Modeling and Numerical Simulation of Electrodeposition
Coupling ion transport, electric field and fluid flow

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Introduction

Electrodeposition

- Widely-used technique for plating electrically conductive objects with metal layers
- Process takes place in electrolytic cells (see Fig. 1) or in so-called galvanic baths at industrial scale.
- Part to be plated is immersed into an electrolyte solution and acts as cathode of the electric circuit.
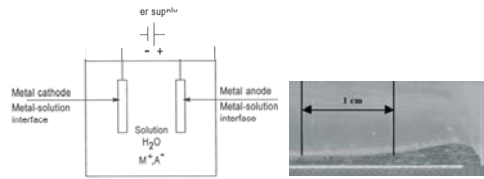

Fig. 1: Sketch of an electrolytic cell (adapted from [1])

Fig. 2: Electrodeposition of copper [2]

Electroforming

- enables deposit thicknesses ranging from millimeters to centimeters (see Fig. 2)
- Application: efficient realization of complex-shaped single-piece components, e.g., in aerospace industry

Multi-Ion Transport

Electrolyte flow

- Movement of electrolyte solution is modeled using the incompressible Navier-Stokes equations.

Multi-ion transport

- Transport of ions in an electrolyte is governed by three mechanisms (see, e.g., [3]): convection, diffusion and migration
- Mass conservation for each ionic species concentration c_k ($k=1,\dots,n_{sp}$):

$$\frac{\partial c_k}{\partial t} + \underbrace{\mathbf{u}\cdot\nabla c_k}_{\text{convection}} - \nabla\cdot(\underbrace{D_k\nabla c_k}_{\text{diffusion}} + \underbrace{z_k\mu_k F c_k\nabla\Phi}_{\text{migration}}) = 0 \quad \text{in } \Omega\times(0,T)$$

- Migration term is nonlinear, since the electric potential Φ is an additional unknown.

Electroneutrality condition

- Common macroscopic approximation considering electrolyte solution to be electrically neutral
- Algebraic constraint:

$$\sum_{k=1}^{n_{sp}} z_k c_k = 0 \qquad \text{in } \overline{\Omega}\times[0,T]$$

Electrode-Surface Kinetics

The metal-solution interface

- Normal current density at an electrode is directly proportional to the rate of electrochemical reaction (i.e., the rate of deposition in this context)
- Driving force for deposition reaction is the so-called overpotential η (see Fig. 3).
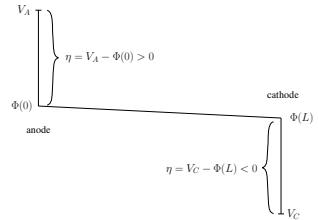

Fig. 3: Schematic distribution of electric potential in an electrolytic cell with overpotential at the electrode-solution interfaces. The applied cell voltage is $\Delta\varphi = V_A - V_C$.

Phenomenological boundary condition

- Butler-Volmer law for normal current density:

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

- Contains nonlinear dependencies on overpotential and on concentration of reactive ionic species

Computational Method

Discretization

- Discretization in time is performed, e.g., with generalized trapezoidal rule or BDF2.
- Stabilized finite element methods are used to discretize the governing equations of all physical fields (for stabilization of electrochemical equations, see [4]).
- A convergence analysis for a diffusion-migration problem in 3D using trilinear shape functions shows second order accuracy in the L^2-norm for all unknown electrochemical quantities (see Fig. 4).
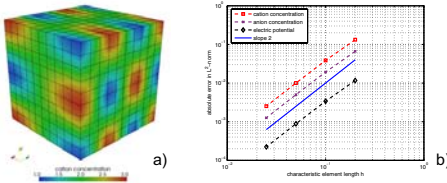

Fig. 4: Convergence analysis for a 3D diffusion-migration problem. The initial field of the cation concentration is depicted in a). The error plot in b) clearly shows second order accuracy in space.

One-way coupling fluid - electrochemistry

- In each time step, do:
  - Step 1: Solve nonlinear fluid equations for the current velocity and pressure field.
  - Step 2: Transfer new velocity field.
  - Step 3: Solve nonlinear electrochemistry model for unknown ion concentrations and electric potential (Newton's method, monolithic approach).
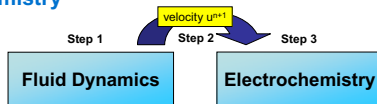
- Linear subproblems to be solved in step 3 possess non-symmetric saddle-point matrix structure due to the electroneutrality condition.

$$\begin{bmatrix} \mathbf{A}_1 & \mathbf{0} & \cdots & \mathbf{0} & \mathbf{B}_1 \\ \mathbf{0} & \mathbf{A}_2 & \ddots & \vdots & \mathbf{B}_2 \\ \vdots & \ddots & \ddots & \mathbf{0} & \vdots \\ \mathbf{0} & \cdots & \mathbf{0} & \mathbf{A}_{n_{sp}} & \mathbf{B}_{n_{sp}} \\ \mathbf{C}_1 & \mathbf{C}_2 & \cdots & \mathbf{C}_{n_{sp}} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \Delta\mathbf{c}_1 \\ \Delta\mathbf{c}_2 \\ \vdots \\ \Delta\mathbf{c}_{n_{sp}} \\ \Delta\mathbf{\Phi} \end{bmatrix} = -\begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_{n_{sp}} \\ \mathbf{r}_E \end{bmatrix}$$

Simulation Results

Parallel-Plate Electrochemical Reactor (PPER)

- Laminar convection (channel flow) acts perpendicular to the electric field.
- Concentration boundary layers develop near the electrode surfaces (see Fig. 5).
- Hydrodynamical conditions influence the concentration boundary layer thickness and thus the normal current density along the electrode (see Fig. 6).
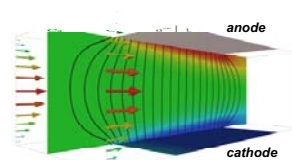

Fig. 5: PPER showing electric field lines, parabolic velocity profile and concentration variations near the electrodes.
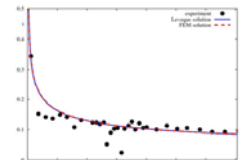

Fig. 6: Normal current density along the cathode. Comparison between simulation and experiment for a PPER-setup given in [5].

Rotating Cylinder Electrode (RCE)

- Configuration with cylindrically-shaped rotating cathode
- Typical electrochemical laboratory device
- Fig. 7 depicts numerical results for a setup specified in [6].
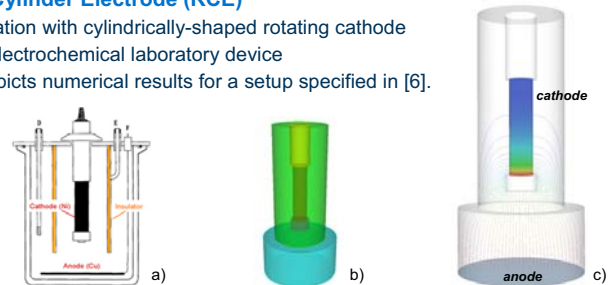

Fig. 7: Rotating cylinder electrode. Experimental setup (a), three-dimensional computational domain (b) and simulation results (c). The latter shows electric field lines and normal current density distribution at the surface of the cathode.

Acknowledgements

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