Numerical Simulation of Natural Convection in Electrochemical Systems

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Introduction

Natural convection in electrochemical systems

- Natural convection is induced by variations of ionic concentration.
- In the case of a weak influence of forced convection, natural convection can have significant effects on the reaction rates.

Use of Non-Conforming Meshes

- The ionic diffusion layer is very thin in the vicinity of the electrode (see Fig. 1).
- Concentration gradients are absent in the bulk of the electrolyte.
- Potential shows a linear behavior outside the diffusion layer.
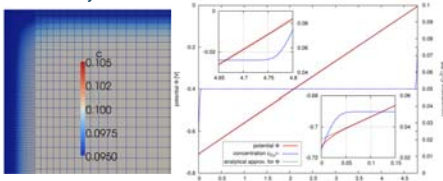- → The mesh size is restricted by the mesh in the diffusion layer.

Fig. 1: Non-conforming meshes in a electrolytic cell (left) and concentration and potential profile along the line y = 0.

Multi-Ion Transport

Electrolyte flow

- Movement of electrolyte solution is modeled using the incompressible Navier-Stokes equations.
- Influence of density variations are modeled by the Boussinesq approximation.

Multi-ion transport

- Transport of ions in an electrolyte is governed by three mechanisms (see, e.g., [1-3]): convection, diffusion and migration

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

Electroneutrality condition

- Closure of the problem:

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

Phenomenological non-linear BC

- e.g. Butler-Volmer law:

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

Concentration – density correlation

- Linear ionic concentration – density correlation:

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

Non-Conforming Meshes

Internal interface with non-conforming meshes

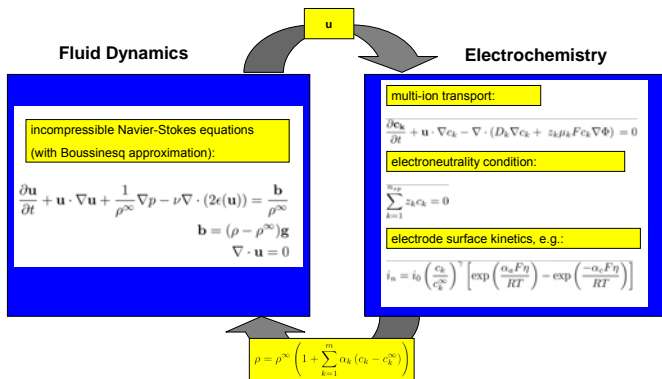- Domain decomposition into sub-domains with an internal boundary [4] (fluid and elec. chem. system):

- Mortar method is used for weakly enforcing coupling constraints by dual Lagrange Multipliers.
- Mortar matrices **M** and **D** (diagonal matrix) are computed once in the beginning of the simulation
  - → **D** is very cheap to invert and therefore, the projection matrix ($\mathbf{P} = \mathbf{D^{-1}M}$) can be computed easily.
- The initial saddle-point system is transformed to a non-saddle-point system by trivial condensation operations.
  - → state-of-the-art solvers and pre-conditioners can be applied to the transformed system.

$$\begin{bmatrix} \mathbf{C}_{\Omega^1,\Omega^1} & 0 & \mathbf{C}_{\Omega^1,\Gamma^1} & 0 & 0 \\ 0 & \mathbf{C}_{\Omega^2,\Omega^2} & 0 & \mathbf{C}_{\Omega^2,\Gamma^2} & 0 \\ \mathbf{C}_{\Gamma^1,\Omega^1} & 0 & \mathbf{C}_{\Gamma^1,\Gamma^1} & 0 & -\mathbf{D^T} \\ 0 & \mathbf{C}_{\Gamma^2,\Omega^2} & 0 & \mathbf{C}_{\Gamma^2,\Gamma^2} & \mathbf{M^T} \\ 0 & 0 & -\mathbf{D} & \mathbf{M} & 0 \end{bmatrix} \begin{bmatrix} \Delta\mathbf{x}_{\Omega^1} \\ \Delta\mathbf{x}_{\Omega^2} \\ \Delta\mathbf{x}_{\Gamma^1} \\ \Delta\mathbf{x}_{\Gamma^2} \\ \lambda \end{bmatrix} = \begin{bmatrix} \mathbf{R}_{\Omega^1} \\ \mathbf{R}_{\Omega^2} \\ \mathbf{R}_{\Gamma^1} \\ \mathbf{R}_{\Gamma^2} \\ 0 \end{bmatrix}$$

Computational Method

Two-way coupling fluid – electrochemistry

u

Fluid Dynamics

Electrochemistry

incompressible Navier-Stokes equations (with Boussinesq approximation):

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} + \frac{1}{\rho^\infty} \nabla p - \nu \nabla \cdot (2\epsilon(\mathbf{u})) = \frac{\mathbf{b}}{\rho^\infty}$$
$$\mathbf{b} = (\rho - \rho^\infty)\mathbf{g}$$
$$\nabla \cdot \mathbf{u} = 0$$

multi-ion transport:

$$\frac{\partial c_k}{\partial t} + \mathbf{u} \cdot \nabla c_k - \nabla \cdot (D_k \nabla c_k + z_k \mu_k F c_k \nabla \Phi) = 0$$

electroneutrality condition:

$$\sum_{k=1}^{n_{sp}} z_k c_k = 0$$

electrode surface kinetics, e.g.:

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

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

u^n

Outer iteration loop

Fluid Solver

p_i^{n+1} u_i^{n+1}

Galvanostatic constraint

Ion-Transport Solver

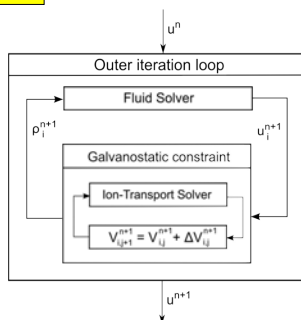$$V_{i,j+1}^{n+1} = V_{i,j}^{n+1} + \Delta V_{i,j}^{n+1}$$

u^{n+1}

Galvanostatic boundary conditions

- Galvanostatic boundary conditions require additional degree of freedom (applied potential).
- BC are implemented by partitioned scheme.
- The inner loop is converged after 3-4 iterations.

$$\mathcal{R}(V) := I_{tot} - I = I_{tot} - \int_{\Gamma_E} i \, dS = 0$$

$$\frac{\partial \mathcal{R}(V)}{\partial V}\bigg|_{V_j} \Delta V_j = -\mathcal{R}(V_j)$$

$$\Delta V_{i,j}^{n+1} = \Delta V_j^C + \Delta V_j^A + \Delta\phi_{\text{bulk},j}$$

Simulation Results

Natural convection between parallel electrodes

- Fig. 2 shows the numerical results for a setup specified in [2, 5].
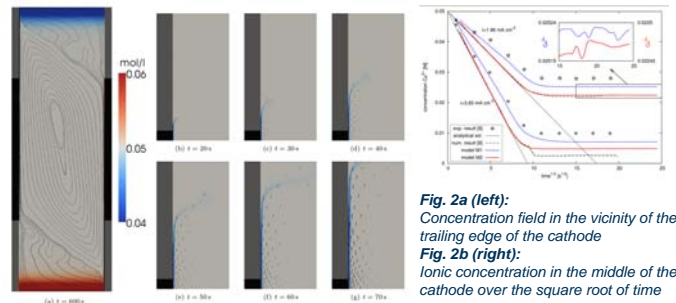
mol/l
0.06
0.05
0.04

Fig. 2a (left):
Concentration field in the vicinity of the trailing edge of the cathode
Fig. 2b (right):
Ionic concentration in the middle of the cathode over the square root of time

Rotating Cylinder Electrode (RCE)

- Configuration with cylindrically-shaped cathode rotates with 1 rad/s.
- Natural convection cannot be neglected for this setup.
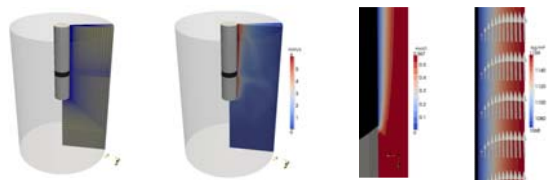- Fig. 3 depicts numerical results for a setup specified in [2, 6].

Fig. 3: Rotating cylinder electrode. Mesh (a), velocity magnitude (b), zoom to the concentration boundary layer which is forming near the surface of the electrode (c) and detailed view of the density field including the velocity field in the vicinity of the cathode (d).

Acknowledgements

References

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