



# Surface evolution of a corroding metal as a moving boundary problem by random assignment of anodic and cathodic sites



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## ABSTRACT

During corrosion a metal surface dissolves when it is immersed in a corrosive electrolyte. The rate of loss of thickness of the metal known as corrosion rate is usually found based on weight loss data from immersion experiments. Similarly, polarization tests also provide an estimate of corrosion current which in turn gives corrosion rate. This type of quantification does not provide information on the unevenness of the corroded surface. In the present work, a simulation is developed based on random assignment of anode and cathode sites. Linearized polarization curves are used with slightly different  $E_{\text{corr}}$  values for anode and cathode sites. A 2D Laplace equation is solved for the electric potential distribution in the electrolyte. Thus uniform corrosion is simulated as a micro-galvanic corrosion process by assuming the ionic conductivity in the electrolyte as the limiting step to determine the anodic current density on the anodic sites and the surface profile is updated as a 2D moving boundary problem. Interesting shapes of the corroding surface are obtained. The average depth of the surface is found to vary linearly with time indicating a constant corrosion rate. On the other hand the standard deviation of the surface profile also increased with time indicating a persistent unevenness of the corroding surface. Sensitivity studies for varying polarization slope and anode fraction are included.

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## 1. Introduction

Corrosion of various types is exhibited by metals depending on the type of corrosive environment. The well known types of corrosion are uniform corrosion, localized corrosion and galvanic corrosion [1]. In uniform corrosion there is active material degradation, in localized corrosion there is either pitting or crevice corrosion, in galvanic corrosion it is dissolution of anodic metal in contact with another cathodic metal and in micro-galvanic corrosion it is dissolution of anodic sites surrounded by cathodic sites. Experimentally, the real time immersion tests are time consuming [2]. Generally Tafel slope method applied to polarization data gives  $i_{\text{corr}}$  and  $E_{\text{corr}}$  from which uniform corrosion rate is calculated [3]. Pitting corrosion was simulated with various assumptions pertaining to diffusional resistance for ionic conduction in the pit as a moving boundary approach [4,5]. In another approach the pits were generated in thin stainless steel foils by applying external potential and the current response was characterized which shows some specific characteristics such as discrete jumps corresponding to under cutting event during pitting [6]. Stochastic models were also applied for tracing the evolution of pits during corrosion [7]. Galvanic corrosion at a junction of dissimilar metal joint was simulated as a moving boundary problem [8]. Micro-galvanic corrosion in alloys such as duplex

stainless steel consisting of two phases namely ferrite and austenite was studied in an artificially prepared template and was shown that the two phases have different  $E_{\text{corr}}$  values primarily which lead to galvanic corrosion at a micro scale [9].

There are several phenomena occurring during corrosion either in pitting or galvanic corrosion. Two major factors are designation of cathode and anode regions and a governing equation for ionic conduction in relation to potential gradient in the electrolyte. There can be ionic flux due to concentration diffusion also. Nevertheless with certain assumption of ionic transport being the rate limiting step, the potential in the electrolyte is governed by Laplace Eq. (10). Subsequently the polarization data of anode and cathode regions is also represented in terms of the relationship between corrosion current or local electric field and the prevalent potential [10]. In some advanced material modeling such as stress corrosion cracking, the microstructure of the alloy is also incorporated [11].

Tafel slopes method of determining the uniform corrosion rate does not provide surface profile pattern during corrosion. In view of above cited literature, there exist a number of models for pitting and galvanic corrosion but no modeling procedure exists for simulating uniform corrosion especially the unevenness of the surface of a metal. It is only a hypothesis that cathodic and anodic sites are developed on a metal in contact with electrolyte during uniform corrosion.

The present work applies a novel approach for simulating uniform corrosion by random assignment of cathodic and anodic regions on

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### Nomenclature

$a$	length of metal surface (m)
$E_{\text{corr}}$	free corrosion potential, volts
$E_{\text{appl}}$	applied potential, volts
$F$	Faraday constant (C/mol)
$i_{\text{corr}}$	current density during free corrosion (Amp/m <sup>2</sup> )
$i$	current density in electrolyte (Amp/m <sup>2</sup> )
$k_d$	coefficient of dissolution (m <sup>2</sup> /s-volts)
mpy	mills per year (milli inches/year)
$t^*$	time (dimensionless)
$u_n$	dissolution speed in normal direction (m/s)
$u_o$	reference dissolution speed (m/s)
$w$	height of electrolyte (m)
$x^*$	x-coordinate of a node on metal surface
$z^*$	z-coordinate of a node on metal surface
$\alpha_a$	polarization length scale of anode (m)
$\alpha_c$	polarization length scale of cathode (m)
$\delta$	fluctuation in $E_{\text{corr}}$ (V)
$\phi$	electric potential at a location in electrolyte (volts)
$\phi^*$	dimensionless electric potential
$\phi_{o,a}$	$E_{\text{corr}}$ of anode (volts)
$\phi_{o,c}$	$E_{\text{corr}}$ of cathode (volts)
$\gamma$	valency of the metal ion (dimensionless)
$\kappa$	ionic conductivity of electrolyte (Amp-m/volts)
$\theta_n$	angle between normal and z-axis on metal nodes
$\rho_s$	density of metal (kg/m <sup>3</sup> )
$\tau_o$	dissolution time constant (s)
$\nabla$	gradient operator
$\nabla^2$	Laplace operator

the metal surface during the corrosion process. For example the polarization data of SS304 in NaCl solution of 16 g/l concentration is shown in Fig. 1(a). Two different runs demonstrate that there is a slight variation of  $E_{\text{corr}}$  as can be observed from the vertically shifted curves. The variation represents that the metal can exhibit unequal ratio of anodic and cathodic regions on a macro-scale during uniform corrosion. In Fig. 1(a) the top curve represents cathodic sites and bottom curve represents anodic sites. Such different polarization curves suits the purpose of simulation of uniform corrosion by the proposed mechanism of random assignment of anodic and cathodic sites. The first reason for this assumption is that the geometric distribution of various phases in metals like stainless steel will also follow a heterogeneous random like distribution in space [1]. The second reason is that the surface of a corroding metal attains non uniform  $E_{\text{corr}}$  due to uneven oxide layer as well as due to uneven concentration polarization.

In addition to above assumption, linear polarization is applied to the polarization characteristic curve of the individual metal sites in order to compute the micro galvanic currents between the neighboring anodic and cathodic sites. The polarization data of Fig. 1(a) is in semi-log axes. If it is represented in linear scale the potential vs absolute of current density would appear as in Fig. 1(b) and it justifies linear polarization assumption since the  $E_{\text{corr}}$  difference between anodic and cathodic sites is very small and of the magnitude of 10 mV. The material responses are assumed to follow linear polarization trend as the potential variation is minimal between the anodic and cathodic sites. The reason for assigning anode and cathode sites is that any metal with homogeneous phase could have different polarization characteristics in various regions of the surface primarily due to the variation of  $E_{\text{corr}}$ . Recalling Fig. 1(a) or (b) it can be considered as  $\phi_{o,a}$  for anodic sites and  $\phi_{o,c}$  for cathodic sites. In this work, only binary characteristics are assumed in a given metal.

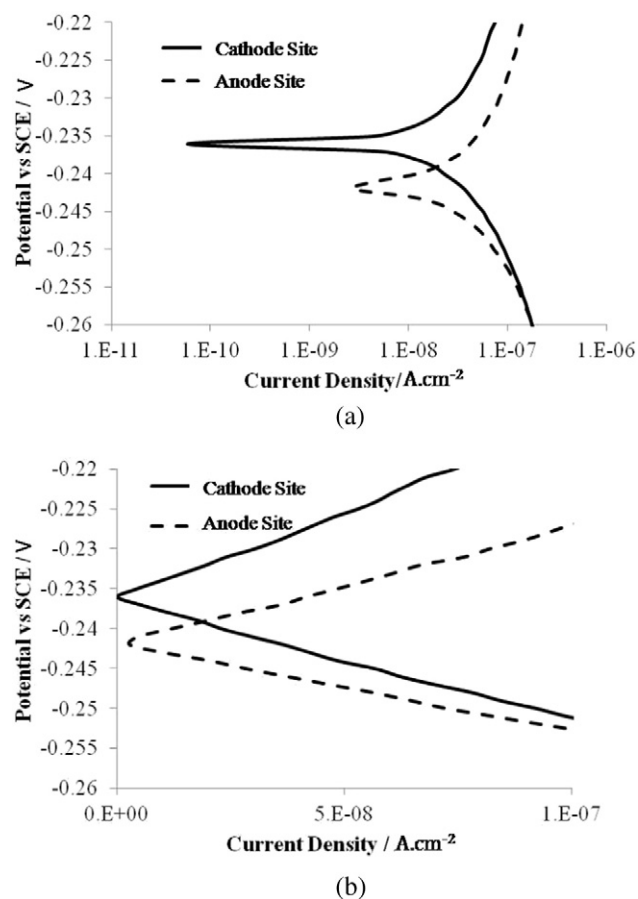


Fig. 1. (a) Polarization plots of SS304 in 16 g/l NaCl solution from two different runs on log scale for current density. (b) Linear polarization plots of SS304 in 16 g/l NaCl solution near  $E_{\text{corr}}$  on a linear scale for current density.

When an anode site dissolves, it could result in a cathode property in the subsequent iteration of numerical simulation. Hence during simulation such a dynamic boundary condition aspect is implemented by randomly assigning anodes and cathodes at every time step using a random number generator with help of software like MATLAB. In addition to this feature, MATLAB also has a PDE toolbox which provides solution to Laplace equation even in a non regular geometry such as the one created during the corrosion process. Here the geometry refers to the electrolyte region bounded by the uneven corroded metal surface at the electrolyte/metal interface.

The surface of the metal is allowed to dissolve wherever there is anodic current. Hence the present approach for modeling uniform corrosion phenomena is similar to many other phenomenon of moving boundary problems such as melting, electro polishing, and anodizing [12]. Other forms of corrosion like metastable pitting can also be simulated by probabilistic approach and cellular spatial distribution of phases [13]. Similarly, a coupled electrochemical-transport-reaction model was recommended to simulate the galvanic corrosion currents [14]. In the following sections a novel simulation approach is developed for a metal surface corroding due to an electrolyte present above it. The objective is to capture the average dissolution speed and unevenness of the metal interface during uniform corrosion.

## 2. Mathematical model

Consider a metal surface covered with electrolyte as shown in Fig. 2. It consists of a two-dimensional metal cross-section with equi-sized elements of anode and cathode assigned randomly on its surface in contact with the two-dimensional electrolyte. The height of electrolyte in

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