Presented at the COMSOL Conference 2009 Milan

Comsol Multiphysics as a General Platform for the Simulation of Complex Electrochemical Systems

A. Lavacchi
Chemistry Department - University of Firenze
alessandro.lavacchi@unifi.it

Overview

- Basics of electrochemical simulation and modeling
- State of the art
- Needs for a general tool
- Application of Comsol Multiphysics

Basics of electrochemical simulation

Electrochemistry is really multiphysics!

Diffusion

Diffusion convection

Migration

Closed form solutions of transport equation don't exist for most of this problems

More Exotic:
Magnetohydrodynamics
Maxwell's electrochemistry
Phase-field modelling

Need for discretization for the non-linear nature of the problems geometry and boundary conditions

State of the art

Finite Differences

- Easy to implement but difficult to extend to multidimentional problems for general boundary conditions

Finite Elements

- Difficult to implement respect the FD
- More general as they allow the straightforward implemementation for the simulation of complex shapes in 2D and 3D.
- Theoretical framework is very well developed allowing error extimation and adaptive techniques

The use of finite elements in electrochemistry shows more generality and it’s the best choice for a tool aiming at general electrochemical simulations.

Needs for a general tool

Flexibility → Finite elements

Flexibility → Equation coupling

Immediacy → No need to be a computer scientist

Applications of COMSOL multiphysics/1
Microelectrode arrays simulation

1) Cyclic Voltammetry (CV) at microelectrodes array
2) Electrodes in the diffusion convection regimes
3) Magnetoelectrochemistry
4) Phase Field modelling of electrodeposition

Applications of COMSOL Multiphysics/2

Cyclic Voltammetry (CV) at microelectrodes array

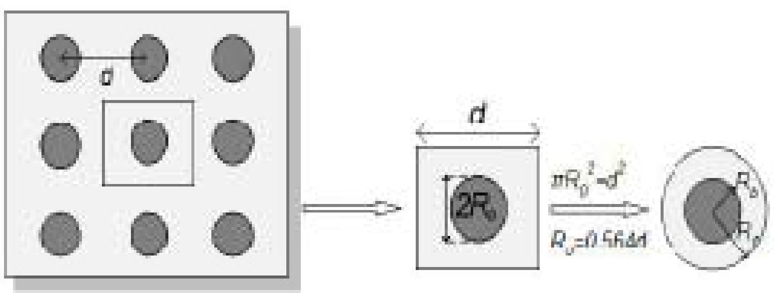


Figure 1. Microelectrode array and the domain wall approximation.

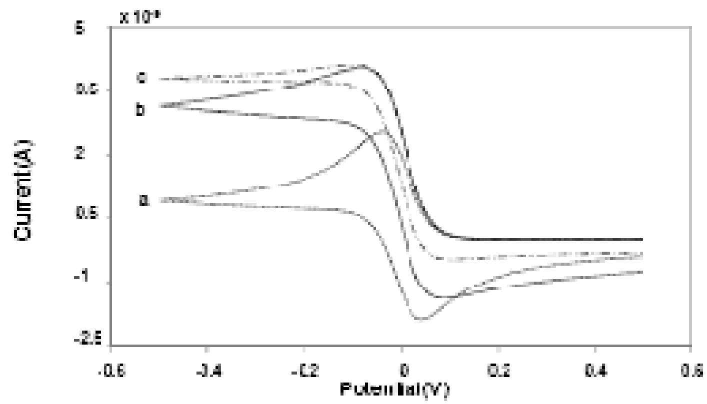


Figure 2. CV's simulated on a microelectrode array with (a) R_b= 10 μm and R_0= 20 μm, (b) R_b= 10 μm and R_0= 50 μm and (c) R_b= 10 μm and R_0= 100 μm

Applications of COMSOL Multiphysics/3

Electrodes in the diffusion convection regimes

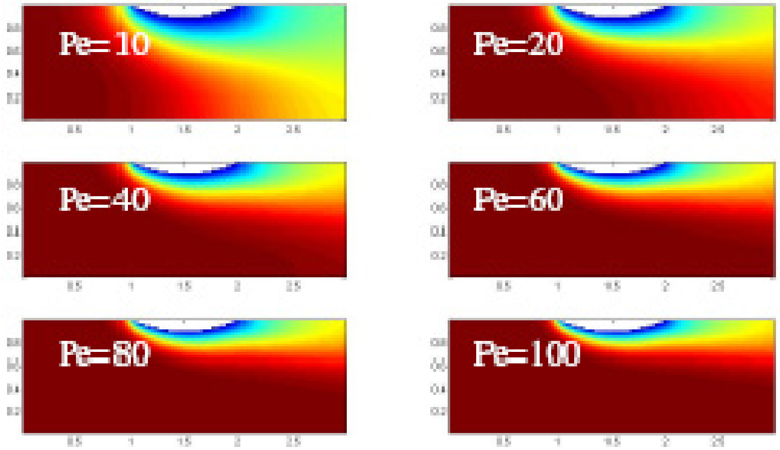


Figure 3. Concentration distribution in the stationary diffusion convection regimes for the bumped electrode.

Peclet Number	Coll. Eff	SS Time Inlaid	Coll Eff	SS Time Bumped
10	41.2	3.1	43.8	3.0
20	26.4	2.4	28.1	2.3
40	16.6	2.3	17.7	2.3
60	12.6	2.4	13.5	2.3
80	10.5	2.5	11.1	2.4
100	9.00	2.7	9.55	2.5

Table 1: collection efficiency and current stabilization times dependence on the Peclet number for bumped and inlaid microelectrodes.

Applications of COMSOL multiphysics/4
Magnetoelectrochemistry

Reverse Flow Occurrence at High Magnetohydrodynamic Numbers

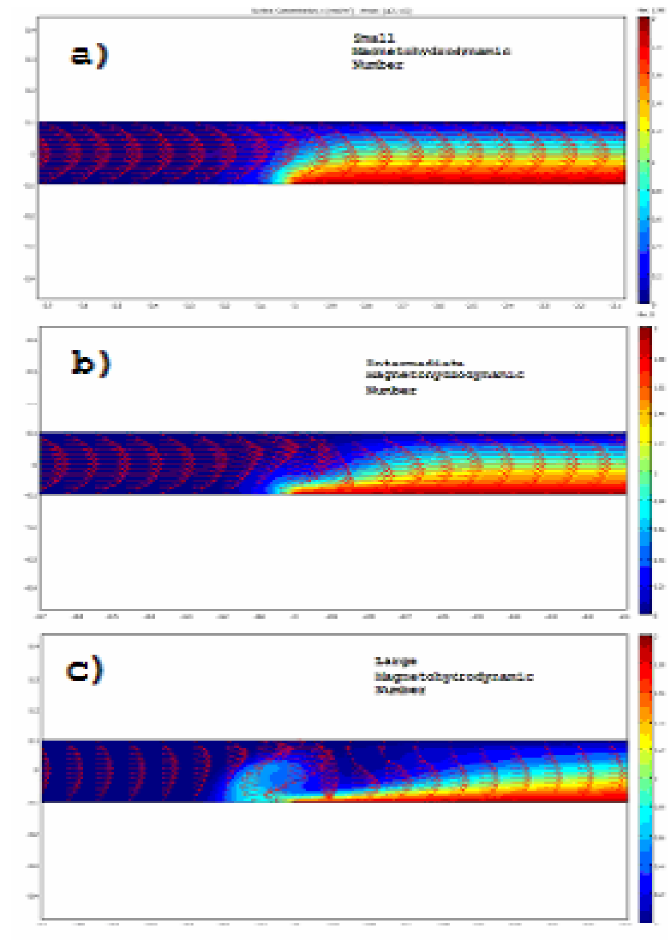
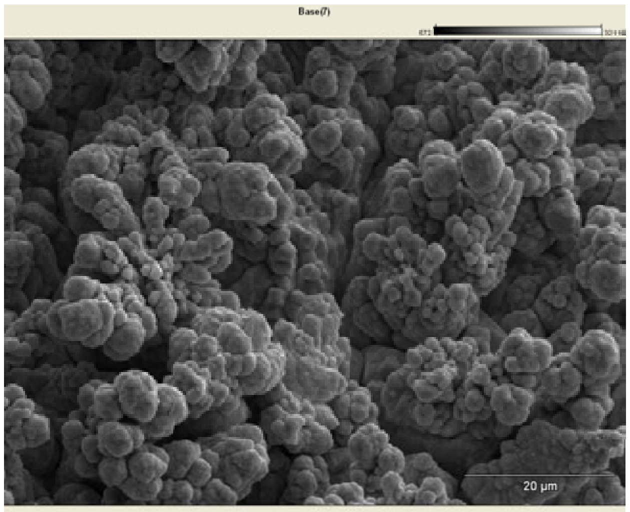


Figure 4. Magnetohydrodynamic convection and reverse flow occurrence in a parallel plates

Applications of COMSOL multiphysics/4
Phase-field modeling of electrodeposition



Electrodeposited Copper

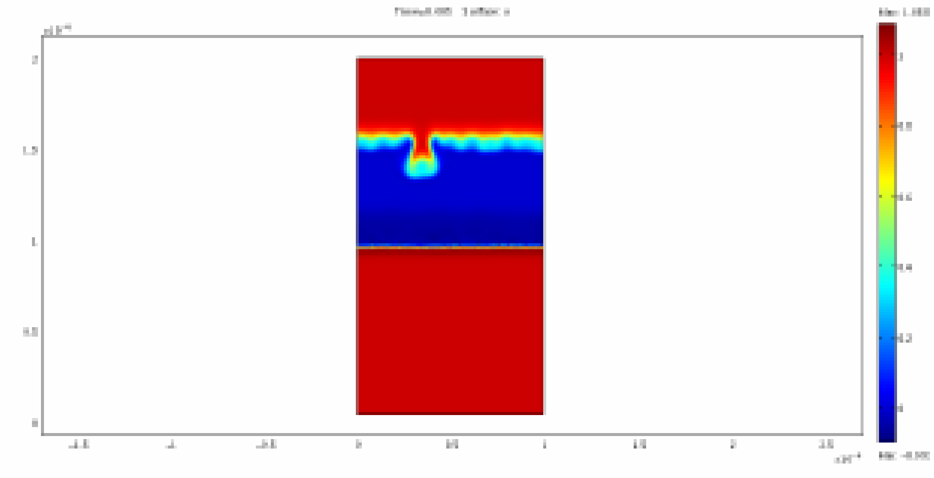


Figure 5. Break-up of morphological stability in the electrodeposition. First stage of the dendritic growth.

Conclusions

- COMSOL multiphysics has been successfully applied to the simulation of a variety of electrochemical experiments

- The same environment provide the possibility of simulating experiments in the whole range of electrochemistry