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LINEARIZATION OF A NONLINEAR PERIODIC BOUNDARY CONDITION RELATED TO CORROSION MODELING*

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Abstract

We study galvanic currents on a heterogeneous surface. In electrochemistry, the oxidation-reduction reaction producing the current is commonly modeled by a nonlinear elliptic boundary value problem. The boundary condition is of exponential type with periodically varying parameters. We construct an approximation by first homogenizing the problem, and then linearizing about the homogenized solution. This approximation is far more accurate than both previous approximations or direct linearization. We establish convergence estimates for both the two and three-dimensional case and provide two-dimensional numerical experiments.

Mathematics subject classification: 35J65, 35Q72.
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1. Introduction

A galvanic current is an electron transport process that occurs between anode and cathode. When anode and cathode are placed in electrical contact, the difference in electrolytic voltage rest potential results in an electron flow from anode to cathode. The anode undergoes oxidation, *i.e.*, the anode loses an electron, while the cathode undergoes reduction, *i.e.*, the cathode gains an electron. The anode is said to be corroded and the electron flow is known as a corrosion current, or galvanic current. Rust is the result of a similar type of oxidation-reduction reaction that occurs between different parts of the *same* surface. In fact, rust-causing current is very similar to a galvanic current on a heterogeneous surface. See [14] for further discussion of the subject.

Mathematically, such galvanic interactions can be modeled by the so-called Butler-Volmer boundary conditions of exponential type. The potential is represented by a function ϕ over a Euclidean domain Ω where a portion of its boundary, Γ, is electrochemically active and composed of anodic and cathodic regions. The potential satisfies the Butler-Volmer boundary conditions over both these regions, but with different material parameters in each region. More specifically, we consider Ω to be a cylindrical domain with base some two-dimensional region. The bottom base of the cylinder is a cathodic plane in which anodic islands are periodically distributed throughout. We denote the anodic part of the bottom base of the cylinder as $\partial\Omega_A$ and the cathodic part as $\partial\Omega_C$, see Fig. 1.1. If we define the bottom base of the cylinder to be

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Γ, then the inert portion of the boundary is $\partial\Omega \setminus \Gamma$. Furthermore, $\Gamma = \overline{\partial\Omega_A} \cup \partial\Omega_C$, where $\partial\Omega_A$ and $\partial\Omega_C$ are open sets such that $\partial\Omega_A \cap \partial\Omega_C = \emptyset$. The electrolytic voltage potential, ϕ, satisfies the following nonlinear problem,

$$
\begin{aligned}
&\Delta\phi = 0 \quad \text{in } \Omega,\\
&-\frac{\partial\phi}{\partial n} = J_A[e^{\alpha_{aa}(\phi - V_A)} - e^{-\alpha_{ac}(\phi - V_A)}] \quad \text{on } \partial\Omega_A,\\
&-\frac{\partial\phi}{\partial n} = J_C[e^{\alpha_{ca}(\phi - V_C)} - e^{-\alpha_{cc}(\phi - V_C)}] \quad \text{on } \partial\Omega_C,\\
&-\frac{\partial\phi}{\partial n} = 0 \text{ on } \partial\Omega \setminus \{\partial\Omega_A \cup \partial\Omega_C\},
\end{aligned}
\tag{1.1}
$$

where the transfer coefficients $\alpha_{aa},\ \alpha_{ac},\ \alpha_{ca},\ \alpha_{cc}$ are such that

$$\alpha_{aa} + \alpha_{ac} = 1, \quad \alpha_{ca} + \alpha_{cc} = 1.$$

The anodic and cathodic polarization parameters J_A and J_C are positive constants and $V_A,\ V_C$ are the anodic and cathodic rest potentials respectively.

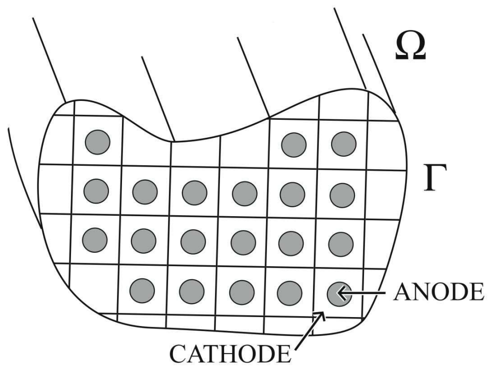

Fig. 1.1. The cylindrical domain, Ω, has a two-dimensional base, Γ, that is made up of anodic islands periodically distributed in a cathodic plane.

This problem has been studied quite a bit in the electrochemistry community. For example, in [12, 13] the authors compute finite element numerical solutions to (1.1). They observe resulting currents for various anodic shapes. Within the applied mathematics community, several aspects of the two dimensional homogeneous problem, including optimal control [9], and singular solutions for negative polarization parameters [7, 11, 15] have been investigated. In [6] we analyzed the periodically heterogeneous problem in two and three dimensions, and suggested a linear correction term. Although the approximations were reasonable and could be shown to converge in various norms, significant error remained in the approximation of the boundary current.

In this paper we suggest a new approximation to (1.1) that consists of the constant solution to the homogenized problem plus a linear correction that is essentially a linearization of (1.1) about the homogenized solution. This approximation, while no more expensive to compute than that of [6], is far more accurate. We demonstrate this both analytically and numerically.