



# Regulation of interfacial chemistry by coupled reaction–diffusion processes in the electrolyte: A stiff solution dynamics model for corrosion and passivity of metals



Infant G. Bosco<sup>a,b</sup>, Ivan S. Cole<sup>a</sup>, Bosco Emmanuel<sup>c,\*</sup>

<sup>a</sup> CSIRO Materials Science and Engineering, Clayton, 3169 Victoria, Australia

<sup>b</sup> Institute for Frontier Materials, Deakin University, Burwood, 3125 Victoria, Australia

<sup>c</sup> CSIR-CECRI, Modelling and Simulation, Karaikudi, 630006 Tamil Nadu, India

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## ABSTRACT

In this paper we advance a stiff solution dynamics [SSD] model to study the regulation of local chemistry near a corroding metal by reaction and diffusion processes in the electrolyte. Using this model we compute the detailed space–time dynamics of the concentrations of metal ions, its hydroxy complexes, H<sup>+</sup> and OH<sup>−</sup> ions near the corroding metal. The time for the onset of passivity for Fe and Zn is presented for free corrosion condition, different impressed currents and initial pH values. The theory advanced provides much physical insight into corrosion and passivity of metals and motivate spectro-electrochemical studies.

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## 1. Introduction

As early as 1972 Pickering and Frankenthal [1] modelled localised corrosion of iron and steel by considering the diffusion and migration of metal ions and hydrogen ions in artificial pits. Galvele and co-workers extended this model to include solution processes such as metal ion hydrolysis and self-hydrolysis of water and studied their role in passivity breakdown [2,3]. These are steady state models involving a known constant current due to metal dissolution at the bottom of the pit. While chemical reactions such as the metal ion hydrolysis leading to H<sup>+</sup> generation in the pit and self-hydrolysis of water are recognised, the cathodic reactions like oxygen reduction or hydrogen evolution and the consequent changes in the solution pH are not considered by these authors. Though these models have led to much useful insights into the conditions under which passivity sets in, two limitations of these models should be noted:

- (1) These models describe only the steady state and consequently cannot capture the time-dependent changes in the pit solution leading to eventual passivity or pitting. For this

reason, they cannot predict properties such as the time for passivity. Importantly passivity may set in before the steady state is reached.

- (2) Only the anodic metal dissolution can be included in their models and the cathodic counter reactions like oxygen reduction:



cannot be included. The reason for the inability of these models to include any cathodic counter reaction can be traced to the fact that Galvele's model is based on the steady state “atom” fluxes and not on the “species” fluxes. For electrode reactions such as (1) where the reactant species as well as the product species are in the solution, the corresponding atom fluxes at the electrode surface turns out to be zero. For example, in the oxygen reduction reaction above, four hydrogen atoms and four oxygen atoms enter as part of the reactants (O<sub>2</sub> and 2H<sub>2</sub>O) and the identical numbers leave as the product (4OH<sup>−</sup>). Though reaction (1) leads to a flux of OH<sup>−</sup> ions going into the solution, Galvele's model which is based on atom fluxes cannot describe this flux. It can capture only the metal ion flux arising from the anodic dissolution of the metal:



Here the metal M is a part of the electrode, while the metal ion is in the solution. Hence there is a non-zero metal atom flux at the metal/solution interface.

\* Corresponding author. Tel.: +91 4565 241480; fax: +91 4565 227779.

E-mail address: [boscoemmanuel@yahoo.co.in](mailto:boscoemmanuel@yahoo.co.in) (B. Emmanuel).

**Nomenclature**

$C_i(x, t)$	concentration of $i$ -th species in the electrolyte, mol/dm <sup>3</sup>	$F_s$	flux of the species $s$ , mol/(dm <sup>2</sup> s)
$K_1, K_2$ and $K_3$	stability constants of reactions in the electrolyte	$I$	impressed current density, A/dm <sup>2</sup>
$D_i$	diffusion coefficient of $i$ -th species, dm <sup>2</sup> /s	$F$	Faraday, C/mol
$R_i$	reaction rate of $i$ -th chemical reaction, mol/(dm <sup>3</sup> s)	$D$	the common diffusion coefficient, dm <sup>2</sup> /s
$k_{if}$	forward rate constant of $i$ -th reaction in the electrolyte	$x, t$	space and time variable, dm, ms to days
$k_{ib}$	backward rate constant of $i$ -th reaction in the electrolyte	$l$	thickness of the thin electrolyte film or the diffusion layer in RDE experiment, dm
$L_M(x, t), L_H(x, t),$ and $L_O(x, t)$	linear combinations of concentrations, mol/dm <sup>3</sup>		

It is clear that for a complete understanding of the passivity phenomenon, the species fluxes (e.g. OH<sup>−</sup> and H<sup>+</sup>) at the electrode surface arising from the cathodic counter reactions such as oxygen reduction and hydrogen evolution should also be included in the model besides the metal ion flux. The proposed SSD model is aimed at achieving this goal and provides a new theoretical methodology for describing the time-dependent changes in the solution composition leading to passivity or pitting. Unlike the earlier models which are applicable only to the impressed current condition the present model is applicable to both the free corrosion condition and the impressed current situation.

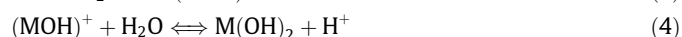
A typical corrosion scenario involves a metal or alloy surface generating a flux of metal ions and hydroxyl ions or consuming hydrogen ions. The metal ions diffuse into the solution, hydrolyse water generating H<sup>+</sup> which in turn modify the self hydrolysis equilibrium of water (H<sup>+</sup> + OH<sup>−</sup> = H<sub>2</sub>O) and react with a host of other ions such as hydroxyl, chloride, bicarbonate and sulphate depending on the composition of the corrosive medium. When the concentration of hydroxy, chloro-hydroxy and other metal complexes exceed certain solubility limits passive layers may deposit on the metal. This will decide between passivity and pitting when these processes take place inside pits, cracks or other voids present in bare or coated metals. On uniform metallic surfaces, general corrosion or passivity will be the result. Precipitation and strong bonding of the precipitate to the corroding metal leading to a compact, non-porous layer will be ideal for corrosion control and self-repair. On the other hand, if the corrosion products are loosely adherent to the metal surface, soft and porous or if they precipitate in the solution, passivity will not set in. Therefore the question of if and when the solubility thresholds are exceeded become important. In fact Cole and Muster [4] undertook an experimental scanning electron microscope/focussed ion beam and in situ Raman study of oxide growth on zinc under seawater droplets. In the in situ Raman they observed rapid (within minutes) growth in the Zn–O bond vibration and somewhat slower growth in sulphate and carbonate bond vibrations (probably associated with gordiate and hydrozincite). The focused ion beam sections demonstrated that solid solution growth of the oxide initially dominated with the growth of a high porous crystalline phase (gordiate or simonkolleite) or precipitation of crystalline phase from solution occurring after some time (around 30 min). The present model is aimed at capturing, in such situations, the solution dynamics leading to passivity or pitting.

In the present work we consider two different geometries: semi-infinite and finite. For corrosion in bulk electrolytes the semi-infinite geometry will be appropriate while the finite geometry will be useful for a metal covered with a thin electrolyte layer [5] or a porous oxide layer [6] and for the Rotating Disc Electrode [7]. However detailed results are presented only for the semi-infinite geometry and work on the other two geometries is in progress [8].

In Section 2, we formulate the detailed mathematical model with its assumptions and approximations clearly spelt out and the analytical solutions of the model for the space–time dependence of the various species concentrations are presented in Section 3. Results, based on this model, for the time evolution of the surface concentration of the metal-ion complexes which can deposit and passivate the metal are presented and discussed in Section 4 for free corrosion condition, different impressed currents and initial pH values for iron and zinc. Typical concentration-versus-distance profiles are also provided for all the species. Conclusions and future perspectives are in Section 5.

## 2. The SSD model framework and the assumptions

The model starts with known fluxes of metal ions and hydroxyl or hydrogen ions at the metal/electrolyte interface. For free corrosion condition the current densities associated with these fluxes balance one another so that there is no net current through the system whereas for the case of impressed current/potential these fluxes will be such as to produce a net current through the system. We report on both these cases. Without loss of generality we treat here the case where oxygen reduction is the cathodic reaction while the case of hydrogen evolution will be taken up in the future work. Thus we have metal ions and hydroxyl ions coming into the solution where they diffuse and undergo solution reactions which are, in the simplest case, the following hydrolysis reactions involving the metal ion M<sup>2+</sup> and the self-hydrolysis reaction of water.



M<sup>2+</sup> may be any divalent metal ion such as Fe<sup>2+</sup>, Zn<sup>2+</sup> and Mg<sup>2+</sup>. For the trivalent metal ions Al<sup>3+</sup> and Fe<sup>3+</sup>, there will be one more hydrolysis step. After labelling the species M<sup>2+</sup>, H<sub>2</sub>O, (MOH)<sup>+</sup>, H<sup>+</sup>, M(OH)<sub>2</sub> and OH<sup>−</sup> respectively by the numerals 1, 2, 3, 4, 5 and 6, the stability constants may be written as

$$K_1 = \frac{C_3 C_4}{C_1 C_2} \quad (6)$$

$$K_2 = \frac{C_3 C_4}{C_1 C_2} \quad (7)$$

$$K_3 = \frac{C_4 C_6}{C_2} \quad (8)$$

where  $C_i$  is the concentration of the  $i$ th species in the reactions (3)–(5) above.

The species 1–6 diffuse in the solution and while diffusing they also undergo chemical reactions. In addition, some of these species will be generated or consumed at the electrode surface by

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