

Hybrid Multiscale Modeling of Corrosion Nanoinhibitors Transport

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Abstract: Until recently, chromium based coatings were in widespread use due to their high mechanical properties as well as corrosion resistance. However, more and more stringent environmental and health regulations demand the substitution of these composites due to their high toxicity. In this direction, progress in coating technology has made possible to develop free-chromate corrosion inhibitors which are capable to smartly migrate when required. In order to support the coating design, we propose a hybrid mathematical model to study the inhibitors release by taking into account the thermodynamics and kinetics involved in the corrosion process. The proposed model is intended to study the transport of such inhibitors, while providing a computational tool for the calculation of useful parameters by avoiding trial and error experimental set ups. Relevant parameters such as the time scale and the amount of inhibitor that is being release could be investigated.

Keywords: Corrosion protection, nanoinhibitors, multiscale modeling, diffusion transport

1 Introduction

Corrosion is an ubiquitous phenomenon that is defined or characterized as the deterioration of a material physical properties or attributes from exposure and interaction with the environment. Unfortunately, it is not uncommon to witness catastrophic failures resulting when corrosion damage undermines the load bearing capability of a structure, or when pollution by corrosion prod-

ucts from lead piping result in possible toxic levels of lead in drinking water supplies just to mention some instances. In industrial settings, such as the aerospace and automotive, corrosion represents one of the biggest economic loss as reported by different companies, furthermore many aluminium alloy structures used in aircrafts and automobiles are still being protected by chromate conversion coatings (CCC), chromate-pigmented organic paints, and other chromate-based chemicals compounds which provide the most efficient corrosion protection, but that represent a threat to humans due to their high toxicity.

According to the German Transport Information Service (TIS), corrosion protection methods can be classified as active, passive, temporary, and permanent. The first two refer to the type of protection, while the others refer to frequency in which a corrosion susceptible system is protected. In the first method protection is achieved by influencing the reactions which proceed during corrosion, while in the second such task is carried out by mechanically isolating the package contents from the aggressive corrosive agents, for example by using protective layers, films or other coatings that do not change neither the general ability of the package contents to corrode nor the aggressiveness of the corrosive agent. In this respect, coating systems have traditionally been designed as passive barrier films. However, recent approaches emphasize the design of hybrid (organic-inorganic) coatings with outstanding abilities, particularly, hybrid multifunctional coatings doped with free-chromate corrosion inhibitors that can be smartly triggered under demand [3, 1].

Such novel technology could not only replace the current corrosion chromate coatings but also add tailored third functions such as abrasion resistance, and low friction or low surface free energy.

To support the production and optimization of such efficient thick layer corrosion protection coatings, we propose a hybrid multiscale model of corrosion nanoinhibitors transport. This model, considers effects at the micro and macroscale based on the nanocomposite properties. Additionally, chemical kinetics and thermodynamic mechanisms, e.g. the corrosion reactions, effective diffusivity (in the coating and in the layer or substrate), chemical equilibrium, and reaction rates are being considered.

2 Model

We assume that the corrosion inhibitors or active components are physically represented as ions encapsulated in a porous polymeric matrix. For the transport of ions, concentration and potential gradients are assumed as the main driving forces. Based on this assumption, we make use of the Nernst-Planck equation to define the mass balance equation for inhibitor species c_i ,

$$\frac{\partial c_i}{\partial t} + \nabla \cdot N_i = \Psi, \quad (1)$$

where flux vector for species i considering the driving forces is given by,

$$N_i = -D_{eff} \nabla c_i - z_i u_{m_i} F \nabla (c_i \nabla V), \quad (2)$$

the mobility u_{m_i} can be calculated as,

$$u_{m_i} = \frac{D_i}{RT}, \quad (3)$$

and the molar fluxes obey the following relation,

$$N_i \cdot \mathbf{n} = \frac{\mu_{ij} I_j}{F}. \quad (4)$$

In equation (3), μ_{ij} represents a stoichiometric coefficient for ionic species i in reaction j , while I_j is the ionic current density. The current densities are assumed to be Butler-Volmer like equations of the form:

$$I_{j_{corr}} = j_{0I} \left\{ e^{-\beta} - \frac{c_\alpha}{c_{0\alpha}} e^\beta \right\}, \quad (5)$$

$$I_{j_{inh}} = j_{0II} \left\{ \frac{c_\gamma}{c_{0\gamma}} e^{-\delta} - e^\delta \right\}. \quad (6)$$

The potential in the vicinity of the anode is assumed to be a time dependent function, in which changes in PH can be tuned by means of constants a and b . We also point out that in what follows it is assumed that the anode is the place where corrosion takes place:

$$V(t) = -a \log(t+b) \text{ for real numbers } a, b > 0. \quad (7)$$

In order to consider transport effects with respect to the radius of inhibitors and their host material, we make use of an effective diffusion coefficient based on the well-known Maxwell-Garnet theory,

$$D_{eff} = D_2 \left[1 + \frac{d(D_1 - D_2)\Phi}{D_1 + (d-1)D_2 - (D_1 - D_2)\Phi} \right],$$

where

$$\Phi = \left(\frac{r_0^i}{r_1^i} \right)^d.$$

Here, D_1 and D_2 denote the diffusion coefficients of inhibitors and host carriers, r_0 and r_1 represent the average radius of inhibitors and carriers respectively, while d is the dimension of the space.

See Fig.(1), for an illustration of the processes of corrosion and self-healing mechanisms that are being considered.

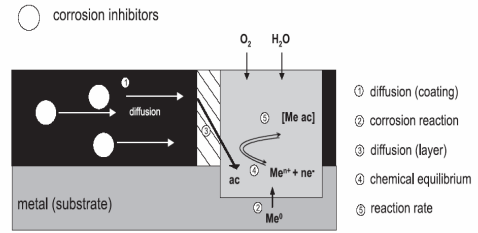


Figure 1: Corrosion mechanisms being considered

2.1 Condition for passivation

In regard of a passivation condition in the vicinity of a corrosion crack, we propose the following relation at the boundary between the intact solid metal and a solution (electrolyte),

$$(I_{j_{inh}} - [c_{solid} - c_{sat}]v) \cdot \mathbf{n} = 0.$$

Assuming that the dissolution rate of material dominates the diffusion process.

3 Numerical simulations

In order to investigate the rate of inhibitor transport, for convenience we consider a simple one dimensional anode-cathode system as shown in Fig.(1)[2].

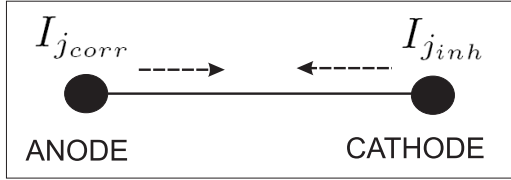


Figure 1: 1D anode-cathode system

A simulation of such a simplified model is shown in Fig.(2), in which, the anode and cathode are thought of as located as extreme points in the x-axis separated by a distance of $10 \times 10^{-3}m$, while the y-axis shows the concentration of inhibitors in the domain for increasing times from top to bottom. The reduction of concentration of inhibitors in the anode (left point) is due to their reaction with other species while exerting a passivation effect in the corrosion area.

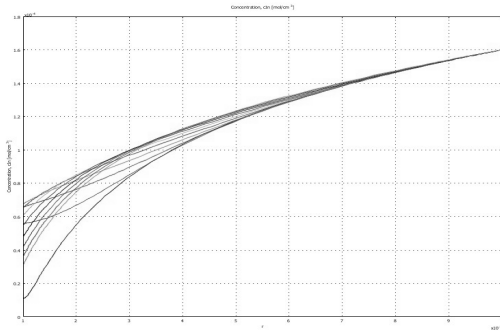


Figure 2: 1D anode-cathode system

Fig.(3) shows the simulation of the system for a 2D domain. Here, the crack present in the coating is noticeable (middle) together with a set of inhibitor reservoirs (circles around the crack) which donate inhibiting species via detecting a change of PH and thus potential around the crack.

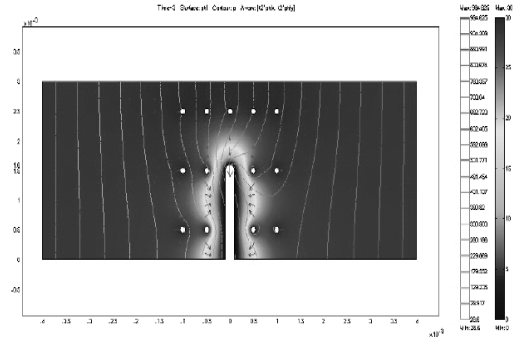


Figure 3: 2D system with corrosion crack and inhibitors transport

In order to obtain information on the mechanisms and kinetics of the self healing and corrosion processes in micro-confined defects, we have made use of the scanning vibrating electrode technique (SVET) and the scanning ion-selective electrode technique (EIS), the first makes use of a micro-probe enabling to calculate current densities via the potential difference between the maximum and minimum of the vibration amplitude Fig.(4).

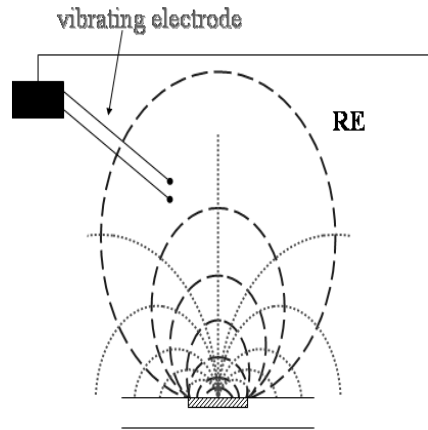


Figure 4: Scanning vibrating electrode technique (SVET)

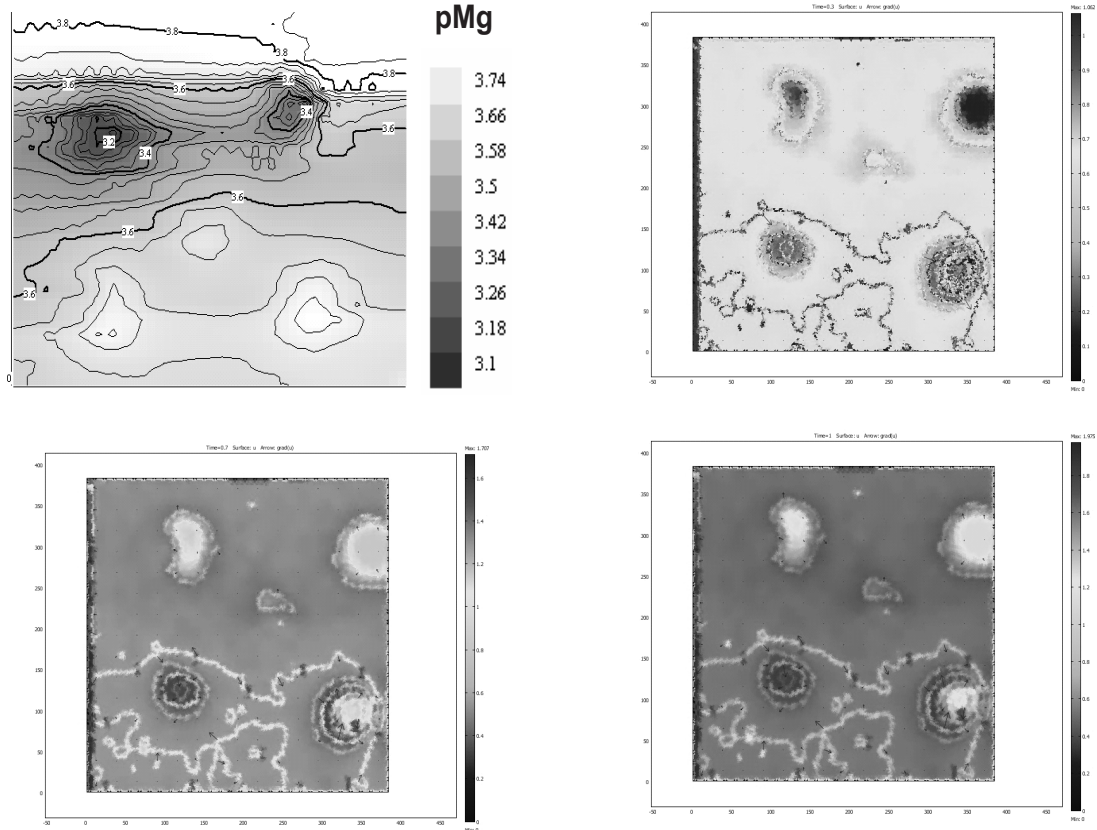


Figure 5: (top, left) SVET experimental data; (top, right) and (bottom) COMSOL simulations showing the effect of inhibitors concentration over time

Fig.(5)(top, left), shows experimental data obtained by SVET, in this image micro defects of sizes 1-2 mm were artificially produced (5)(top, right) and (5)(bottom) shows numerical simulations of the effect of inhibitors by taking initial conditions in the inhibitors transport model.

4 Conclusion

We have introduced a hybrid transport model for corrosion inhibitors ions that considers effects at different spatial scales, and in which different inhibitors reservoirs distributions can be studied by using COMSOL capabilities. Such a model takes advantage of novel experimental techniques for the study of confined micro-defects. This model offers enough flexibility for the study of additional flux terms, such as in the case of porosity and tortuosity of coatings, as well as the study of conducting polymer coatings. This issues are currently under investigation.

References

- [1] M.A. Jakab and J.R. Scully, *On demand release of corrosion inhibiting ions from amorphous Al-Co-Ce alloys*, Nature Materials **4** (2005), 667–670.
- [2] C. Trenado and D.J. Strauss, *Multiscale multiphysics modeling*, In proceedings: Energetyka Zeszyt tematyczny (2007), 73–77.
- [3] M.L. Zheludkevich, M. Serra, M.F. Montemayor, K.A. Yasakau, I.M. Miranda-Salvado, and M.G.S. Ferreira, *Nanos-structured sol-gel coatings doped with cerium nitrate as pre-treatments for AA2024-t3 corrosion protection performance*, Electrochim. Acta **51** (2005), 208–217.

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