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Corrosion Science

Three dimensional discrete stochastic model of occluded corrosion cell

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ABSTRACT

We present a stochastic three dimensional (3D) model for corrosion at a mesoscopic scale. The competition between uniform and localized corrosion is studied, with special emphasis given to the connection between the anodic and cathodic reactions. Even if the reactions happen at different places, they are linked and occur simultaneously, maintaining an electric balance. We focused on the particular case of an occluded corrosion on a metal covered by a non reactive layer, where two growth regimes are evidenced and controlled by the diffusion of species in the electrolyte.

1. Introduction

Cellular automata (CA) modelling is used as an alternative method to model corrosion. The main feature of this method is the probabilistic factors which are well adapted to describe the stochastic properties of electrochemical corrosion. They have been used to describe the morphological evolution of corrosion [1]. The first CA models appeared about two decades ago [2,3] and with simple transformation rules describing only dissolution and passivation. Progressively, an evolution could be noticed [4], models became more exhaustive: more phenomena that influence corrosion were included [5–8], results became quantitative [9,10] and 3D based models became predominant [11].

A 3D description is fundamental to better describe localized corrosion, especially pitting corrosion, where the asymmetrical corroded morphology is roughly simplified in 2D models. This type of corrosion is considered as a undesirable event, where the initiation time and the place of the attack are often unpredictable [12]. This work illustrates the 2D to 3D extension of a previous CA model that involves the main mechanism of corrosion, that is anodic and cathodic reactions. These reactions are driven by an electric potential difference. When they are homogeneously distributed over the surface, the result is an uniform corrosion. In contrast when external factors (e.g. variations of pH) concentrate each reaction in different places, it can lead to a localized form of corrosion. Some typical examples are pitting or crevice corrosion where the anodic reaction occurs in a specific area. Previous CA models described the anodic and cathodic reactions as a simplified single location event [6,10,11,13,14]. We represent this mechanism as two simultaneous electrochemical semireactions to see the influence of two events at different locations but intrinsically dependent. These are randomly distributed over the metal surface to mimic the stochastic character of corrosion.

The model was first presented by Vautrin et al. in 2004 [15]. They studied the incubation time due to the stochastic character of the phenomena and clearly evidenced the spontaneous separation of the acidic and basic zones. Following this, Aarão et al. [16] implemented a scaling theory to reproduce simulation results. Stafiej et al. [17] studied the effect of the spatially separated reactions on the incubation time of localized corrosion. Following their first works, Vautrin et al. [18] studied the case when the anodic and cathodic reactions occur at the same place, showing that the detached metals that appear in the CA modelling can be related with the chunk effect on metals [19]. Such metal inclusions in oxide layers have been found in archaeological analogues and have been predicted up to now only by CA approaches [20].

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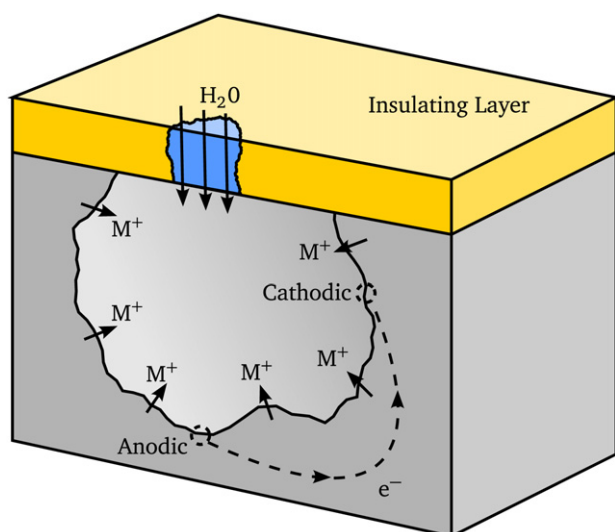
Fig. 1. Illustration of the occluded corrosion cell. Anodic and cathodic reactions occur inside the cavity, where electrolyte may reach the metal surface, through a defect in the insulating layer.

The case under study is an occluded corrosion cell. It is illustrated in Fig. 1. This confined scenario is created when an insulating layer (such as a porous paint or the agglomeration of non conductive porous corrosion products), covers the surface of the metal. This layer plays an important function because it allows the development of corrosion in the metal while it imposes an open circuit condition. The electrochemical reactions generate an electron transfer in the metal and an ion transfer in the electrolyte. The inert protective layer is considered non conductive thus, electron transfer occurs only inside the confined environment. The insulating layer acts also as an ion barrier, letting only the inclusion of electrolyte solution inside the cavity and ensuring its electro-neutrality. The interaction of positive and negative ions, that annihilate when coming into contact, is governed by diffusion. This mass transfer mechanism is not fully efficient for large cavity sizes, leading to a spontaneous acidic and basic zones separation. When the characteristic size of the cavity exceed a threshold value, then an auto-catalytic asymmetric growth of the cavity sets, that this model can predict.

In this work we do not consider specific types of steels or electrolytes. Instead we focus on the coupling effect of basic process such as diffusion and the separated electrochemical reactions on propagation of corrosion. Let's note that this corrosion model can be viewed as a particular case of more general diffusive reactive systems, that may generate complex patterns [21,22].

This paper is organized as follows: Section 2 describes the physico chemical basis of the model, Section 3 presents the characteristics and parameters of the CA model, Section 4 presents the implementation approach of the CA model, Section 5 presents the main results and discussions. Conclusions and future work are discussed in Section 6.

2. Physicochemical model

This section introduces to the basic features of the model and the modifications from previous versions [15,17,18,23–25]. This model lies on several assumptions: simplified electrochemical reactions (anodic and cathodic) and simplified chemistry no pollutants, only H^+ and OH^- ions). These features do not depend on the detailed nature of the metal they are general for aqueous corrosion. Other phenomena influence corrosion like for instance IR drop or

precipitation of salt film due to the concentration at the surface of the cavity but they are not considered in the present model.

2.1. Mesoscopic scale

The present approach uses a mesoscopic scale that enable to highlight the general corrosion tendencies and to:

(i) Show the larger scale effects of a microscopically generated corrosion.
(ii) Simulate longer corrosion times than the ones used at microscopic scale.
(iii) Represent the corrosion stochastic character as it can not be described at a macroscopic scale.

2.2. Electrochemical reactions

Metal corrosion is governed by local electrochemical semireactions. These reactions can occur at two different sites of the surface, that are electrically connected through the metal. The anodic and cathodic reactions are randomly distributed over the surface. As they are separated, they are called Spatially Separated Electrochemical (SSE) reactions. In acidic or neutral medium, the anodic semireaction is metal oxidation.

$$M \longrightarrow M^+ + e^- \tag{1}$$

followed by cation hydrolysis

$$M^+ + H_2O \longrightarrow MOH_{aq} + H^+. \tag{2}$$
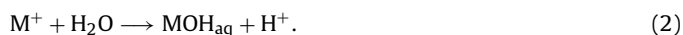
Metal cations produced in (1) undergo an hydrolysis in (2) leading to acidification. Anions from the electrolyte migrate close to the dissolving surface to compensate the charge of dissolved cations. The anodic dissolution of metals is characterized by low pH and abundance of aggressive anions. The two step semireaction can be simplified in the following equivalent chemical expression for acidic and neutral environments

$$M + H_2O \longrightarrow MOH_{aq} + H^+ + e^-. \tag{3}$$
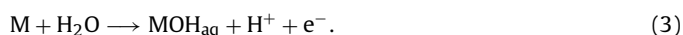
In a basic medium, the metal oxide products have lower solubility, thus the semireaction corresponds to the precipitation of the hydroxide
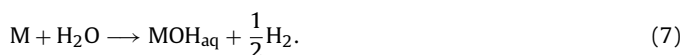
$$M + OH^- \longrightarrow MOH_{solid} + e^-. \tag{4}$$

The associated cathodic semireaction corresponds to the reduction of hydrogen or water depending on the local acidity. In acidic or neutral environments, pH $\leq$ 7, the cathodic process is mainly the reduction of hydrogen ions

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2. \tag{5}$$

Meanwhile, for basic electrolyte, pH > 7, the reduction of water can be expressed as follows

$$H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^-. \tag{6}$$

Even if they occur in different conditions, both (5) and (6) are chemically equivalent. Following the 2D model, we also consider the case when the anodic and cathodic semireactions occur at the same place, we use the reference spatially joint (SJ) reactions. In this case, the local pH remains constant as a consequence of the chemical equilibrium of the reaction. In acidic or neutral environment, the equivalent reaction is the sum of (3) and (5)

$$M + H_2O \longrightarrow MOH_{aq} + \frac{1}{2}H_2. \tag{7}$$