

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

A. Lavacchi*

Department of Chemistry, University of Firenze, Via della Lastruccia, 3 – 50019 – Sesto Fiorentino (FI) Italy

*email address: alessandro.lavacchi@unifi.it

Abstract: Microelectrodes demonstrate that modeling is crucial for understanding the behavior of complex electrochemical systems. Here the finite element method superseded finite differences for its ability to handle complex geometries. By the way the use of the finite element methods in electrochemistry may be of much more general interest. In this context a software such as COMSOL Multiphysics® allows a straightforward way to the set up models including coupling of phenomena from different branch of physics. In the opinion of the author this is an extraordinary promising tool which will allow the simulation of virtually any conceivable electrochemical experiment, providing a general platform for the electrochemical modeling. I present here a variety of simulated electrochemical experiments with a special emphasis on diffusion and diffusion convection in electroanalytical device, magneto-electrochemistry, and the morphology evolution in metal electrodeposition.

Keywords: Electrochemistry, Microelectrodes, Phase Field Modeling, Magneto-electrochemistry, Electrodeposition.

1. Introduction

The advantage of the finite element methods (FEM) as compared with finite differences is that complicated geometries and general boundary conditions can be handled relatively easily. This is a key issue in electrochemistry since the rising complexity of the electrochemical experiments require general tools for the data interpretation. Further the theoretical basis of FEM add reliability and in many case make possible the estimation of the error in the approximations leading to adaptive methods [1-4]. Many commercial software packages for the finite element discretization of partial differential equation exist. This issue is particularly relevant

since it provides straightforward way to manage complex electrochemical problems without the need of arranging a dedicated program code. The choice of Comsol Multiphysics® was motivated by its versatility in setting up models involving equations of different branch of physics, e.g. diffusion, fluid dynamics and electrostatics in magneto-electrochemistry. Then it has a well developed and intuitive Graphic User Interfaces (GUI's) also offering a large variety of post-processing opportunity.

The main results of models coming from different field of electrochemistry are considered here. The common task of simulation in microelectrode system is first considered. Here the diffusion equation together with the electrode kinetic determine the current density. In complex geometries numerical simulations are unavoidable for designing such devices. Convection diffusion is sometimes used in microelectrode systems in order to get stationary answer and larger current densities in order to enhance the sensitivity. Here numerical modeling addresses to the solution of the diffusion-convection according to the velocity profiles derived by the solution of the Navier-Stokes equations. A real multiphysics field in electrochemistry is magneto-electrochemistry. Here the Maxwell's equations are coupled with the Navier-Stokes equations and the diffusion equation. A model aimed at characterizing the flow pattern occurring in various conditions is shortly described. The last case considered here is the phase field modeling of the electrodeposition processes. The model has been implemented to show how the finite elements method can be applied to systems where changes in the topology of the domain occur.

The models presented here are not described in too much detail as it would not be possible to do that in a limited space. A detailed description is out of the purpose of the paper which is mainly focused in demonstrating how COMSOL

Multiphysics[®] fits the requirements for a general modeling and simulation platform for electrochemical research.

2. Models

2.1 Diffusion

The use of microelectrode systems in electrochemistry is quickly rising. Main reasons are a better signal to noise ratio and a lower capacitance compared to that of large planar electrode. Stationary waveforms are easily obtained for Cyclic Voltammeteries (CV's) also at high potential scan rates. These features make microelectrode arrays an attracting choice for electroanalytical sensors. Anyway the theoretical determination of the electrochemical response of is not straightforward as in the case of 1D geometries. Only analytical approximated expressions have been derived for the prediction of the current-potential relationship. Since the optimum signal is obtained under radial diffusion conditions the simulation play here a crucial role in a "a priori" determination of the physical and geometric condition which provide such propagation. In the case of the arrays the overlap of the diffusion clouds from neighborhood electrode can destroys this radial behavior providing a linear diffusion with lower current density and peak shaped CV's. So when operating with arrays it is very important to work in conditions avoiding this overlap. The simulations reported here aim at a theoretical assessment of the behavior of such arrays as a function of the array geometric parameters understanding if radial or linear diffusion dominate.

The simulation of such systems should require a 3D model. The reduction of the problem from a 3D to a 2D axial symmetry one is performed applying the domain wall approximation [5] reported in fig.1.

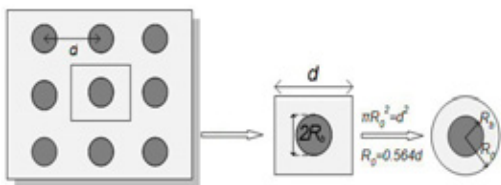


Figure 1. Microelectrode array and the domain wall approximation.

Simulations have been performed at a constant electrode radius ($R_b = 10 \mu\text{m}$) and varying the distance among the electrode centers. It was found that the CV is dominated by the linear diffusion for $R_o = 20 \mu\text{m}$ (Fig. 2a), and progressively approach to a stationary waveform when R_o is increased to 50 (Fig. 2b) and $100 \mu\text{m}$ (Fig. 3c).

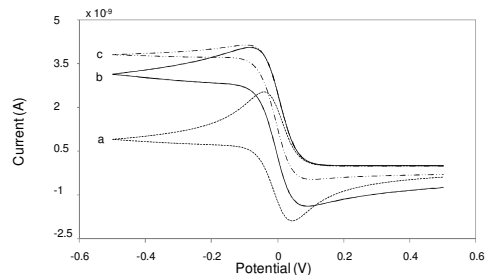


Figure 2. CV's simulated on a microelectrode array with (a) $R_b = 10 \mu\text{m}$ and $R_o = 20 \mu\text{m}$, (b) $R_b = 10 \mu\text{m}$ and $R_o = 50 \mu\text{m}$ and (c) $R_b = 10 \mu\text{m}$ and $R_o = 100 \mu\text{m}$

2.2 Diffusion-Convection

Unlike the case of microdisks, it is known that diffusion cannot provide a stationary current response in microbands. By the way a stationary current is a desirable property for analytic purposes and can be attained in microband configurations, only providing a steady convective flow of the electrolyte. Only approximated expression have been derived for steady state currents in linear sweep voltammetry and mass transport controlled potential step experiments. The complexity of the system preclude the possibility of finding general analytic expression for both the transient and the stationary regime. Numerical methods have been recognized to be much more general as they overcome the need for the assumptions required for the derivation of the approximated formulas. The modelling of the current response of band microelectrodes under such potential steps is essential both for assessing the system performance and optimizing the device design [6].

In the present work numerical modelling has been employed to analyze the following points:

- i) how long after the potential switch on the current response take to get stationary;
- ii) how the collection efficiency depends on the Peclet number and the microband profile;

The first point defines the minimum required amount of sample, a critical issues in microanalysis. The second aims at providing a quantitative estimation of the effect of the shape of the band for both recessed and inlaid electrodes. The effect of the finiteness of the channel height is also considered since it is a condition commonly encountered in real devices, both for the restriction imposed by the fabrication technologies and the need for large collection efficiency to optimize the sensitivity. The mathematical framework of the problem requires the diffusion convection and the Navier-Stokes equation. The advantage of the finite element methods (FEM) as compared with finite differences here is evident as we can change the geometry of the electrodes introducing protrusion in a easy way.

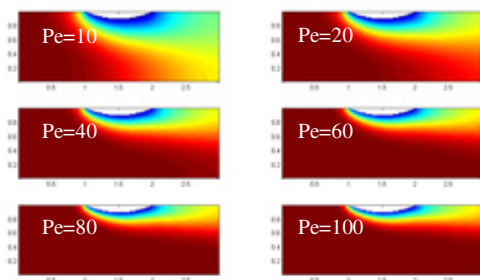


Figure 3. Concentration distribution in the stationary diffusion convection regimes for the bumped electrode.

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.

In the simulations I assumed that concentration at the electrode surface is 0 and the fluid which moves from left to right carries the reacting specie with a dimensionless concentration set to 1. Simulations have been performed for a set of values of the Peclet number ranging from 10 to 100. The Reynolds number was fixed and set to 0.1. Such values are common in microchannels. Fig. 3 shows the results of the simulation. It is evident that for low Peclet numbers the concentration profiles reaches the bottom of the cell. This aspect enlarge the time required for the stabilization in the answer as shown in table 1. For peclet number larger than 40 the effect of the finiteness of the cell is negligible. Obsiously the collection efficiency is larger at low Peclet numbers. Table 1 also show the effect of the bump. For the same Peclet number a protruded geometry produce a larger collection efficiency and the time required for the stabilization of the current is slightly shorter.

Data could be analyzed much more in detail, but even this short description gives a clear indication of the importance of having a general tool for the modeling. Concretely there is the possibility of designing devices with a careful choice of the geometries and an accurate choice of the operating conditions. Experimental work experiments saving activities which are usually much more expensive and time consuming than modeling.

2.3 Magnetochemistry

It is recognized that magnetic field can affect electrochemical reactions in four different ways [7]. An externally driven magnetic field can influence the interface reaction kinetics, change the electrolyte properties, affect the deposit structure and enhance mass transport rates. The first three effects are more fundamental and are related to surface chemistry and the structure of matter. Concerning the fourth point, it has been observed that when electrolysis is carried out in the diffusion controlled regime, the imposition of a magnetic field with intensity even lower than 1 T [8-15] significantly enhance mass transport rates. This is explained by the influence of the induced electromagnetic forces on the hydrodynamics of flow. The objective here is showing the results of the mathematical model accounting for the coupling between the mass

transport equation and the Navier Stokes momentum equation. The assumed system is a parallel plate electrochemical reactor where the convection is provided by magnetohydrodynamic. The electrodes are faced and the concentration is set to 0 for the anode located at the top of the channel. The flow pattern is then examined. At low magnetohydrodynamic numbers the flow is almost a fully developed parabolic flow between the plates as indicated by the red arrows in fig. 4a. As the Magnetohydrodynamic number increases the flow start to show pattern modifications and distorsion in the concentration profile occur fig. 4b. Finally a dramatic change in the flow pattern occurs at large magnetohydrodynamic number and locally reverse flow appears fig 4c. The evidence of a vortex is also showed by the shape of the concentration profiles. The obtained results are in good agreement with what found in ref. [7]. It is expected that such kind of modeling will provide a suitable tool for designing magnetochemical devices such as sensors with enhanced sensitivity.

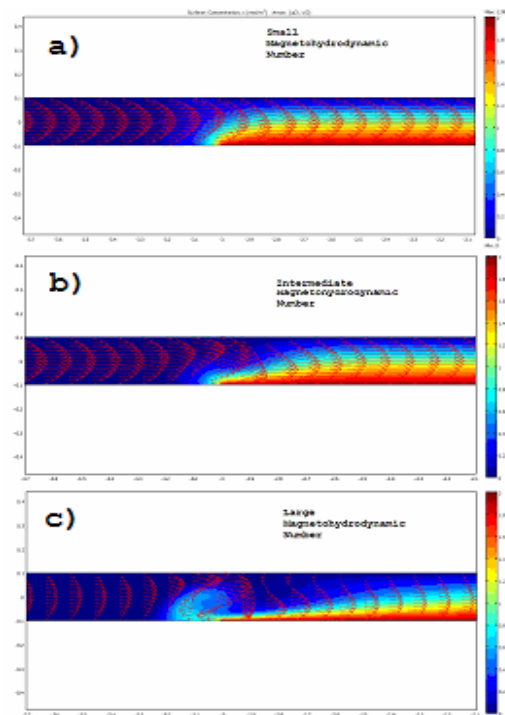


Figure 4. Magnetohydrodynamic convection and reverse flow occurrence in a parallel plates

.electrochemical reactor immersed in a cross magnetic field.

2.4 “Phase Field” Modelling of Electrodeposition

Phase Field modelling has been widely applied to the modelling of the solidification of metals and alloys. Recently many other application in different fields have also been reported e.g. the calculation of the equilibrium shape of membranes. The main advantage of this modelling technique consists in the fact that the boundary conditions don't explicitly appear in the definition of the model. For such reason they have been recently successfully applied to the simulation of the electrochemical interface where the definition of the boundaries is somewhat difficult due to the diffuse nature of the double layer and to the evolution of the interface morphology. Some “phase field” models aimed at the calculation of fundamentals electrochemical properties such as the differential capacitance and the composition of an electrodeposited alloy under diffusion control have been recently reported as shown in the works of J.E. Guyer and al. [16,17]. The basic idea here is that the driving forces governing solidification from melt is somehow similar to the overpotential in electrochemical deposition. The main difference occurring among the two systems concerns the presence of charged species which need to be explicitly considered by the addition of a specific constraint, increasing the complexity of the equation system. Here I report the result of a phase field model of the first stages of the dendrite growth in the electrodeposition of copper from hydrosulphuric and copper sulphate water based electrolytes on metallic copper substrates Fig. 5. Here the evidence of unstable growth is clear and roughening of the surface spontaneously occurs during electrodeposition. Such aspect is considered mainly to explore the effect of the deposition conditions on the morphology evolution. This issue is particularly relevant for the rising interest in the highly dispersed materials which, in the case of copper, are used as media for Thermal Solar Energy capture.

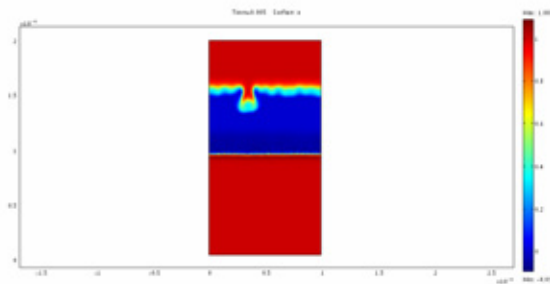


Figure 5. Break-up of morphological stability in the electrodeposition. First stage of the dendritic growth.

4. Conclusion

The results of models from different field of electrochemistry have been presented. It has been shown that COMSOL Multiphysics® is a suitable tool for general electrochemical modeling. The main reasons are the multiphysics nature of the software, allowing an easy coupling of the fundamental equations and the use of the finite elements algorithm. A large choice of solvers for linear and non linear systems allows the optimization of the solution time and accuracy. Further the post processing capabilities provide a straightforward data analysis and presentation tool giving a fundamental help in the exploitation of the simulation results.

5. References

- 1) K. Harriman, D. J. Gavaghan, P. Houston, E. Suli, Adaptive finite element simulation of currents at microelectrodes to a guaranteed accuracy. Theory, *Electrochemistry Communications*, **2**, 2000, Pages 157-162
- 2) K. Harriman, D. J. Gavaghan, P. Houston, E. Suli, Adaptive finite element simulation of currents at microelectrodes to a guaranteed accuracy. First-order EC' mechanism at inlaid and recessed discs, *Electrochemistry Communications*, **2**, 2000, Pages 163-170
- 3) K. Harriman, D. J. Gavaghan, P. Houston, E. Suli, Adaptive finite element simulation of currents at microelectrodes to a guaranteed

accuracy. ECE and EC2E mechanisms at channel smicroband electrodes *Electrochemistry Communications*, **2**, 2000, 576-585

4) D. J. Gavaghan, K. Gillow, E. S. Suli, Adaptive Finite Element Methods in Electrochemistry, *Langmuir* 2006 **22**, 10666-10682

5) A. Lavacchi, U. Bardi, C. Borri, S. Caporali, A. Fossati, I. Perissi, Cyclic Voltammetry Simulation at Microelectrode Arrays with COMSOL Multiphysics®, *Journal of Applied Electrochemistry*, 2009, doi: 10.1007/s10800-009-9797-2

6) A. Lavacchi, Finite Element Simulation of Diffusion-Convection at Inlaid, Protruded and Recessed Band Microelectrode, in preparation.

7) G.B. Ngo Boum, A. Alemany, Numerical Simulations of Electrochemical Mass Transfer in Electromagnetically Forced Channel Flows, *Electrochimica Acta*, **44**, 1999, 1749-1760

8) S. Mohanta, T.Z. Fahidy, Mass Transfer in a Magneto-electrolytic Flow Cell, *Electrochimica Acta* **19**, 2000, 835-840.

9) R. Aogaki, K. Fueki, T. Mukaibo, Application of Magnetohydrodynamic Effect to the Analysis of Electrochemical Reactions. 2. Diffusion Process in MHD Forced Flow of Electrolyte solution, *Denki Kagaku*, **43**, 1975, 509-514.

10) R. Aogaki, K. Fueki, T. Mukaibo, Diffusion Process in Viscous Flow of Electrolyte Solution in Magnetohydrodynamic Pumps Electrodes, *Denki Kagaku*, **44**, 1976, 89-94.

11) S. Mohanta, T.Z. Fahidy, Mass Transfer in a Cylindrical Magneto-electrolytic Cell, *Electrochimica Acta*, **21**, 1976, 149-152.

12) A. Olivier, J.P. Chopart, J. Douglade, C. Gabrielli, Investigation of Magnetic Effects on Mass Transport at the Electrode/Electrolyte Interface by Impedance techniques, *Journal of Electroanalytical Chemistry*, **217**, 1987, 443-452.

13) S. Mori, K. Satoh, M. Takeushi, A. Tanimoto, Electrolytic mass transfer around inclined cylinder in static magnetic field, *Electrochimica Acta*, **39**, 1994, 2789-2794.

14) S. Mori, K. Satoh, A. Tanimoto, Enhancement of electrolyte mass transfer around spheres by applying static magnetic fields, *Journal of Chemical Engineering of Japan*, **27**, 1994, 803-807.

15) S. Mori, M. Kumita, M. Takeushi, A. Tanimoto, Effects of Pulsating Magnetic Fields on Electrolyte Mass Transfer Around Cylindrical Cathodes, *Journal of Chemical Engineering of Japan*, **29**, 1996, 229-234.

16) J. E. Guyer, W. J. Boettinger, J. A. Warren, and G. B. McFadden, Phase field modeling of electrochemistry. I. Equilibrium, *Phys. Rev. E* **69**, 2004, 021603

17) J. E. Guyer, W. J. Boettinger, J. A. Warren, and G. B. McFadden Phase field modelling of electrochemistry. II. Kinetics, *Phys. Rev. E*, **69**, 2004, 021604