

Modeling Galvanic Corrosion

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Abstract: Galvanic corrosion is an electrochemical process that occurs when at least two dissimilar metals (electrodes) are in electrical contact with one another while immersed in a conducting environment known as an electrolyte. This paper describes modeling work on galvanic corrosion where the corrosion rate is calculated from the values of electrochemical potential and electric current at the metal surfaces. The values of potential and current at the surfaces are obtained by solving Laplace's equation for the potential field inside the electrolyte subject to appropriate current-potential relationships commonly used in electrochemicals. The results obtained are in excellent agreement with previous results obtained by other methods for a specially selected test problem. The paper then describes results of several other examples that clearly show the versatility of the finite element method.

Keywords: galvanic, corrosion, electrochemistry,

1. Introduction

Electrochemical reactions are chemical reactions that involve release and uptake of electrons from/to an external circuit. One electrode acts predominantly as anode (electron and cation producing) and is the component of the galvanic couple that undergoes material dissolution while the other acts predominantly as cathode and is the site where a cathodic (electron and anion consuming) reaction takes place. The electrons produced by the anodic reaction are exactly used up by anions at the cathode by the cathodic reaction.

Galvanic corrosion is an electrochemical process that occurs when at least two dissimilar metals (electrodes) are in electrical contact with one another, and are in a conducting environment known as an electrolyte [1], (see also Figure 1).

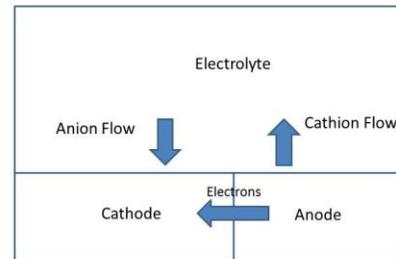


Figure 1. Schematic representation of electrochemical phenomena in a galvanic junction.

The amount and rate of dissolution of the anode material is directly related to the electrochemical potential distribution at the anode-electrolyte interface. Assuming a stagnant electrolyte, the equation governing the distribution of electrochemical potential inside it, is obtained combining the equation conservation of charge with the constitutive equation relating the electric field distribution to the electrochemical potential gradient. The result is Laplace's equation. The equation must then be solved subject to appropriate boundary conditions.

2. Theory

Under steady state conditions, the potential distribution within the electrolyte of a galvanic system is determined by the charge conservation equation for in the electrolyte.

$$\nabla \cdot i = 0$$

Where i is current density and t is time. Since the current density is related to the electric field (E) by Ohm's Law, $i = \sigma E$, where σ is the electrical conductivity of the electrolyte and the electric field is related to the electrochemical

potential ϕ by $E = -\nabla\phi$, the equation governing the potential distribution in the electrolyte becomes Laplace's equation (for constant conductivity)

$$\nabla^2\phi = 0$$

The governing equation for the potential must be solved subject to appropriate boundary conditions. At any electrode-electrolyte interface, both anodic and cathodic processes take place simultaneously and the current density through the interface is the result of the electronic exchanges in both processes. In a galvanic couple, the cathodic process dominates in the more noble metal (the cathode) while the anodic process is dominant in the less noble metal (the anode). The Butler-Volmer equation [2] gives the total current density at any electrode-electrolyte interface as

$$\begin{aligned} i_{\text{net}} &= i_{\text{anodic}} + i_{\text{cathodic}} = \\ &= i_0 \exp[a_{\text{anodic}} zF(\phi - \phi_0)/RT] - \\ &\quad i_0 \exp[-a_{\text{cathodic}} zF(\phi - \phi_0)/RT] \end{aligned}$$

where i_0 is the exchange current density, a_{anodic} , a_{cathodic} are the transfer coefficients for the anodic cathodic reactions, respectively and ϕ_0 is the equilibrium electrode potential. Moreover, z is the number of electrons involved in the reaction, F is Faraday's constant, R is the gas constant and T is temperature. The current density at the electrode surface is directly proportional to the normal component of the electrochemical potential gradient at the interface

$$\partial\phi/\partial n = -i_{\text{net}}/\sigma$$

One thus obtains a non-linear Neumann boundary condition for Laplace's equation. The current density is assumed negligible at all other domain boundaries.

3. Use of COMSOL Multiphysics

For model calibration and validation purposes the coefficient form PDE mathematics module of COMSOL Multiphysics was used to recreate the two-dimensional galvanic corrosion geometry studied in [3]. The input data are shown in Table 1. The default triangular quadratic elements were used and the default normal mesh produced mesh insensitive results.

Table 1 Input Data Used for Model Validation

Property	Value	Units
Tafel Parameters:		
α_A anodic reaction of metal A	0.05	V
α_B anodic reaction of metal B	0.05	V
β_A cathodic reaction of metal A	0.05	V
β_B cathodic reaction of metal B	0.05	V
σ conductivity of the electrolyte	10	$\Omega^{-1}\text{m}^{-1}$
$i_{0,(A)}$ free current density of metal A	1	Am^{-2}
$i_{0,(B)}$ free current density of metal B	1	Am^{-2}
a surface length of metal A	0.01	m
b surface length of metal B	0.01	m
w thickness of the electrolyte	0.01	m
$\phi_{0,(A)}$ free corrosion potential of metal A	0.5	V
$\phi_{0,(B)}$ free corrosion potential of metal B	-0.5	V

4. Results

Using the given data together with the Butler-Volmer (B-V) relationships for the current densities at the electrode surfaces produced the potential distribution in the electrolyte shown in Figure 2. These results are in excellent agreement with those reported in [3].

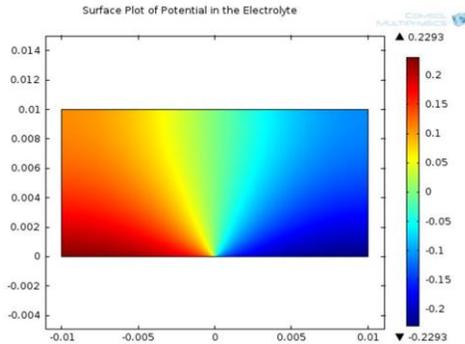


Figure 2. Computed electrochemical potential field in the electrolyte for the test problem used for validation.

Once the potential has been computed, the current density at the electrode-electrolyte interfaces is calculated from the Butler-Volmer equation. Moreover, since according to Faraday's law, the (anodic or cathodic) reaction rate v at the electrode surface is given by

$$v = i/zF$$

an estimate of the corrosion rate is readily obtained. Reaction and corrosion rates are only developed for the anodic surface of each system, because only the anode corrodes.

COMSOL was then used to develop several other models of galvanic corrosion systems. In [3], the effect of applied electrode polarization was also investigated. The COMSOL model was easily modified to simulate the situation resulting from applied polarization of 4.5V. In order to apply the polarization, the zero flux condition on the upper boundary was replaced with a Dirichlet boundary condition that fixed the potential at that boundary to 4.5V. The resulting potential distribution in the electrolyte is shown in Figure 3. The effect of the imposed polarization is clearly shown and the numerical results are again in excellent agreement with those previously reported.

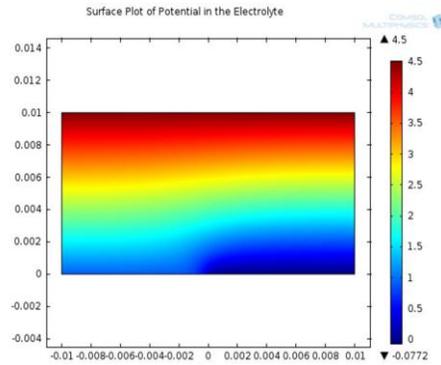


Figure 3. Computed results: system subjected to polarization.

Next, the effect of varying electrode orientation was investigated by modeling two non-coplanar electrodes. Electrode 1 extends further into the electrolyte at a 90 degree angle to the surface of Electrode 2. This geometry could be representative of an area where two plates are not flush to one another.

Figure 4 shows the potential distribution in the electrolyte that was produced using the data in Table 1.

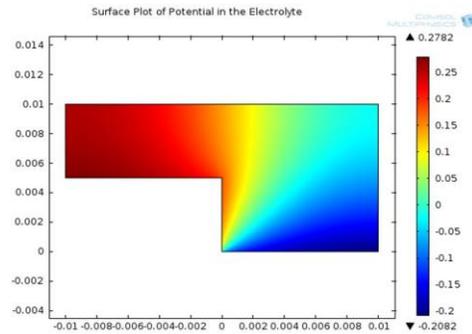


Figure 4. Computed results: system with a step.

Interestingly, the distortion of the electrochemical potential field produced by the new geometry leads to an increase in the corrosion rate of the anode.

An elliptical step was also investigated. Using again the data in Table 1, the results in Figure 5 were obtained

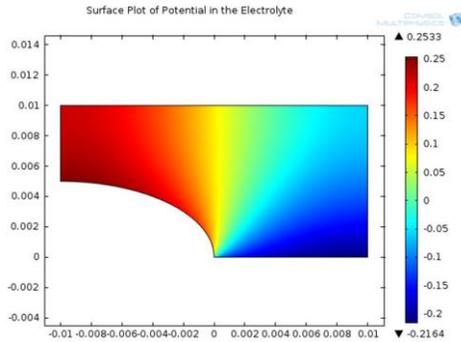


Figure 5. Computed results: system with an elliptical step.

Just as in the case of the discontinuous step, the corrosion rate at the anode increases by just about the same amount.

The next case assumed a 2D axisymmetric geometry. This geometry could be representative of a pipe joint involving two different metals. Using again the input data in Table 1 yields the potential distribution shown in Figure 6.

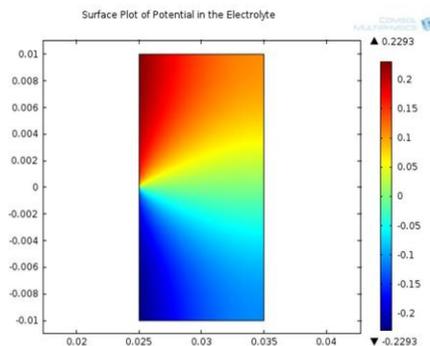


Figure 6. Computed results: axisymmetric electrode geometry.

Several other galvanic corrosion systems were investigated. Detailed descriptions and results can be found in [4].

5. Conclusions

Once the fundamental electrochemistry of the galvanic corrosion problem was clearly

understood and the mathematical problem was correctly stated, COMSOL Multiphysics allowed rapid development of finite element models. Once validated, these models became useful tools for experimentation and discovery.

6. References

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7. Acknowledgements

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