

## A Unified Theory for Passivity and Passivity Breakdown

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Traditionally, the phenomena of passivity and passivity breakdown have been described from quite different theoretical perspectives [1]. Thus, the existence of passive films has most commonly been described in terms of equilibrium thermodynamic concepts, most notably by Pourbaix in terms of potential-pH diagrams [2]. However, more recent analyses [3] demonstrate that passive films are thermodynamically meta-stable entities whose existence depends upon a judicious relationship between the rate of formation and the metal/barrier layer (m/bl) and the rate of destruction at the barrier layer/solution (bl/s) interface. This finding has introduced a new, kinetic theory for the growth of the barrier layer (bl) that is equally applicable in describing all passivity and passivity breakdown phenomena. From the Point Defect Model [1,3], the rate equation for describing barrier layer growth can be written as (for  $\text{pH} < \text{PZC}$ , where the PZC is the pH of zero charge):

$$\frac{dL}{dt} = \Omega k_3^0 e^{a_3 V} e^{-b_3 L} e^{c_3 \text{pH}} - \Omega k_7^0 e^{a_7 V} e^{c_7 \text{pH}} \left( \frac{C_{H^+}}{C_{H^+}^0} \right)^n \quad (1)$$

where  $\Omega$  is the mole volume of the barrier layer per cation,  $k_3^0$  is the standard rate constant for the generation of oxygen vacancies at the m/bl interface,  $L$  is the bl thickness,  $k_7^0$  is the standard rate constant for the dissolution of the bl,  $a_3$ ,  $b_3$ ,  $c_3$ ,  $a_7$ , and  $c_7$  are constants that depend upon fundamental parameters in the model,  $C_{H^+}$  is the concentration of hydrogen ion at the bl/s interface,  $C_{H^+}^0$  is the standard state concentration (1 mol/l), and  $n$  is the kinetic order of the bl dissolution reaction with respect to hydrogen ion. In reduced form, and for constant  $V$  and  $\text{pH}$ , this equation can be written as

$$\frac{dL}{dt} = A e^{-b_3 L} - C \quad (2)$$

where the constant  $A = \Omega k_3^0 e^{a_3 V} e^{c_3 \text{pH}}$  and the dissolution rate becomes  $C = \Omega k_7^0 e^{a_7 V} e^{c_7 \text{pH}} \left( \frac{C_{H^+}}{C_{H^+}^0} \right)^n$ .

Under steady state conditions  $dL/dt = 0$  and this may be used to define the steady state thickness of the bl as;

$$L_{ss} = -\frac{1}{b_3} \ln \left( \frac{C}{A} \right) \quad (3)$$

Now, the barrier layer cannot be negative, so that the condition that the barrier layer exists is simply that  $A > C$ . The quantity  $A$  is simply the rate of growth of the bl at the m/bl interface at zero bl thickness and, as previously stated,  $C$  is the destruction rate of the bl at the bl/s interface. This simple inequality,  $A > C$ , is the condition that must exist if a metal or alloy is to exhibit a passive state.

Implicit in the above discussion is the phenomenon of passivity occurs over a macroscopic area and, indeed, depassivation arising from  $C > A$  does occur over such dimensions (e.g., transpassive dissolution, electro-polishing, erosion-corrosion, fretting corrosion), but the same concepts can be applied at microscopic dimensions to describe localized corrosion processes, such as pitting corrosion, stress corrosion cracking, and corrosion fatigue, as will be shown in this paper.

1. D. D. Macdonald, "Passivity: The Key to Our Metals-Based Civilization", *Pure Appl. Chem.*, **71**, 951 (1999).
2. M. Pourbaix, "Atlas of Electrochemical Equilibria", NACE international, Houston, TX, 1974.
3. D. D. Macdonald. "On the Existence of our Metals-Based Civilization: I. Phase Space Analysis," *J. Electrochem. Soc.*, **153**(7), B213 (2006).