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 $\eta$ (see Fig. 3).

Phenomenological boundary condition

- Butler-Volmer law for normal current density:
  \[
  i = \frac{\alpha_f \phi^2}{RT} \exp \left( \frac{\alpha_f \phi}{RT} \right) \exp \left( \frac{\alpha_f \phi}{RT} \right)
  \]
- Contains nonlinear dependencies on overpotential and on concentration of reactive ionic species

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

Introduction

Electrochemistry

- Linear subproblems to be solved
- One-way coupling fluid - electrochemistry

Stabilized finite element methods are used to discretize the governing equations

- Application: efficient realization of complex-shaped single-piece components, e.g., in aerospace industry

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 bilinear shape functions shows second order accuracy in the $L^2$-norm for all unknown electrochemical quantities (see Fig. 4)

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

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 $c_i$ ($i=1,...,n_{sp}$):
  \[
  \frac{\partial c_i}{\partial t} + \nabla \cdot (D_i \nabla c_i) - \nabla \cdot (c_i \mathbf{u}) = 0 \text{ in } \Omega \times (0,T)
  \]
- Migration term is nonlinear, since the electric potential $\phi$ is an additional unknown.

Electroneutrality condition

- Common macroscopic approximation considering electrolyte solution to be electrically neutral
- Algebraic constraint:
  \[
  \sum_{i=1}^{n_{sp}} c_i = 0 \text{ in } \Omega \times (0,T)
  \]

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. 3: Schematic distribution of electric potential in an electrolyte cell with overpotential at the electrode-solution interfaces. The applied cell voltage is $\Delta V = V_c - V_i$.

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.

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].

References