A stabilized finite element method for the numerical simulation of multi-ion transport in electrochemical systems

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ARTICLE INFO

ABSTRACT

A stabilized finite element method for the simulation of instationary and stationary multi-ion transport in dilute electrolyte solutions is presented. The proposed computational approach accounts for all three ion-transport phenomena, that is, convection, diffusion and migration, as well as nonlinear electrode kinetics boundary conditions. The governing equations form a set of coupled nonlinear partial differential equations subject to an electroneutrality condition. The latter establishes an algebraic constraint to the problem formulation. Derived from the variational multiscale method, we introduce stabilization terms which prevent potential spurious oscillations arising in the convection-dominated case when a standard Galerkin finite element method is used. For various numerical examples, it is demonstrated that the proposed computational method is robust and provides accurate results.

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1. Introduction

For the modeling of many electrochemical systems, the consideration of ion-transport phenomena plays a fundamental role. Within macroscopic models based on a continuum hypothesis, three different ion-transport mechanisms are typically considered for dilute electrolyte solutions (see, e.g., [1]): convection, diffusion and (electro-) migration. The latter effect describes movement of ions caused by an electric field. In this work, we focus on electrochemical systems where the influence of convection is not negligible. One example is electrodeposition of metals, an important and widely-used electrochemical technique for coating electrically conductive objects with layers of metal by using electrical current. In many industrial plating baths, it is aimed at keeping the electrolyte solution well-mixed by using various agitation and stirring techniques. Rotationally symmetric parts to be plated are usually also rotated to achieve more uniform plating results. As a consequence, rather complex, often turbulent flow conditions arise, directly influencing the ion-transport processes inside the electrolyte solution. Hence, a mathematical model describing such electrochemical systems has to take into account the apparent coupling to fluid flow.

Over the last decades, various numerical approaches for the simulation of multi-ion transport in dilute electrolyte solutions have been developed; in the following, some of these approaches will be addressed. In [2], a fractional-step algorithm using a finite-difference scheme for spatial discretization was proposed. Steady-state studies for a two-dimensional parallel plane flow channel were performed in [3] using a new multi-dimensional upwinding method for the analysis of multi-ion electrolytes controlled by diffusion, convection and migration. A finite-difference method with upwinding was developed in [4] for the simulation of convection-dominated multi-ion transport. Using that method, various two-dimensional electrochemical problem settings including convection were studied (see, e.g., [4,5] and references therein). In [6], a three-dimensional model of an electrochemical sensor was investigated. A finite-volume software package was used for solving the Nernst–Planck/Poisson–Boltzmann system of equations coupled to the Navier–Stokes equations. A finite-volume method for solving three-dimensional diffusion-migration problems on irregular domains with moving boundaries was proposed in [7].

In [8], a finite element method (FEM) was used to simulate current–density distributions in three-dimensional microchannels. However, their model did not account for migration, and a constant conductivity of the electrolyte solution was assumed. Ion-diffusion mechanisms in porous media were modeled via FEM in [9], using the Nernst–Planck–Poisson system of equations. Only diffusion and migration were considered in the ion-transport model. A rotating cylinder Hull cell was investigated in [10] using a commercial

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finite element software package. Steady-state current distributions for a 2D axial-symmetric model were computed. Only the concentration of a single ionic species was considered, and no flow field was computed, since the corresponding mass transport model was based on a Nernstian diffusion layer expression. An adaptive multilevel finite element algorithm was proposed in [11] and applied for solving various controlled-current experiments in one spatial dimension. In [12], finite element discretizations for a Navier–Stokes–Nernst–Planck–Poisson system were investigated theoretically. Recently, in [13], we presented a finite element method suitable for three-dimensional electrochemical problem configurations including all three ion-transport effects as well as nonlinear electrode kinetics at the same time. The apparent (one-way) coupling to fluid flow and its numerical treatment was particularly addressed in [13].

It is well-known that a standard Galerkin finite element method (SGFEM) applied to transport equations with a dominating convective term can lead to oscillations. To account for this, stabilized finite element methods were developed for the numerical solution of convection–diffusion-reaction equations and the incompressible Navier–Stokes equations, e.g., the Streamline-upwind Petrov/ Galerkin (SUPG) method in [14]. For an overview on existing methods, the reader is referred to, for instance, [15]. Stabilized methods may be considered particular methods derived from the more general framework of the variational multiscale method (VMM) as originally introduced in [16]. The present authors successfully developed methods based on the variational multiscale framework for the challenging problems of turbulent incompressible flow, e.g., in [17], and turbulent variable-density flow at low Mach number, e.g., in [18,19], among others.

Concerning electrochemistry, particularly coupled multi-ion transport problems, very few publications addressing stabilized finite element methods exist. In [20], a mixed finite element method for the numerical simulation of electrophoresis separation phenomena was proposed. Therein, different ion-separation processes in one- and two-dimensional configurations were studied. An SUPG approach was proposed as the stabilizing technique. However, no coupling to the Navier–Stokes equations was included in that solution approach, and no boundary conditions for modeling electrochemical reactions at electrode surfaces were considered in the mathematical model. Transport of charge carriers within semiconductor devices is often described with the popular drift–diffusion model. The governing equations exhibit similarities to the governing equations of multi-ion transport in dilute electrolyte solutions. In [21,22], for instance, stabilized finite element formulations were used for the spatial discretization of the arising drift–diffusion equations. However, one of the main differences to multi-ion transport is the absence of a convective term which is establishing the one-way coupling to fluid flow in our case.

In the present study, a novel formulation based on the variational multiscale method (VMM) for the coupled multi-ion transport problem will be developed, which extends the method proposed previously in [13]. To the authors' best knowledge, such a comprehensive methodical approach for robust and accurate simulations of multi-ion transport in dilute electrolyte solutions including all transport phenomena, convection, diffusion, and migration, as well as nonlinear electrode boundary conditions has not yet been presented.

The outline is as follows. In Section 2, we recall the governing equations for modeling multi-ion transport and electrode reactions in electrochemical systems and introduce them into a weak problem formulation, which forms the basis for our new computational approach. Our newly developed stabilized finite element method based on the variational multiscale framework is presented in Section 3. Within that section, we emphasize the issue of defining appropriate stabilization terms for the system of coupled nonlinear partial differential equations. The numerical approach is tested for several numerical examples in Section 4. Finally, conclusions are drawn in Section 5.

2. Problem formulation

2.1. Governing equations

We consider fluid flow and multi-ion transport for the time interval $[0, T]$ in a polyhedrally-shaped and bounded domain $\Omega \subset \mathbb{R}^d$, where $d \leqslant 3$ is the number of space dimensions. As usual, the boundary of Ω is denoted by $\partial \Omega$. The closure of Ω is given by $\overline{\Omega} := \Omega \cup \partial \Omega$. The incompressible Navier–Stokes equations provide an adequate model to describe the flow of a dilute electrolyte solution in an electrochemical cell at a macroscopic scale (see, e.g., [1]). The solution variables are the velocity field $\mathbf{u}$ and the pressure p, which are governed by

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} - \nabla \cdot (2\nu \boldsymbol{\varepsilon}(\mathbf{u})) + \nabla p = \mathbf{g} \quad \text{in } \Omega \times (0, T), \tag{1}$$

$$\nabla \cdot \mathbf{u} = 0 \quad \text{in } \Omega \times (0, T), \tag{2}$$

where ν denotes the kinematic viscosity of the electrolyte solution, $\mathbf{g}$ the specific volume force and $\boldsymbol{\varepsilon}(\mathbf{u})$ the symmetric strain rate tensor given by

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

Based on the partition $\partial \Omega = \Gamma_D \cup \Gamma_N$, with $\Gamma_D \cap \Gamma_N = \emptyset$, appropriate boundary conditions read as follows:

$$\mathbf{u} = \mathbf{u}_D \quad \text{on} \quad \Gamma_D \times (0, T),$$
$$(-p\mathbf{I} + 2\nu \boldsymbol{\varepsilon}(\mathbf{u})) \cdot \mathbf{n} = \mathbf{t} \quad \text{on} \quad \Gamma_N \times (0, T).$$

Here, $\mathbf{u}_D$ is the velocity prescribed on the boundary part Γ_D, $\mathbf{n}$ the unit outer normal to the boundary and $\mathbf{t}$ the traction vector on Γ_N. Finally, an initial condition in the form

$$\mathbf{u} = \mathbf{u}_0 \quad \text{in } \overline{\Omega} \times \{0\}$$

is required for instationary flow problems, with $\mathbf{u}_0$ being a solenoidal initial velocity field.

For the electrochemistry part of the mathematical model, solution variables to be determined are the molar concentrations c_k for each ionic species $k = 1, \ldots, m$ present in the electrolyte solution. The electric potential field Φ inside the electrolyte solution is an additional unknown physical field. Note that the corresponding electric field $\mathbf{E}$ is given by the negative gradient of the electric potential, that is $\mathbf{E} = -\nabla \Phi$. Based on mass conservation, each concentration field c_k with $k = 1, \ldots, m$ is governed by a convection–diffusion-migration equation (Nernst–Planck equation) that reads in its convective form as:

$$\frac{\partial c_k}{\partial t} + \mathbf{u} \cdot \nabla c_k + \nabla \cdot \mathbf{N}_k^{\mathrm{d+m}} = 0 \quad \text{in } \Omega \times (0, T). \tag{3}$$

The ionic mass flux contribution due to diffusion and migration is given by

$$\mathbf{N}_k^{\mathrm{d+m}} := -D_k \nabla c_k - z_k \mu_k F c_k \nabla \Phi. \tag{4}$$

Here, D_k is the diffusion coefficient of ionic species k with respect to the solute, z_k is the corresponding charge number (valence), μ_k the mobility constant, F Faraday's constant (96,485 C/mol) and $\mathbf{u}$ the velocity of the electrolyte solution governed by the incompressible Navier–Stokes equations. Thus, the convective term in (3) establishes a one-way coupling of each ion-transport equation to the flow. As usual in dilute-solution theory, the mobility constant μ_k is expressed in terms of the diffusivity D_k, the absolute temperature T and the universal gas constant R by the Nernst–Einstein relation