-elements. Three node triangle elements with one degree of freedom per node are considered for two-dimensional formulation. The triangle element can be rotated arbitrarily and can therefore approximate boundaries not aligned with coordinate axes well. For approximating the concentration field within the element, linear shape functions are used.

The enrichment functions are taken from equation (3.7), and elemental matrices for enriched elements are computed at each time step. One additional degree of freedom is introduced to each enriched node. The enriched element cut by the interface is divided into subtriangle and subquadrilateral. The integration is performed on both the subelements with three and four Gauss quadrature points for subtriangle and subquadrilateral, respectively. Penalty matrices are computed along the evolving interface at each time step. Elemental matrices are computed
for all the elements using isoparametric mapping and are assembled into global matrices. The assembled set of equations is solved for concentration field \( c(x,t) \) using direct time integration. The initial condition is \( c(x,0) = 0 \text{ mol l}^{-1} \) in \( \Omega_{\text{pit}} \) at time \( t = 0 \text{ s} \). The Dirichlet boundary condition for concentration \( c(x,t) = 0 \text{ mol l}^{-1} \) is prescribed on the horizontal surface \( x = 0 \). The interface concentration condition imposed is \( c(x^{-},t) = c_{\text{sat}} = 5.1 \text{ mol l}^{-1} \) for \( x \in \Gamma^{-}_{\text{int}}(t) \). Zero flux conditions are assumed both Neumann boundaries along interface and solid metal. Solid metal concentration \( c_{\text{solid}} = 143 \text{ mol l}^{-1} \) is prescribed on \( \Gamma_{\text{solid,dc}} \) and is assumed to be a distance of \( d_{s} = 5 \mu \text{m} \) away from the interface. The level set mesh is a finite difference grid composed of 800 square elements. The analysis mesh for two-dimensional-level set update is the same as shown in figure 12. The level set function \( \phi \) is constructed such that \( \phi(x,t) = 0 \) when \( x \in \Gamma^{-}_{\text{int}} \) and the boundary condition for constructing the scalar velocity field is \( V_{\text{nor}} = v \) along the interface \( \Gamma_{\text{int}} \).

The pit depth and pit width evolution with time are shown in figure 13. Experimental results from the pencil electrode [42] for artificial two-dimensional pit growth measured at 10\(^{\circ}\)C, 20\(^{\circ}\)C in 1 M Nacl 600 mV are taken as the reference for comparing the numerical results. The obtained finite-element solutions were also compared with finite volume solutions from [10,22], as there are no analytical solutions for the two-dimensional case. The proposed model (level set method) predicted the interface shape and location shape with high accuracy. Results matched exactly with finite volume solutions and are in good agreement with experimental data. It is observed that pit growth in depth varies parabolically with time but in width varies linearly with time. Parabolic variation of pit depth signifies that it is a purely diffusion controlled process with salt film formation at the pit surface. Diffusion-controlled dissolution of the salt film governs the metal...
dissolution rate at the pit surface. The surface underlying the salt film continues with pit growth under diffusion control. The process of passivation and re-passivation of the pit surface results in the formation of a lacy cover, which is not governed by the diffusion process, emphasizing the linear variation of pit width with time. The dominance of lacy cover formation in the two-dimensional case is clearly visible from the graphs, where one-dimensional pits grow faster than two-dimensional pits. This is because the lacy cover does not exist for the one-dimensional pitting case. Lacy cover formation affects the pit growth rate to a large extent. One-dimensional analysis compliments the two-dimensional case by highlighting the effect of lacy cover formation on pit growth. The complete behaviour of the lacy cover is not completely understood as it depends on various parameters such as porosity, bulk solution, electrochemical potential.

**Figure 13.** Two-dimensional pit depth and width evolution with time: (a,b) comparison with experimental results at 10°C and 20°C, respectively.

(c) Pitting potential results

For stainless steel 304, standard potential \( E_0 = +80 \text{ mV} \), model parameters \((a, b, c, d)\) for model 1 and 2, are determined from equations (6.5) and (6.6)

**Model 1:**
\[
\begin{align*}
    a_1 &= 665.0263 \\
    b_1 &= -1.9631 \\
    c_1 &= -0.25 \\
    d_1 &= 8.2764,
\end{align*}
\]

**Model 2:**
\[
\begin{align*}
    a_2 &= 197.4651 \\
    b_2 &= -13.0516 \\
    c_2 &= 0.0903 \\
    d_2 &= -2.9932.
\end{align*}
\]

**Figure 15** compares model 1 and model predictions with experimental results, which are obtained from [46]. Pitting potentials for 304 SS in 1 M NaCl solution were recorded in the experiments. As model 1 predicted the pitting potential variation close to the experimental data, we chose model 1 for studying the concentration, temperature and pH effects on pitting potential. **Figure 15** is
Figure 14. Two-dimensional concentration profile (mol l$^{-1}$) in the pit at temperature 20$^\circ$C after time 1000 s.

Figure 15. Pitting potential variation with temperature for both the models and comparison with experimental data: fixing $c = 5.1$ mol l$^{-1}$ (pit boundary), pH 9.

Pitting potential $E_p$ is measured in millivolts with temperatures taken in K and concentration taken in mol l$^{-1}$ units. The model is valid for the temperature range 25–80$^\circ$C, pH range 6–9 and for concentrations within the pit solution. Figure 16 shows the pitting potential profile within the pit at different temperatures and pH 9. Figure 17 shows the pitting potential profile within the pit at different pH values and $T = 50^\circ$C. The isolines represent the potential with its value written near the isoline. The isolines also represent the concentration with its value shown in the legend below the plots. In simple words, observing figure 15 for 30$^\circ$C: the grey line represents the isoline for potential with value $+71.26$ mV and for concentration with value

$$E_p = 665.0263 - 1.9631T - 0.25(T \log(c)) + 8.2764(pH \log(c)).$$

(7.1)
Figure 16. (a–d) Pitting potential profile with in the pit: fixing pH 9 and at various temperatures. Pitting potential (mV) at the concentration (mol l\(^{-1}\)) isolines. (Online version in colour.)

Figure 17. Pitting potential profile within the pit: fixing \(T = 50^\circ\text{C}\) and at various pH values. Pitting potential (mV) at the concentration (mol l\(^{-1}\)) isolines. (Online version in colour.)

0.425 mol l\(^{-1}\). Dependence of pH on \(E_p\) can be understood from figure 18; it is clear that \(E_p\) increases with pH for a constant concentration and temperature. Figure 19 shows the variation of \(E_p\) with concentration within the pit. It is observed that \(E_p\) depends linearly on the logarithm of concentration for a constant pH and temperature. Potential is highest near to the pit surface and lowest at the pit boundary. From these graphs, it can be emphasized that concentration,
temperature and pH affect the potential values in the pit. The potential value for any value of concentration, temperature and pH (falling in the prescribed range) can be obtained from equation (7.1).

8. Conclusion

For stable pit propagation, with a moving boundary, a combined extended finite-element and level set model is developed. Only three inputs, solid metal concentration, saturation concentration of dissolved metal ions and diffusion coefficient, are required to solve the set of coupled partial differential equations for concentration profile and pit boundary evolution. In
XFEM, the discontinuities in the gradient of the concentration across the interface is captured through a discontinuous-derivative enrichment formulation, which eliminates the necessity for explicit representation of the interface, front-conforming mesh and re-meshing. The level set method updates the interface location in time without significant computational expense. Numerical analysis of stainless steel 304 showed that the model produced accurate results for concentration field and interface motion, and are in good agreement with experimental results, exact solution and some approximate solutions. Pit depth and width evolution with time are studied, along with current density and its reciprocal. Dependence of temperature, pH and concentration is studied using the proposed pitting potential model. The model predicted potential values close to experimental results. By understanding the complete behaviour of lacy cover formation and pit morphology, the proposed method can be extended for three-dimensional problem with nonlinear pit kinetics, which is the ongoing research work.

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