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A 3D FINITE ELEMENT METHOD FOR THE COUPLED NUMERICAL SIMULATION OF ELECTROCHEMICAL SYSTEMS AND FLUID FLOW: ION TRANSPORT IN ELECTRODEPOSITION

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Abstract. Multi-ion transport is a fundamental aspect for the modeling of many electrochemical systems. An important electrochemical application is electrodeposition of metals. where electrically conductive objects are coated with layers of metal by using electrical current. In macroscopic models based on the continuum hypothesis, the unknown physical fields to be solved for are the respective ionic species concentrations as well as the electric potential inside the electrolyte solution. Chemical reactions, that is, the deposition process in the present context, are typically limited to the electrode surfaces and modeled by nonlinear boundary conditions depending on the solution variables. The governing equations form a coupled system of nonlinear partial differential equations supplemented with an algebraic constraint. For electrochemical systems where the influence of convection is not negligible, an inherent coupling to fluid flow exists. Several challenges have to be faced when solving the resulting system of coupled equations as described above. Here, we present the development of a stabilized finite element formulation for the coupled nonlinear system of ion transport and incompressible Navier-Stokes equations. After presenting the computational approach, results from various three-dimensional numerical examples will be provided, demonstrating that our numerical method is robust and provides accurate results. Finally, we discuss challenges, advances and future steps of our current work towards the development of a predictive tool for industrial electrodeposition applications.

1 INTRODUCTION

The inclusion of ion-transport phenomena plays a fundamental role for the modeling of many electrochemical systems. Typically, three different ion-transport mechanisms are considered in dilute electrolyte solutions [1]: convection (movement with bulk electrolyte solution), diffusion (movement caused by concentration gradients) and migration (movement of ions due to an applied electric field). In this presentation, we focus on electrochemical systems where the influence of convection is not negligible. One example for such electrochemical systems is electrodeposition. This is an important and widelyused electrochemical technique for coating electrically conductive objects with layers of metal by using electrical current. There is a broad spectrum of industrial applications, and plating mainly serves function, corrosion-control and/or decorative purposes. Typically, the process of electrodeposition takes place in so-called electrolytic baths. Therein, the part to be plated acts as the cathode of the electrical circuit and is immersed in a solution (electrolyte) containing one or more metal salts as well as other ions that permit the flow of electricity. The applied electrical current causes the positively charged metal ions in the solution to move to the cathode's surface, where they are reduced and finally plate out. In many industrial plating baths, it is aimed at keeping the electrolyte solution well-mixed by using different agitation techniques such as jet systems and stirring devices. Rotationally symmetric parts to be plated are usually also rotated to achieve more uniform plating results. As a consequence, quite complex, often turbulent flow conditions arise, directly influencing multi-ion transport inside the electrolyte solution. Hence, a mathematical model describing such electrochemical systems has to take into account the apparent coupling to fluid flow. Chemical reactions, that is, the deposition process in the present context, are typically limited to the electrode surfaces and modeled by nonlinear boundary conditions depending on the solution variables. Several challenges have to be faced when solving the system of coupled equations as described above. Especially when electrodeposition is a critical aspect of the overall manufacturing process, reliable numerical simulations can not only lead to better understanding of plating processes but also provide promising and relatively cheap opportunities for designing new or optimized existing electrodeposition facilities.

2 PROBLEM FORMULATION

2.1 Electrolyte flow

Electrolyte flow and multi-ion transport in a polygonally-shaped and bounded domain $\Omega \subset \mathbb{R}^d$, where $d \leq 3$ is the number of space dimensions, is considered for the time interval [0, T]. The incompressible Navier-Stokes equations are used to describe the flow of an electrolyte solution in an electrochemical cell. The solution variables are the velocity

field \mathbf{u} and the pressure p, which are governed by

0

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

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

where ν denotes the kinematic viscosity of the electrolyte, **b** the specific volume force and ε (**u**) the symmetric strain rate tensor given by

$$\boldsymbol{\varepsilon}\left(\mathbf{u}\right) = \frac{1}{2} \left(\nabla \mathbf{u} + \left(\nabla \mathbf{u}\right)^{T}\right). \tag{3}$$

Appropriate boundary and initial conditions complete the fluid flow model.

2.2 Multi-ion transport in dilute electrolyte solutions

The temporal and spatial variation of the molar concentration c_k of each ionic species k = 1, ..., m present in an electrolyte solution is governed by the three ion-transport phenomena addressed above: convection, diffusion and migration. Based on mass conservation, the following set of m nonlinear partial differential equations is obtained:

$$\frac{\partial c_k}{\partial t} + \mathbf{u} \cdot \nabla c_k + \nabla \cdot \mathbf{N}_k = 0 \quad \text{in } \Omega \times (0, T) \,, \quad k = 1 \dots m \tag{4}$$

where

$$\mathbf{N}_k := -D_k \nabla c_k - z_k \mu_k F c_k \nabla \Phi.$$
(5)

Here, D_k is the diffusion coefficient of ionic species k, z_k is the valence (charge number), μ_k the mobility constant, F Faraday's constant, Φ the electric potential inside the electrolyte solution and **u** the solenoidal velocity field governed by the incompressible Navier-Stokes equations. Thus, the convective term in (4) establishes the aforementioned one-way coupling of each ion-transport equation to fluid flow. Beside the ionic species concentrations c_k , the electric potential Φ is an additional unknown physical field in (4). The system of equations is typically closed with the so-called electroneutrality condition. This condition is an algebraic constraint originating from the assumption that the electrolyte solution is locally electrically neutral:

$$\sum_{k=1}^{m} z_k c_k = 0 \qquad \text{in } \overline{\Omega} \times [0, T] \,. \tag{6}$$

For the transient case, initial conditions for all ion concentrations have to be specified, which obey the electroneutrality condition. On the boundaries of the computational domain, essential (Dirichlet) or natural (flux) boundary conditions have to be imposed. For details, the reader is referred to [2], for example.

2.3 Electrode surface kinetics

At electrode surfaces, the rate of electrochemical reaction is directly related to the normal current density i_n to this surface. Thus, for electroplating applications, the deposition rate at the cathode is directly proportional to i_n . Inert ionic species have zero mass flux at these boundaries, while the mass flux of reactive species at electrode surfaces is linked to the normal current density. For the case of one single electrochemical reaction taking place at the electrode, the boundary conditions read

$$-\mathbf{N}_k \cdot \mathbf{n} = \begin{cases} 0 & : & \text{inert ionic species} \\ \frac{i_n}{z_k F} & : & \text{reactive ionic species} \end{cases}$$
(7)

Here, **n** denotes the unit outer normal vector at the boundary. The normal current density i_n on the associated boundary parts is determined by some (often nonlinear) phenomenological kinetic model that typically depends on the solution variables. An important example is the Butler-Volmer law in the form specified in [1]:

$$i_n = i_0 \left(\frac{c_k}{c_k^{\infty}}\right)^{\gamma} \left[\exp\left(\frac{\alpha_a F}{RT} \left(V - \Phi\right)\right) - \exp\left(\frac{-\alpha_c F}{RT} \left(V - \Phi\right)\right) \right].$$
(8)

The parameters involved are the exchange current density i_0 , some reference concentration for the reactive ionic species c_k^{∞} , an exponent γ for weighting the concentration dependency, an anodic constant α_a , a cathodic constant α_c and the so-called overpotential $V - \Phi$, with V being the electric potential applied on the metal side of the metal-solution interface.

3 NUMERICAL CHALLENGES AND SOLUTION APPROACHES

If convection has to be accounted for, the one-way coupling of fluid flow and ion transport has to be appropriately performed. We use matching spatial discretizations for both fluid and electrochemistry system with the same ansatz function order. Since equal-order shape functions for velocity and pressure are used, stabilization/ multiscale techniques are required for the flow solver (see, e.g., [3, 4]). In each time step, we first solve the nonlinear Navier-Stokes system for the current velocity and pressure fields. After providing the determined velocity field, the nonlinear electrochemistry equations can be solved for the current time step. A sketch of the coupling algorithm is provided in Fig. 1. The



Figure 1: One-way coupling fluid flow - electrochemistry

same order is also used for solving stationary problem formulations without proceeding in time. This one-way coupled approach is all that is needed for the current model. For future applications, however, the proposed coupling scheme will be extended to a twoway-coupled partitioned scheme. A possible application that requires such an extension is the consideration of electrode shape changes due to deposition processes. Furthermore, local electrolyte density variations due to concentration variations near the electrodes result in natural convection phenomena. Both effects influence the flow field, the first one due to a moving-boundary problem, the second one due to a varying density.

Beside the well-known challenges linked to the numerical solution of the incompressible Navier-Stokes equations, the ion-transport model reveals three difficulties that need proper numerical treatment. Equations (4) together with (5) and initial and boundary conditions define a volume-coupled system of nonlinear partial differential equations subjected to an algebraic contraint given in (6). The first challenge is related to the nonlinearity of the ion-transport equations due to the electromigration term as well as the nonlinear boundary conditions applied at electrode surfaces. Second, the presence of the algebraic constraint (6) leads to the fact, that linear equation systems that have to be solved in the nonlinear solution loop possess a non-symmetric saddle-point matrix structure. As a third point, one has to account for the convection-dominated regime, since it is well-known that spatial discretizations based on the standard Galerkin method become unstable in this case. We use stabilized finite element formulations for the spatial discretization of the ion-transport equations to achieve stable solutions for convection-dominated problems. For this purpose the streamline upwind/Petrov Galerkin (SUPG) method for convectiondiffusion equations [5] was extended for the system of ion-transport equations coupled to electroneutrality and electrode kinetics. A similar method for ionic transport was proposed in [6] in the context of electrophoresis separation techniques. Details of the stabilized finite element formulation and the computational approach are provided in [2].

4 NUMERICAL EXAMPLES

4.1 Rotating cylinder electrode

An important example is the rotating cylinder electrode (RCE), where the cylindershaped cathode of the electrolytic cell is rotating in the center of the cell configuration. Due to rotation, fluid flow is induced, which in turn influences the rate of deposition at the surface of the cathode. For an RCE configuration specified in [7], tertiary current distribution and fluid flow conditions are investigated. A stationary problem configuration is addressed here. Rotationally symmetric boundary conditions allow the usage of the flexible computational approach based on Cartesian coordinates also for rotationally symmetric applications. Thus, a solver implementation based on cylinder coordinates is not required. In Fig. 2, the resulting wedge-shaped computational domain with an angle of 15° can be seen. Simulation results for velocity and copper concentration fields for the cell operating at limiting current density are shown. The computed mean current density



Figure 2: Simulation results for an rotating cylinder electrode configuration: velocity magnitude (a), copper ion concentration (b) and zoom to the concentration boundary layer that is forming near the surface of the cathode (c).

along the cathode surface is 708 A/m², which is in excellent agreement with the value of 709 A/m² reported in [7]. According to Faraday's law, the corresponding average deposition rate of copper is $2.33 \cdot 10^{-4}$ kg m⁻²s⁻¹, with a surface growth rate of 93.6 μ m/h.

4.2 Oscillating shear flow cell

As a second example, we consider unsteady tertiary current distributions governed by oscillating shear flow. In the following, an excerpt of the simulation results presented in [2] is given. The setup of the problem as well as experimental conditions are described in [8]. A two-dimensional sketch of the cell configuration is depicted in Fig. 3. Here, the cathode with length 2L = 0.25 mm is part of the bottom plane that is oscillating in its own plane. The fixed counter electrode is placed above the working electrode with distance H = 16 mm. In the experiments carried out in [8], the anode $(20 \times 13 \text{cm})$ and the bottom plane are very large compared to the line-shaped cathode $(2L \times 2 \text{cm})$. Thus, the planes at top and bottom can be assumed infinitely long. However, the computational domain has to be limited by two artificial boundaries located at $x_1 = -(D + L)$ and $x_1 = D + L$. The value for D has to be chosen sufficiently large for not introducing errors due to these artificial boundaries. Here, D = 20mm is used.

Copper deposition from a 3.0 mM $CuSO_4 + 0.3$ mM H_2SO_4 electrolyte solution under potentiostatic conditions is considered. As in [8], complete dissociation is assumed. Thus, an instationary multi-ion transport problem involving three different ionic species (Cu²⁺, SO_4^{2-} , H⁺) has to be solved. This example is especially interesting, since not only the



Figure 3: Two-dimensional sketch of the oscillation shear flow cell (not drawn to scale).

one-way coupling of ion transport to fluid flow for an unsteady problem is tested, but also all three mechanisms of ion transport. In addition, a nonlinear kinetic model of Butler-Volmer type is used at the cathode surface. In [8], a linear approximation to the convective velocity field was used in the vicinity of the cathode, which was derived analytically. In contrast, we actually solve the instationary incompressible Navier-Stokes equations combined with periodic boundary conditions to provide the current flow field. In [8], two-dimensional simulations using finite-difference schemes where performed. We use an appropriate three-dimensional "slice" as computational domain for testing our three-dimensional implementation and proving that our approach can also deal with essentially two-dimensional problem setups. In total, the mesh consists of 12, 296 hexahedral elements with trilinear shape functions and 25, 148 nodes. With four degrees of freedom per node for the fluid problem (velocity **u**, pressure p) and four degrees of freedom per



Figure 4: Locally refined mesh near the cathode surface.



Figure 5: Temporal evolution of space-averaged cathodic current density. Comparison of computed results with experimental data provided in [8].

node for the electrochemistry fields (c_1, c_2, c_3, Φ) , in total, more than 200,000 degrees of freedom have to be determined within each time step.

Data evaluation was performed after initial transients had vanished and the quasi-static periodic solution had been reached. In Fig. 5, the temporal evolution of the spatially averaged current density at the cathode surface is shown over two periods of oscillation. The comparison with the experimental data given in [8] shows excellent agreement for both values of applied cell voltages. Fig. 6 depicts the computed copper cation concentration profiles near the cathode for the potential V_C at the metal side of the cathode being set to $V_C = -0.245$ V. Snapshots at four different times are provided that clearly reveal the influence of the oscillating shear flow on the shape of the concentration boundary layer. The periodic changes in the boundary layer thickness cause the observed oscillatory behavior of mass flux and current density at the cathode surface.



(a) t = 146.1s (= 15 T)



(b) t = 148.5s



(c) t = 151.0s



(d) t = 153.4s

Figure 6: Concentration boundary layer of Cu^{2+} forming near the cathode surface: snapshots at various times within one oscillation period (T = 9.74s).

5 CONCLUSIONS

We presented a new finite element approach to the numerical simulation of electrochemical systems, with special emphasis on electrodeposition applications. Our computational approach addresses all modelling aspects of multi-ion transport subjected to electroneutrality. The coupled effects of convection, diffusion, migration as well as the potential use of any nonlinear phenomenological boundary conditions at electrode surfaces are included. Our solution approach is also capable of dealing with the one-way coupling of fluid flow to electrochemistry that is arising whenever ion transport due to convection has to be considered. The finite element method is used for the spatial discretization of all governing equations, that is, the electrochemistry equations as well as the Navier-Stokes equations. The computational method presented is capable of solving for stationary and instationary tertiary current distributions including ionic concentrations and electric potential field in three-dimensional geometries. It has been successfully tested for several numerical examples. Further benefit of the finite element method will be gained when considering more complex geometries in the future. In particular, this work is part of our effort towards the development of a predictive tool for industrial electroplating applications. When effects such as moving boundaries due to the deposition process and density variations due to concentration gradients in the solution are also included, fluid and electrochemical equations will become fully (two-way) coupled. This extension is part of our current work.

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