Thin Layer Elecrodeposition: Hydrodynamics, Electrochemistry and Chemical Coupled Aspects. From the Mesoscopic to the Micronic Scale.

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Abstract.

There are many electrochemical techniques in which the electrode moves with respect to the solution. Those systems, like the rotating electrodes, vibrating electrodes or whose in which there is a forced solution flow passing a stationary electrode, are called hydrodynamic electrochemical processes. The aim of the present work is to model and to numerically simulate the hydrodynamics, electrochemical and chemical phenomenon which are occurring during the electrodeposition process. The mesoscopic results obtained are the flow and composition field in the vicinity of the electrode surface. It is then possible to evaluate with a Monte Carlo method, the local fractal value which is directly related to the roughness and porosity of the material obtained.

Then, the hydrodynamic and chemical studies of the electrodeposition process upon a rotating electrode, an oscillating electrode and a simply stable electrode is presented in this work. A mathematical modelling associated with those two aspects is presented and demonstrated. The mathematical resolution of the equation system obtained is made using the finite volume method of Patankar, using the Fluent code®.

First, a hydrodynamic study is necessary to evaluate the convection transport of chemical species. Transitional and stationary velocity fields are calculated for three rotating velocities values $\dot{\omega} \in \{10^0;\ 10^1;\ 10^2\}$ rad.s^{-1}. It has been found a good agreement with the classical estimation for the rotating electrode in its vicinity, but for an axial distance of about 1 mm the good estimate is lost for $\dot{\omega}=10^0$ rad.s^{-1}.

Electrochemical and chemical processes are then taken into account, obeying a classical EC scheme. Both precipitation and complexation phenomena are taken in the numerical example chosen: the zinc oxide elecrodeposition. Results show that, because of volumetric precipitation and complexation reactions, the classical Levich diffusion theory, which correlates boundary layer depths for the rotating electrode, are lost and chemical boundary layer thicknesses are greatly modified in the reacting case.

In a last point, this study uses the mesoscopic scale results to define local weighted probability for working particles which form the material layer, allowing the local porosity and rugosity estimation by fractal calculation.

Key words: Electrodeposition, chemical kinetics properties identification, hydrodynamics, moving electrode, mesioscopic scale, micronic scale

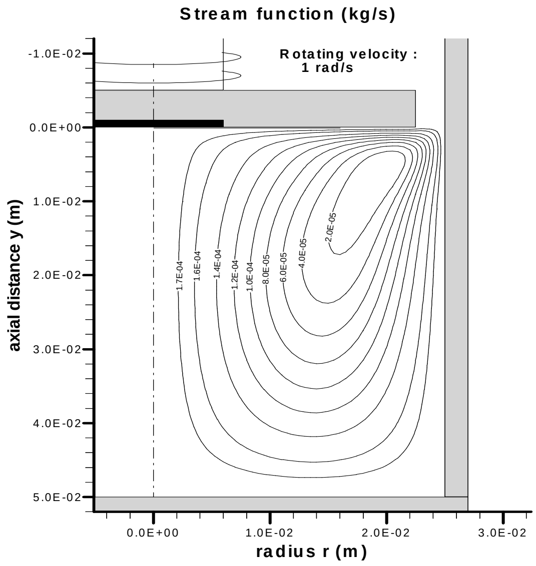

Figure 1: Stationary stream function evolution with the rotating velocity $\dot{\omega}=1$ rad.s^{-1}

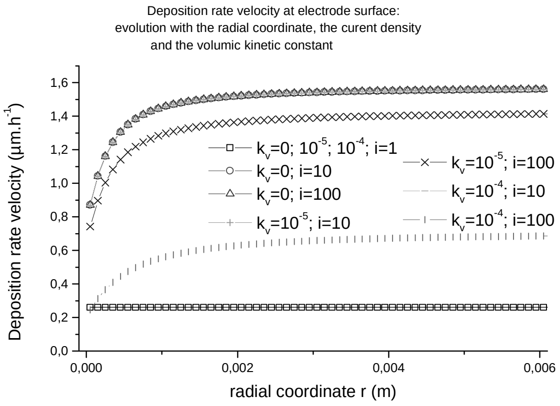

Figure 2 : Deposition rate velocity at the electrode

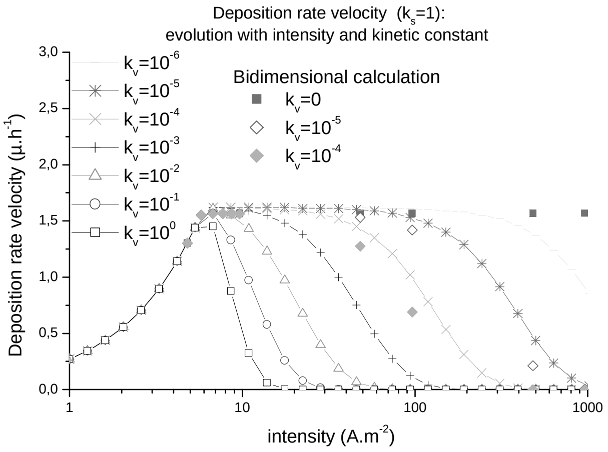

Figure 3 : Deposition velocity : variation with the current density