Mathematical modeling of galvanic cells beneath organic coatings

K. N. Allahar[*], M. F. Hurley[*], E. D. Sapper[+], D. P. Butt[*]

[*]Department of Materials and Science Engineering,
Boise State University, Boise, ID 83725, USA.

[+]Boeing Research and Technology
PO Box 3707, M/C 42-30, Seattle, WA 98124, USA.

The corrosion at buried metal-coating interfaces under an open circuit condition occurs through the galvanic interaction between anodic and cathodic sites. The requirements include pathways for electronic conductivity and ionic transport between the sites and a driving electrochemical force for the electrochemical reactions that exceeds the *iR* drop. A mathematical model of a galvanic cell is presented that addresses the ionic transport between anodic and cathodic sites beneath an organic coating on an aluminum substrate.

Reports in literature addressing the transport of ions in organic coatings have indicated that the corrosion at the metal-coating interface is influenced by the local ionic concentration and coating condition at the interface.[1] Experimental galvanic cells between coated zinc and coated steel were used to demonstrate the polarization of the metal-coating interfaces with the zinc dissolution being balanced by cathodic reactions at the steel surface.[2]

Numerous models of the electrochemistry in electrolyte-metal systems have been presented in literature with only limited models for the transport of ionic species in organic coatings.[3] Recently, a one-dimensional model was presented by Allahar *et al.*[4] that simulated the transient electrochemistry in an electrolyte-coating-metal system under open-circuit conditions of balanced anodic and cathodic current densities. In this model, the corrosion potential and corrosion current density were functions of the local pH at the metal-coating interface.

A model of a two-dimensional, electrolyte-coating-metal system is presented here. The local polarization behavior, a function of pH, was coupled to the global polarization behavior by the constraint of a net zero current density. The casting of the local polarization behavior as a function of pH allowed the system to evolve to an open-circuit condition in response to changes in the system. This mathematical model provides a framework to describe the mechanisms involved in the evolution of galvanic cells beneath organic coatings.

Mathematical Model

A two-dimensional, transient mathematical model was developed to simulate the transport of ionic species in an electrolyte-coating-metal system. The model used the Nernst-Planck equation for the flux of a species i,

$$N_i = -z_i u_i c_i F \nabla \Phi - D_i c_i \tag{1}$$

where u_i is the mobility, D_i the diffusion coefficient, z_i the charge number, c_i the concentration, Φ the solution potential and F Faraday's constant. The contribution of convection was considered negligible. The porosity of the coating was accounted for in the diffusion coefficient of the species, D_i^*, in the coating by using

$$D_i^* = \varepsilon^{1.5} D_i \tag{2}$$

where ε is the porosity of the coating. The conservation of a species was expressed as

$$\frac{\partial(\varepsilon c_i)}{\partial t} = -\nabla \cdot \left(\varepsilon^{1.5} N_i\right) + R_i \tag{3}$$

where the accumulation term is on the left-hand side and the net input of the flux and net rate of production of species by homogeneous reactions are on the right hand side, respectively. In the electrolyte domain, the porosity was set at unity. Homogeneous reactions were not considered with the ionic species being Na^+, Cl^-, OH^- and Al^{3+}.

The experimental polarization behavior of 99.99% Al in de-aerated NaCl at different pH values was used to cast the polarization behavior of aluminum dissolution and hydrogen evolution as functions of pH.[4,5] The current density at the metal coating interface i_{Al} for the aluminum dissolution reaction was calculated using a modified Tafel expression

$$i_{Al} = \omega_A \omega_{Al} i_{Al}^o 10^{(V - E_{Al}^o)/\beta_{Al}} \tag{4}$$

where β_{Al} is the Tafel slope, and E_{Al}^o, a reference potential and i_{Al}^o, a reference current density, were functions of pH. Weighting parameters ω_A and ω_{Al} were used to account for the surface area available for the heterogeneous reaction and the reduction in the current density at the interface, respectively. The electrochemical potential V is defined as $V = E - \Phi$, where E is the metal potential. A similar expression was used for the hydrogen evolution reaction. The governing equations of conservation of species and electroneutrality were solved using a finite difference approach with the program developed in FORTRAN.

Galvanic cells between anodic and cathodic sites were simulated by weighting the current densities differently. The open-circuit transient behavior was simulated by finding the metal potential at which the global anodic and cathodic current densities were balanced. Simulations showed the evolution of the electrochemistry and metal potential associated with a galvanic cell to an open circuit condition in response to changes in the bulk pH and polarization conditions.

References
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