



A temporal semi-stochastic model for pitting corrosion



Harpatap Singh ^{*}, Seiichiro Nakabayashi

Department of Chemistry, Faculty of Science, Saitama University, Saitama 338-8570, Japan

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ABSTRACT

We have proposed a mechanism that could possibly mimic the well known phenomenon of the halide ions induced oscillations in Me|nM H₂SO₄ system. It is assumed that close to the Flade potential region or anodic side far from the Flade potential are the scenarios wherein the applied potential is greater than the pitting potential. Consequently, the pitting initiation process occurs with unit probability and hence the stochastic pitting growth process becomes independent from the instantaneous pit depth. This pitting growth phenomenon is captured by time dependent stochastic functions (double exponential) along with the deterministic component. The consequences of mimicking the spatial features of oxide film breakdown by using the time dependent stochastic functions, are also discussed. Furthermore, the additional results have been provided to validate the proposed temporal semi-stochastic form of the model.

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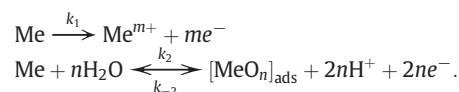
1. Introduction

Pitting term is commonly used for the corrosion process that is a life threatening activity for the metals and alloys. Shibata and Takeyama had suggested that this complex behavior can be considered as a stochastic process [1]. They employed a variable known as transition probability of pit formation to explain the time dependent nature of pitting phenomenon observed in their experiments involving chloride ions. Consequently, numerous stochastic models had been proposed wherein the pitting mechanism was regarded as a homogeneous Poisson process [2], non-homogeneous Poisson [3,4] and non-homogeneous Markov process [3–5] to explain the pitting corrosion dynamics such as pit depths, induction times, corrosion rates, and current–voltage fluctuations. Moreover, the other types of statistical approaches involving physicochemical analysis are also found in the literature such as Monte Carlo technique [6], memory field theory [7], reaction–diffusion equation [8,9], and perturbation method [10], etc. In contrast, Hudson and Mikhailov group put forward the idea of cooperative stochastic behavior both theoretically [7,11,12] and experimentally [11,13,14] wherein the pitting corrosion was considered as well as demonstrated as a consequence of the interactions between metastable pits in both temporal space and spatio-temporal space. In addition, the chaotic current–voltage dynamics observed in steel chloride system [15] suggests that this complex pitting behavior might have deterministic origin. Therefore, in addition to its hazardous behavior (that cause structure failure), the pitting corrosion is also interesting to study in the case of self-sustained oscillators under stochastic forcing like a limit cycle electrochemical system in the halide environment. From the last two decades,

in series of papers [16–24], the research group of Pagitsas and Sazou, had shown that the repeated pitting process, i.e., localized corrosion of iron in acid solutions in the presence of halide ions, induces a variety of dynamics such as periodic, aperiodic, quasi-periodic, and chaotic. Although the literature is well documented with the experimental findings and the theoretical explanations, the mathematical model that can reproduce these results numerically, has not been given so far (to the best of our knowledge).

2. Model and theory

In the present work, we are making an effort to demonstrate the pitting induced dynamics numerically using a semi-stochastic temporal model. For this, we have chosen Koper–Slyuyters 3D model [25] as a basis to develop the present mechanism or one can say to mimic the halide free environment (i.e., metal only in the acidic solution). Koper–Slyuyters model [25] is based upon dissolution–precipitation mechanism [26], i.e., active–passive transition of metal electro-dissolution occurs in two parallel processes:



Moreover, the assumptions (other than the Koper–Slyuyters model [25]) on which the proposed model stand, are:

A. The rate constants k_1 (corresponds to electro-dissolution, process 1), k_2 (denotes oxide layer formation via an electro-dissolution–precipitation mechanism, forward process 2) and k_{-2} (represents breakdown of oxide layer, backward process 2) also depend upon the fractional coverage (θ)

^{*} Corresponding author.

E-mail address: harpatap@mail.saitama-u.ac.jp (H. Singh).

of the electrode's surface by the passive oxide layer in addition to the electrode potential (v), i.e.,

$$k_1 = k_1^0 e^{[(v-v_1^0)/2-g_1\theta]} \quad (1)$$

$$k_2 = k_2^0 e^{[(v-v_2^0)/2-g_2\theta]} \quad (2)$$

$$k_{-2} = k_{-2}^0 e^{[-(v-v_2^0)/2+g_{-2}\theta]} \quad (3)$$

Where g_1 , g_2 , and g_{-2} are the heterogeneity factors (other parameters have same sense as in Koper–Sluyters model [25]) that are generally ignored in the models using Langmuir adsorption isotherm. This assumption implies that the Gibbs energy of activation and adsorption depends linearly on θ [27].

B. System has a single electro-active species, i.e., H^+ ions. This is a frequently used assumption [25] since the H^+ ions are usually regarded as most mobile ions that carry almost all the current and their transference number could be considered as unity [25]. This means that the halide ions do not participate in any of the two processes that are mentioned above. Consequently, the halide ions do not contribute to the Faradaic flux. However, they effect the flux indirectly by effecting k_1 , k_2 and k_{-2} through θ , i.e., assumption **A**.

C. Pitting process occurs only in the passive film, i.e., this process only enhances the reaction kinetics like a catalyst which is consistent with the assumption **B**. Therefore, pitting corresponds to the attack on oxide film that results into the metal electro-dissolution (corrosion).

D. When the applied potential lies in the active region, i.e., close to the Flade potential (active/passive region) or in the completely passive region, i.e., far from the Flade potential towards anodic side, the probability of the pit initiation event is unity. This means that the condition of critical potential (pitting potential) for pitting initiation is always satisfied in the present case. In other words, there is no chance wherein a pit can re-passivate. However, pit grows in time with randomly varying exponent after the pit nucleation. This is somewhat consistent with the point defect model (PDM) [28] wherein a vacancy in the passive film (formed due to halide ions attack) will grow if the applied potential is greater than the pitting potential which is the present scenario. Moreover, this assumption transforms the complex spatio-temporal pitting corrosion system into a temporal system because pit can grow without any pit depth threshold. Hence, the pitting corrosion dynamics can be demonstrated without incorporating the partial derivatives which represent the local coupling between the pit nuclei (in case of pitting corrosion phenomenon). However, under this assumption, there is a drawback, i.e., the model cannot differentiate between the different pitting tendencies [28] and dynamics [18,20] of the halide ions, i.e., F^- , Cl^- , Br^- and I^- (or any other attacking/inhibiting species like nitrate ion [29]). In addition, our model cannot demonstrate the alteration in induction (transient) time that has been observed [17, 21] for the low and intermediate concentrations of halide ions. This is because, here the induction time also depends upon the re-passivation behavior (i.e., a spatial feature) along with the pitting potential.

E. There exists a recovery time for the concentration of free halide ions to be high enough to re-attack the film. This recovery time plays a crucial role in the pitting corrosion dynamics. Moreover, the 'recovery time' parameter (extrinsic) allows the film to rebuild and stores energy that is observed in the form of spiking behavior during re-pitting. This assumption is motivated from the theory [15,23,28] that the halide ions form complex with the Fe ions while pitting and we believe that this complex must take some time to dissociate into free halide ions.

Following these assumptions (**A** to **E**) and Koper–Sluyters 3D model [25], the dimensionless equations of motion for the Me|nM H_2SO_4 system in the halide (other pitting species) environment, are:

$$\frac{dv}{dt} = \frac{V-v}{0.1} - 100[k_1(1-\theta) + k_2(1-\theta) - k_{-2}\theta h] \quad (4)$$

$$\frac{dh}{dt} = 1-h + \frac{v-V}{10} + k_2(1-\theta) - k_{-2}\theta h \quad (5)$$

$$\frac{d\theta}{dt} = 200[k_2(1-\theta) - k_{-2}\theta h] - F\theta \quad (6)$$

The variable v depicts the electrode potential whereas h represents the concentration of H^+ ions in the vicinity of the electrodes' surface with in the diffusion layer. The dimensionless parameter V in Eq. (4), denotes the magnitude of applied potential and also considered as a bifurcation parameter of the system. The rate constants k_1 , k_2 and k_{-2} are given in Eqs. (1)–(3), wherein the parameters are chosen as: $k_1^0 = .01$, $k_2^0 = .01$, $k_{-2}^0 = .001$, $v_1^0 = 0$, $v_2^0 = 20$, $g_1 = 0.6$, $g_2 = 0.6$, and $g_{-2} = 0.6$. Based on the assumptions **B** and **C**, the dissipative bold term in Eq. (6), $-F\theta$ (where θ is same as θ), shows that the attacking species removes the coverage of passive film which enhances the metal electro-dissolution, i.e., the pitting corrosion in temporal space. Moreover, **F** is the stochastic term or one can say stochastic forcing to the electrochemical cell and it has a form:

$$F = c_1 e^{c_2\eta_1} e^{\frac{(v-V)}{2}} = c_1 e^{c_2\eta_1 + \frac{(v-V)}{2}} \quad (7)$$

The dimensionless parameter c_1 represents the concentration of free halide ions (other pitting species) that can do pitting process. Here, η_1 is a random number (that can attain values between 0 and 1) varying with time t , i.e., the time at which the system's intrinsic dynamics: $v(t)$, $h(t)$ and $\theta(t)$, evolve. In addition, **F** is also modulated with the change in electrode potential v with respect to the applied potential V . In other words, **F** is effected by the change in IR drop, where $I (= \frac{V-v}{0.1})$, in the present case) is the total current (dimensionless) and R is the uncompensated resistance of the electrolyte. The importance of this dependence lies on the previous experimental observations wherein they reported that the pitting behavior is found to be sensitive towards the change in applied potential [1,30] and consequently on the electrode's potential. The exponential dependence form, i.e., $e^{\frac{(v-V)}{2}}$, is motivated from the Shibata and Takeyama's second and third transition probabilities of the pit formation [1]. However, the present form is different in three ways: I. since the applied potential is assumed to be greater than the critical potential (assumption **D**), pitting potential is replaced by V ; II. the term $(v-V)$ yields the negative values that induce response (like inertia) of the system towards the forcing, by reducing the stochastic term ($c_2\eta_1$) and III. the exponent of magnitude less than 1, i.e., $\frac{1}{2}$, makes sure that this deterministic part should not dominate over the stochastic component. In addition, this dependence also enables **F** to sense the change in the stability (thickness) of the passive film that increases with increase in V [17,31] (in the temporal space). Furthermore, the employed form of varying exponent c_2 that induces the non-uniformity in the distribution function **F** is

$$c_2 = e^{\eta_2 t} + e^{\eta_2(1-t)} \quad (8)$$

The choice of exponentially varying exponent comes from the fast growing property of the double exponential. Moreover, it should be noted that the stochastic component of **F** is quite different from the Gumble distribution function [32] which is commonly used to explain pitting behavior [2,4,32], though both have similar form of double exponential. In the present case, the double exponential (stochastic component of **F**) should not exhibit decreasing behavior (which is the case of Gumble distribution [32]) to mimic the drilling nature of halide ions in the passive (oxide) film after nucleation in the temporal space. Furthermore, the change in dimensionless parameter T (Eq. (8)) that shows the total time evolution ($T = \int_0^t dt$) does not affect the asymptotic dynamics of the system, though the transient behavior could be changed slightly. This dimensionless parameter T has been set at 200 (i.e., dimensionless time) for the presented results. Moreover, the random number η_2 (whose values lie between 0 and 1) in Eq. (8), depicts

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