STABLE PITTING CORROSION OF STAINLESS STEEL AS DIFFUSION-CONTROLLED DISSOLUTION PROCESS WITH A SHARP MOVING ELECTRODE BOUNDARY

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Summary. *This contribution is devoted to explanation and prediction of corrosion pit propagation or stable pit growth, governed by ion transport properties in electrolytic solutions by deriving the (3D) mass balance for a body hosting a sharp dissolution front which separates the solid electrode from liquid electrolyte. The model is completed by Fick's law of diffusion, governing the behavior of the dissolved metal ions.*

1 INTRODUCTION

Corrosion plays an adversary, but central role in different technological fields, concerning biomedical implants, automobile industry, metallic coatings, and engine parts. On the civil engineering side, reinforced and post-tensioned concrete bridges may suffer durability problems due to steel corrosion of post-tensioning tendons in prestressed concrete bridges and/or from corroding reinforcing bars.

Steel corrosion is an electrochemical process, initiated by certain electrochemical conditions in the proximity of the steel member: depassivated steel surface, sufficient humidity, and sufficient electrochemical potential. If the passive layer is destroyed locally (e.g. due to the presence of chlorides at the steel surface), while humidity and electrochemical potential prevail constantly at a sufficient level, stable pitting corrosion will occur.

2 PREDICTION MODEL

The very existence of a sharp boundary separating the intact solid metal (electrode) from a solution (electrolyte) requires the dissolution process to be infinitely fast with respect to the diffusion process [8]. Such a problem is called to be of Stefan-type [11], and it refers to diffusion-controlled or stable pitting corrosion. Instantaneous dissolution results in a constantly saturated solution at the fluid side of the dissolution front, the movement of which depends only on the diffusion of the dissolved species. Its proper simulation requires formulation of mass balance for a domain hosting two subdomains (solid metal and electrolyte), separated by a sharp surface of discontinuity Σ (see Fig. 1).
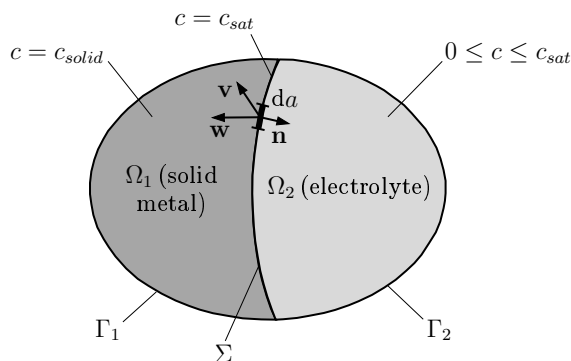
Figure 1: Definition of a domain separated into two subdomains Ω_1 and Ω_2 with boundaries Γ_1 and Γ_2; the subdomains are separated by the surface of discontinuity Σ

Subdomain 1, Ω_1, relates to the solid steel, subdomain 2, Ω_2, relates to the dissolved metal ions. Thus, mass balance is expressed by the local continuity equation,

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{J} = 0 \ \text{ with } \ 0 \leq c \leq c_{sat} \ \text{ in } \ \Omega_2, \tag{1}$$

and the jump, or Rankine-Hugoniot condition,

$$([\mathbf{J}] - [c_{solid} - c_{sat}]\mathbf{v}) \cdot \mathbf{n} = 0 \ \text{ with } \ c = c_{sat} \ \text{ on } \ \Sigma. \tag{2}$$

Combination with Fick's law of diffusion [1],

$$\mathbf{J} = -D\nabla c, \tag{3}$$

yields a prediction model with only three input values, namely the ion concentration in the solid metal, $c_{solid} = 144.0 \, \text{mol/l}$ [7], the saturation concentration of the dissolved metal ions in the electrolyte, $c_{sat} = 5.1 \, \text{mol/l}$ [2], and the diffusion coefficient of dissolved metal ions, $D = 0.85 \times 10^{-5} \, \text{cm}^2/\text{s}$ [4].

3 RESULTS

By solving Eqs. (1) – (3) for appropriate initial and boundary conditions, either analytically or numerically by the Finite Volume Method (FVM) [8], experimental results of Ernst and Newman [2, 3], Laycock and Newman [5, 6] (see Fig. 2(a)), and Pistorius and Burstein [9] (see Fig. 2(b)) can be satisfactory predicted, showing the diffusion-control of corresponding experiments. Moreover, knowledge of the lacy cover porosity allows pit shape prediction (see Fig. 3).

4 CONCLUSIONS

Pit depth and pit width evolutions are governed (almost) exclusively by a diffusion-controlled dissolution process, i.e. they depend on the solid metal concentration, on the
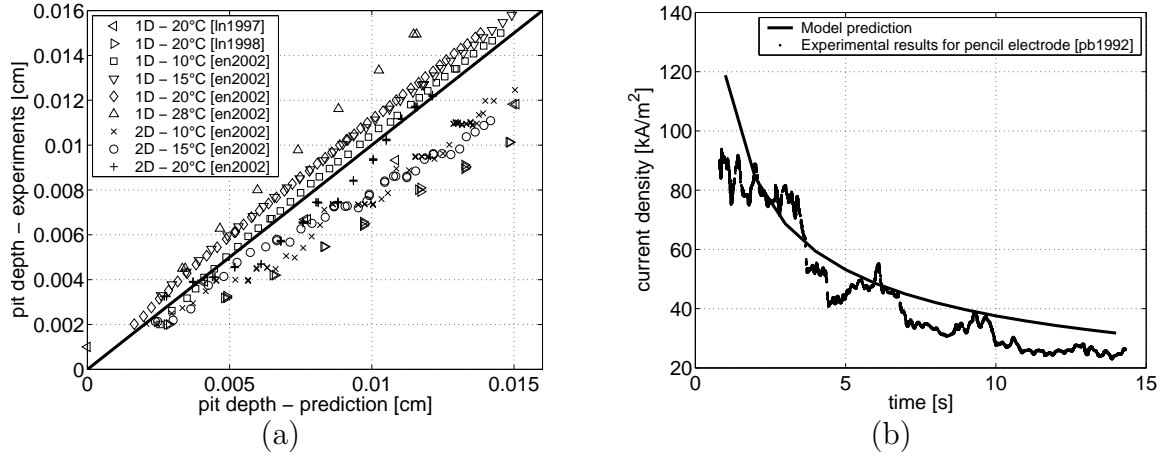
Figure 2: (a) comparison of the predicted pit depth [10] with the experimental values for (1D) pencil electrodes [2, 3, 5, 6] and (2D) foil electrodes [2, 3], (b) early stages of pit growth: comparison of the model prediction [10] with the measured current density [9] at an applied potential of 0.56 V
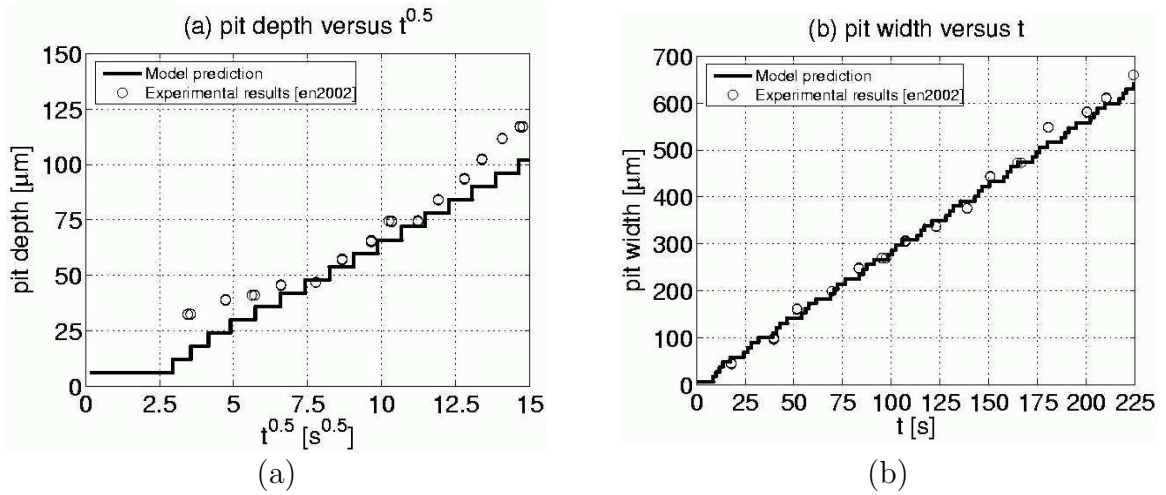

Figure 3: Results of the model predictions [10] for a 2D pit compared with respective experiments [2, 3]: (a) pit depth is a linear function of $\sqrt{t}$, (b) pit width is a linear function of t

saturation concentration of dissolved metal ions, and on the diffusion coefficient of the ionic solution, as well as on the boundary conditions for ionic flux. In the case of 2D pits with lacy covers, the latter probably depend on complex depassivation-repassivation phenomena which require further electrochemical analyses [1]. However, once the extent of lacy cover perforation is known, the entire pit propagation problem reduces to a classical Stefan-type problem with a sharp moving electrode boundary separating the solid electrode from the liquid electrolyte. The introduced simulations are believed to enhance predictability of steel corrosion in concrete bridges, supporting the decision process on appropriate measures for bridge maintainance and repair. They are probable to play a

role in the design and corrosion protection of any metallic parts (or materials susceptible to corrosion) in engineering.

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