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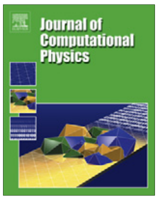

A computational approach for the simulation of natural convection in electrochemical cells

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ABSTRACT

A novel computational approach for the numerical simulation of electrochemical systems influenced by natural convection phenomena is presented. A stabilized finite element framework for multi-ion transport mechanisms including convection, diffusion and migration coupled to an incompressible flow solver is developed. The role of a galvanostatic Butler–Volmer condition including the interaction of ionic concentration at the surface of the electrode and the surface overpotential is emphasized, to obtain a non-uniform surface overpotential distribution. Additionally, a three-dimensional rotationally-symmetric boundary condition is used for modeling rotating cylinder electrodes. The computational framework is tested for various numerical examples exhibiting two- and three-dimensional electrochemical cell configurations including dilute $CuSO_4$ electrolyte solutions with and without excess of supporting H_2SO_4 electrolyte.

1. Introduction

Natural convection induced by variations of ionic concentrations plays a fundamental role in electrochemical cells. In general, ionic mass transfer is based on three different transport mechanisms, as outlined, e.g., in [1]: ionic mass transport as a result of a velocity field (convection), mass transfer as a result of concentration gradients (diffusion), and mass transfer as a result of an electric field (migration). The convective effect can be distinguished in forced convection and natural convection. Forced convection originates from particular fluid boundary conditions such as in- and outflow conditions, whereas natural convection is induced by buoyancy phenomena. In electrochemical cells, local density variations are caused by local variations of the ionic concentration. Such concentration gradients occur especially near electrode surfaces, where electrochemical reactions take place. In the case of a weak influence of forced convection, natural convection can have significant effects on the reaction rates along the electrodes or on the limiting currents.

The influence of natural convection in electrochemical cells was already considered theoretically and experimentally in the year 1949 in [2]. Therein, the influence of natural convection on the current distribution along the cathode and on the limiting current was investigated based on the boundary-layer theory. The effect of migration on the limiting current in the presence of supporting electrolyte was studied, e.g., in [3]. Concentration and velocity profiles near vertical electrodes were investigated, e.g., in [4,5]. Local current density distributions along the cathode were studied, e.g., in [6]. Recently, concentration profiles were measured experimentally by interferometry, e.g., in [7].

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In recent years, natural convection phenomena have also been investigated numerically. The influence of natural convection on the current density and the ionic concentration at the electrode was investigated, e.g., in [8]. Therein, the Laplace (electric potential field), the ion-transport (excluding migration effects), and the fluid equations were solved individually by a finite difference scheme. A galvanostatic boundary condition was introduced to keep the current flow at the electrodes constant over time. The numerical results were experimentally validated in [9]. In [10], the Butler–Volmer law was added as a kinetic boundary-condition model. The importance of including density gradients for modeling rotating cylinder electrodes was emphasized in [11]. The steady state ion-transport (excluding migration effects) and fluid equations were solved using a commercial software. Another finite difference scheme to simulate ion transfer (including migration effect) under the influence of natural convection was proposed in [12]. In [13], the tertiary current density distribution in the case of multi-ion electrodeposition was studied for high-aspect-ratio cells including convection, diffusion and migration. Therein, the flow, the ionic concentration and the potential field were strongly coupled by an iterative (two-dimensional) finite volume scheme. Natural convection phenomena were also investigated in [14] using a finite volume scheme, including an ion-transport equation for binary electrolyte solutions, an equation for the electric potential and the Butler–Volmer law as a kinetic boundary-condition.

In the present study, the finite-element-based computational approach recently proposed in [15,16] is extended to include natural convection effects. The equations for multi-ion transport including convection, diffusion and migration and the Navier–Stokes equation are coupled in the form of a partitioned scheme. Additionally, galvanostatic Butler–Volmer conditions are introduced to enable a non-uniform potential distribution along the electrodes. The outline of this study is as follows. The mathematical model is introduced in Section 2. In Section 3, the computational method in the form of a stabilized finite element method is presented. The method is tested for two-dimensional and three-dimensional electrochemical cells in Section 4, comparing the results to experimental and numerical results available in the literature. Finally, conclusions are provided in Section 5.

2. Problem statement

Multi-ion transport in a dilute electrolyte solution is considered for the time interval $[0, T_{\mathrm{end}}]$ in a polygonally-shaped and bounded domain $\Omega \subset \mathbb{R}^d$, where $d \leqslant 3$ is the number of spatial dimensions. The boundary of Ω is denoted by $\partial\Omega$ and is assumed sufficiently smooth. The closure of Ω is defined as $\overline{\Omega} := \Omega \cup \partial\Omega$. As emphasized in [1], a divergence-free velocity field is a valid approximation for dilute electrolyte solutions, where only small density variations occur at the electrode. Therefore, the so-called Boussinesq approximation (see, e.g., [17]) is also valid for the electrolyte solutions considered here. Consequently, the influence of density variations is neglected in all terms of the momentum equation, except for the body-force term. After all, continuity and momentum equation of the Navier–Stokes equation are written in the following form:

$$\nabla \cdot \mathbf{u} = 0,$$

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} + \frac{1}{\rho^\infty}\nabla p - 2\nu\nabla \cdot \boldsymbol{\varepsilon}(\mathbf{u}) = \frac{\mathbf{b}}{\rho^\infty}. \tag{1}$$

Herein, natural convection is accounted for by local density variations in the body-force term

$$\mathbf{b} = (\rho - \rho^\infty)\mathbf{g},$$

where ρ represents the density field, varying in space and time, ρ^∞ the reference density of the bulk electrolyte solution, and $\mathbf{g}$ the gravitational acceleration. In addition, $\mathbf{u}$ denotes the fluid velocity, p the pressure, t the time, ν the kinematic viscosity, and $\boldsymbol{\varepsilon}(\mathbf{u})$ the symmetric strain rate tensor,

$$\boldsymbol{\varepsilon}(\mathbf{u}) = \frac{1}{2}\left(\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathrm{T}}\right).$$

It is emphasized that the density field ρ is not a solution variable but depends on the local ion concentrations in an electrolyte solution via

$$\rho = \rho^\infty\left(1 + \sum_{k=1}^{m}\alpha_k\left(c_k - c_k^\infty\right)\right). \tag{2}$$

Usually $m \geqslant 2$ ionic species with molar concentrations c_k $(k = 1, \ldots, m)$ are present in electrolyte solutions. Furthermore, α_k denotes the densification factor and c_k^∞ the bulk concentration of ionic species k.

Based on a partition $\partial\Omega = \Gamma_{\mathrm{D}} \cup \Gamma_{\mathrm{N}}$, where $\partial\Gamma_{\mathrm{D}} \cap \partial\Gamma_{\mathrm{N}} = \emptyset$, Dirichlet and Neumann boundary conditions can be formulated as

$$\begin{aligned} &\mathbf{u} = \mathbf{u}_{\mathrm{D}} \quad \text{on} \quad \Gamma_{\mathrm{D}} \times (0, T_{\mathrm{end}}), \\ &\left(-\frac{p}{\rho^\infty}\mathbf{I} + 2\nu\boldsymbol{\varepsilon}(\mathbf{u})\right) \cdot \mathbf{n} = \mathbf{t} \quad \text{on} \quad \Gamma_{\mathrm{N}} \times (0, T_{\mathrm{end}}), \end{aligned} \tag{3}$$

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