A model for multi-ion transport simulations in 3-dimensional electrochemical reactors

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Introduction

Several authors (see for example references [1-3]) have presented results for stationary multi-ion transport and reaction simulations in vareous 2-dimensional reactor configuration cross-sections. These simulations where performed for aqueous solutions containing up to 15 ions, with non-linear boundary conditions to account for electrode reaction kinetics. For more complex reactor configurations however, 2-dimensional cross-sections can no longer deliver accurate ion concentration and potential distributions. As a consequence, also the reaction current density distributions over the electrodes (derived quantities) will become highly inaccurate. The purpose of this work is to illustrate the capabilities and challenges induced by the transition from 2-dimensional to 3-dimensional multi-ion simulations.

Description of model

The conservation of mass for each ion in a diluted solution is expressed by equation (1) :

$$\frac{\partial c_k}{\partial t} = -\nabla . \bar{N}_k + R_k \qquad (1)$$

where total flux of ion *k* considers the contributions of diffusion, convection and migration as given by:

$$\bar{N}_k = -D_k \nabla c_k + c_k \bar{u} - z_k F u_k c_k \nabla U \qquad (2)$$

The electroneutrality condition completes the set of equations:

$$\sum_k^{NIons} z_k c_k = 0 \qquad (3)$$

The electrode reaction kinetics is introduced in the model by the non-linear boundary conditions (often of Butler-Volmer type) using the dependence between local reaction current densities and the overpotential.
Often a forced electrolyte flow is applied and in this case the velocity field for the convection contribution in total flux of ion *k* is obtained solving the Navier-Stokes for incompressible flow:

$$\nabla \bar{u} = 0 \qquad (\bar{u}\nabla)\bar{u} + \frac{1}{\rho}\nabla p = \nu \nabla^2 \bar{u} \qquad (4,5)$$

Electrochemical and fluid flow models are both discretized using a Finite Element approach, with upwind contributions for the convection terms [3]. The two models are solved decoupled: first the velocity vector field is calculated from Navier-Stokes equations (4,5), next the electrochemical model (1-3) is solved to obtain the ion concentration and field results.

To validate the 3D implementation, a 0.3 M copper sulphate + 0.9 M sulphuric acid solution has been considered (yielding 4 ion species in total: Cu^{2+}, H^+, HSO_4^- and SO_4^{2-}), with copper deposition as the only cathodic electrode reaction:

$$Cu^{2+} + 2\,e^- \rightarrow Cu$$

A tubular reactor with cylindrical cathode is considered (Fig. 1). This configuration is entirely axisymmetrical. A laminar fluid flow is computed for an inlet velocity of 0.01 m/s (Re = 150), and the electrochemical model is solved for the above 4 ion system.

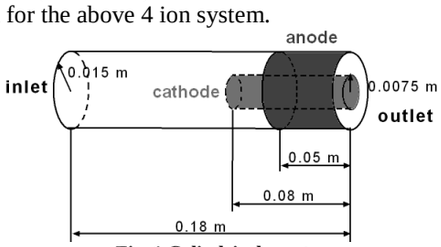

Fig. 1 Cylindrical reactor

The agreement between the results obtained in with a full 3-dimensional and with an axi-symmetrical model approach is very good.

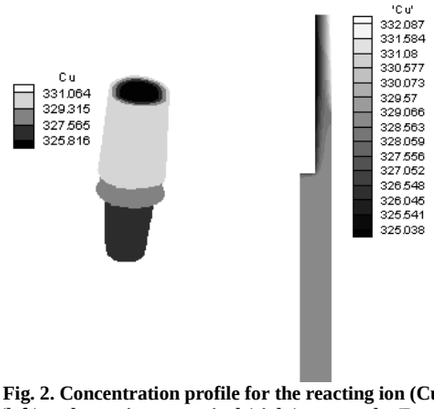

Fig. 2. Concentration profile for the reacting ion (Cu^{2+}) with a 3D (left) and an axi-symmetrical (right) approach. For the 3D profile (left) only the upper part of reactor is represented.

The relative error (around 2%) between these simulations is mainly due to the quality of the grid as used for the 3 dimensional simulations. Because the 3D simulations require a large amount of computation resources, the total number of nodes in grid is limited and the quality of the results in the boundary layer was affected (the number of tetrahedral elements in the diffusion boundary layer becoming to scarce).

Conclusion

Three-dimensional simulations are very expensive in memory and calculation (CPU) time and further work is required for parallelization and model decomposition to allow simulations of industrially relevant reactor configurations.

Acknowledgment

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