3D ELECTRODE SHAPE CHANGE SIMULATION IN ELECTROPLATING

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Key words: Electroplating, 3D modeling, Electrode shape change, Potential model, Boundary element method.

This paper proposes a general applicable numerical technique for the simulation of three-dimensional (3D) electrode shape changes obtained during the electroplating processes. The shape of the electrode is found displacing each mesh node proportional with, and in the direction of the local current density according to Faraday's law. The local growth rate is obtained solving numerically the potential model using Boundary Element Method (BEM). An example dealing with the 3D simulation of electroplating near an insulator (singularity) is presented and compared with measurements and two-dimensional (2D) simulations.

1. **INTRODUCTION**

In the electroplating cells, metal deposit occurs at the cathodes. The high non-uniform current density, due to the edge effects, transfers to a pronounced non-uniform deposition layer. In order to predict and mitigate such effects suitable mathematical model and simulating software are necessary.

Dilute solution theory provide the general equations describing the electrochemical processes, as described in detail in [1]. Most of the published papers present a more or less simplified mathematical model. For example, when the electrode reactions take place at low rates, such that the concentration gradients are neglected, the potential distribution may be found only using Laplace's equation. Hence, the resulting model describes the ohmic effects in the electrolyte and is known as the potential model (PM) [2]. Several authors applied the PM to compute the current density distribution and hence the electrode growth rate for electroplating applications. Alkire *et. al.* applied in [3] the finite element method (FEM) to solve the resulting Laplace equation, with nonlinear boundary conditions that account for electrode charge transfer reactions. Deconinck *et al.* [2] discretized

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the equations of the PM using the BEM in order to compute the changing electrode profile for nonlinear boundary conditions. They also presented a complete study of the electrode evolution function of the electrode reactor dimension for different angles between the electrode and an adjacent insulator. Using the finite difference method (FDM), Bozzini and Cavallotti [4] presented numerical simulations for the Cr-plating process on corner-shaped cathodes.

Most of the works presented above applied an Euler scheme for the integration of Faraday's law with respect to the time, combined with the displacement of the discretization nodes of the electrode surface. This method, referred as the string theory in [5], derives from the Lagrangian approach of changing boundary problems that implies the grid boundary to be attached to the moving front.

Lee *et al.* in [6] and Purcar *et al.* in [7, 8] proposed level set method (LSM) for the calculation of the electrode shape changing. Both approaches used the PM for the computation of the current density distribution. LSM does not explicitly distort the profile of the interface but implicitly compute it as a solution of a scalar advection equation [5].

A limited number of publications deal with three dimensional (3D) current density distribution simulations in electrochemical reactors, but in the field of 3D electroplating they are very scarce. Applications that consider current density distributions for more complex 3D geometries can be found in the field of cathode protection and wafer plating [9, 10]. Purcar and Bortels [11–13] applied the principles of advanced CAD integrated approach for 3D electrochemical machining simulations.

Although during the last decade significant progress in the developing of the simulation tools of the electrochemical process has been made, there is still a high need for effective software and compact integration of these tools in the product design-development chain in order to minimize the computational time, which is extremely long for the 3D problems. This paper presents a general simulation approach of the 3D electroplating applications with strong non-linear boundary conditions including reaction efficiency and illustrates the basics principles of the 3D electrode shape change algorithm.

2. MATHEMATICAL MODEL AND NUMERICAL SOLUTION METHOD

The electrochemical process (*e.g.* electroplating, electroforming, electro erosion etc.) develops continuously in time. In order to simulate the evolution of the electrode profile, the continuous process time must be divided into a sequence of discreet time steps [13]. For each time step two problems should be usually solved:

1) the electrochemical model (a steady state problem for calculating the local electrode growth rate) and

2) the electrode growth problem (a time dependent problem for calculating the shape of the electrode surface at each time step).

The electrode growth rate, provided by Faraday's law, ensures the coupling of the two problems.

2.1. ELECTROCHEMICAL MODEL

In most practical cases (e.g. 3D simulations), the dilute solution theory which describes the migration, convection, diffusion and electrode reactions in electrolytes [1] is subjected to important simplifications. Hence, considering the electrolyte solution very well stirred (situation often met in the practical situations) concentration gradients can be neglected (except for a very thin layer near the electrodes where the electrochemical reactions occurs). Assuming charge conservation in the bulk and the conductivity of the electrolyte constant, potential model yields.

The potential model is described by the Laplace equation for the electrolyte potential U, whereas the phenomena occurring in the diffusion layer and at the electrode interface [1] (*e.g.* the electrochemical reactions) are included in the boundary conditions.

$$\nabla^2 U = 0 \quad \boldsymbol{J} = -\sigma \cdot \overline{\nabla} U \,, \tag{1}$$

where σ represents the conductivity of the electrolyte in [$\Omega^{-1}m^{-1}$], U the electrolyte potential in [V] and $\boldsymbol{J}$ the current density in [A/m^2].

2.1.1. BOUNDARY CONDITIONS

The boundary conditions in equation (1) are divided into insulators and electrodes [2, 7, 8]. As no current can flow through the gaseous medium in contact with the electrolyte and electrochemical cells walls (the normal current density J_n is zero, see Fig. 1):

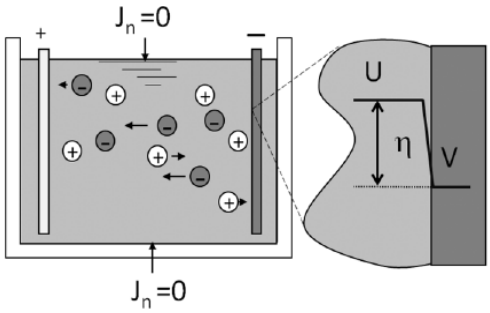

Fig. 1 – Boundary conditions at the electrodes [10].

At the interface between the electrode and the electrolyte, known as double layer [1], electrochemical reactions occur. The electrochemical reaction driving force is expressed at each point of the electrode by a difference between the solution U and electrode potential V (Fig. 1) and is called the charge transfer overpotential or polarization η [1, 2, 7, 8]. The following expression of the overpotential generally holds for a given reaction at the electrodes:

$$\eta = V - U - E_0 = f(c_0, J_n), \tag{2}$$

with U the potential of the solution adjacent to the electrode, outside to the double layer, V the metal potential, E_0 the equilibrium potential, c_0 the surface concentration of the ion(s) involved in the reaction in [mol/m^3] and J_n the normal current density at the electrode (Fig. 1).

Function of the overpotential sign, oxidation (positive η) or reduction (negative η) occurs at the electrodes. Study of the kinetics of the electrode reaction generally reveals a strong non-linear behaviour in (2). The electrochemical reaction (2) is incorporated in the PM as a non-linear boundary condition and in the most general situation is written as:

$$J_n = f(\eta). \tag{3}$$

Such function is usually obtained measuring the physicochemical parameters of the electrolyte and approached with a spline function as in [2, 7, 8].

2.1.2. ELECTRODE GROWTH RATE

The amount of material reduced at the cathode is directly proportional to the amount of the electrical charge flowing between the electrodes. This can be expressed using Faraday's law:

$$m = \frac{M \cdot I \cdot T}{z \cdot F}, \tag{4}$$

with: m – the dissolved or deposited mass [kg], I – the total current that flows between the electrodes [A/m^2], T – the total process time [s], M – the atomic weight of the metal [kg/mol], F – the Faraday's constant [96 485 C/mol] and z – the electric charge [C].

Considering the deposited mass $m = \rho \cdot \mathrm{d}V$, where ρ is metal density [kg/m^3] defined on an infinitesimal $\mathrm{d}V = \mathrm{d}h \cdot \mathrm{d}S$ volume, the local electrode growth $\mathrm{d}h$ can be simply computed from (4) as:

$$\mathrm{d}h = \theta \cdot \frac{M \cdot T \cdot J_n}{\rho \cdot z \cdot F}, \tag{5}$$

where $J_n = I/\mathrm{d}s$ is the normal current density through an infinitesimal surface ds at the electrode surface. For a more general definition of the electrochemical reactions (3) (*e.g.* incorporating the side effects like gas evolution), the efficiency θ is introduced. In that case the efficiency θ is below 100 %.

2.2. NUMERICAL SOLUTION METHOD

The equations (1–3) describe geometries with arbitrary boundary conditions which cannot be solved analytically. The solutions can be obtained using different discretization techniques (*e.g.* BEM, FEM, FDM etc.), which assume the approximation of the continuous solution as a set of quantities at discrete locations, often on an irregularly spaced mesh.

The computational environment, ESCFrameWork V1.1, developed by the authors, is object-oriented and can handle any 3D single or multiple domain models. A flexible grid generator [14] is used to create an unstructured triangular mesh separately on each face of the computational domain. The mesh is optimally refined towards the zones where a steep variation of field variables is expected but generates coarse elements at any other position, see Fig. 3 (right). The computation of the equation system (8) is implemented both for an iterative and for a direct LU solver (http://www.boost.org/).

2.2.1. BEM FOR ELECTROLYTE AND ELECTRODE REACTIONS

In order to solve the simplified charge conservation equation (1), BEM is more suitable over other discretization methods (FEM and FDM) because the conductivity of the electrolyte is considered constant. One of the BEM advantages is that only the boundaries of the computational domain must be discretised. Another advantage, in particular for electrochemical systems, is that the current density distribution along the electrodes is a direct unknown to the problem, rather than a variable that must further be computed from the derivative of the potential field at the electrodes.

The boundary S_Γ of the computational domain is meshed with N_e non-overlapping elements defined by nodes $\chi_i = (x_i, y_i, z_i)$ in $\mathbb{R}^3$ ($i = 1 \ldots N_p$). The characteristic BEM equation for the contribution to a point i is [15, 16]:

$$c^i U^i + \sum_{e=1}^{N_e} \int_{S_e} U \frac{\partial w^*}{\partial n} \mathrm{d}\, S_\Gamma = \sum_{e=1}^{N_e} \int_{S_e} w^* Q \,\mathrm{d}\, S_\Gamma \,, \tag{6}$$

with $w^*=1/(4\pi r)$ the 3D Green function (r being the position relative to point i), $Q = \partial U/\partial n$ the inward flux on the boundary nodes and c^i is an integration constant for point i. The index e ranges over all elements of the domain and integration is performed over the surface S_e of each element. Triangular elements with linear

shape functions for the unknown potential U and flux field Q are used, hence, restricting the unknowns to the nodal values i.

BEM equation (6) results into the system of equations:

$$[\boldsymbol{H}]\cdot[\boldsymbol{U}]=[\boldsymbol{G}]\cdot[\boldsymbol{Q}], \tag{7}$$

where $\{\boldsymbol{Q}\}$ is a vector of size N_p containing the values of the electric field normal to the boundary S_Γ in each point, $\{\boldsymbol{U}\}$ is a vector of size N_p containing the value of the potential in each node and $[\boldsymbol{H}]$ and $[\boldsymbol{G}]$ are square matrices of size N_p x N_p.

Including in (7) the boundary conditions on the electrodes (overpotentials) and insulators the system (7) is reordered such that all unknowns are put to the left hand side:

$$\begin{bmatrix}[\boldsymbol{H}] & -[\boldsymbol{G}]\\ [\boldsymbol{0}] & [\boldsymbol{1}]\end{bmatrix}\cdot\begin{Bmatrix}\boldsymbol{U}\\ \boldsymbol{Q}\end{Bmatrix}=\begin{Bmatrix}\{\boldsymbol{0}\}\\ \boldsymbol{f}(\boldsymbol{\eta})\end{Bmatrix}. \tag{8}$$

As for most of the electrochemical process the overpotential η is non-linear, a Newton-Raphson iterative algorithm is applied to solve the system (8).

Numerical validation of the BEM model has been performed in [6]. Results showed a very good agreement with the analytical values, with a relative error below 2 % in direct relation to the surface mesh refinement.

2.2.2. ELECTRODE SHAPE CHANGE COMPUTATION

In order to compute the electrode profile, the continuous process time T is divided into a discreet sequence of time points t_m (m = 0, 1, ... N_t). Knowing at each nodal point of the boundary the current density, equation (5) reduces to N_p equations, one for each nodal point i. The electrode growth rate becomes:

$$\frac{\mathrm{d}\,\boldsymbol{h}(\chi_i,t)}{\mathrm{d}\,t}=-\left[\theta\cdot\frac{M}{\rho\cdot z\cdot F}\right]\cdot\sigma\cdot J_n(\chi_i,t)\cdot\mathbf{1}_n, \tag{9}$$

where the unit normal $\mathbf{1}_n$ is oriented outwards from the computational domain.

Equation (9) is the Lagrangian formulation of the interface evolution and represents the basic equation of the nodal displacement method (NDM) [13]. For t = 0 the initial condition $\boldsymbol{h}(\chi_i, t=0)=0$ is imposed. Replacing the differential in the formulation (9) with a simple forward difference approximation, results:

$$\boldsymbol{h}_i^{t_{m+1}}=\boldsymbol{h}_i^{t_m}+\lambda\cdot\sigma\cdot J_{n,i}^{t_m}\cdot\boldsymbol{1}_n\cdot\Delta t_m, \tag{10}$$

with $\lambda=-\theta\cdot M/(\rho\cdot z\cdot F)$ and $\Delta t_m=t_{m+1}-t_m$ the time step.

Equation (10) represents the explicit Euler integration scheme which is in fact the first order Taylor expansion of the solution of equation (9). The new boundary

is easily found displacing each node on the electrode proportional with and in the direction of the local growth rate (Fig. 2). This is easy to fulfil if the connectivity does not change and the surface elements are not highly distorted.

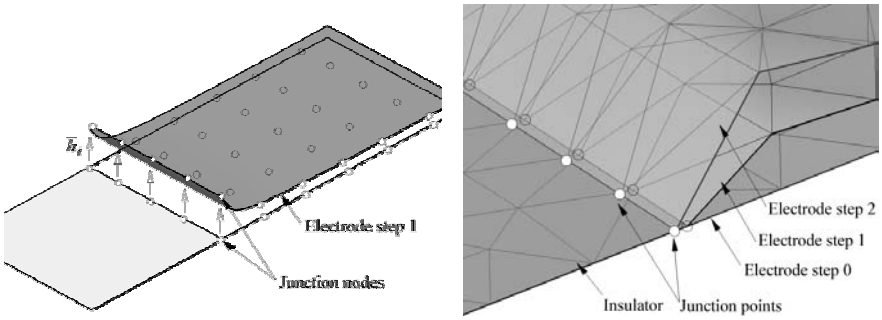

Fig. 2 – Displacement of the boundary nodes.

3. **ELECTROPLATING SIMULATION NEAR A SINGULARITY**

This example presents the 3D copper electroplating simulation in the vicinity of a insulator singularity. A similar example has been studied in references [2, 7] for 2D numerical simulations based on different computational methods. These comparisons will be used to validate the 3D electrode shape change model presented in this paper.

3.1. MODEL DEFINITION AND PROCESS CONDITIONS

The cell in the experimental set-up [2] and simulations [2, 7] is given in Fig. 3 (left). The distance between the cathode and anode is 12 cm. The length of the cathode and anode is 19.9 respectively 30.7 cm. The reactor's width is 0.79 cm.

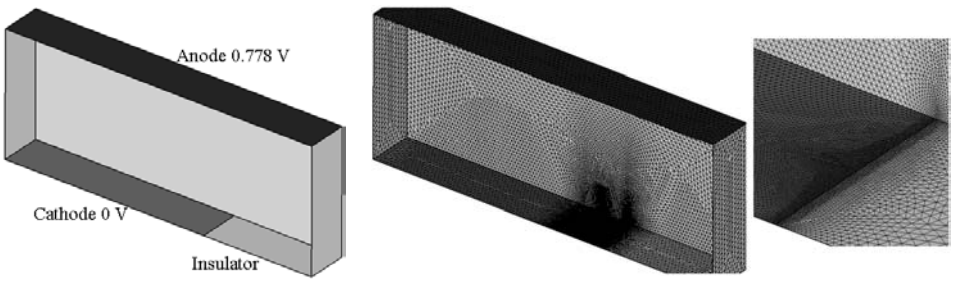

Fig. 3 – Geometry of the electrochemical cell in the vicinity of the singularity (right) and the triangular surface mesh of the computational domain (left).

The experiment described in [2] ran for 86.98 h to a constant voltage $U = 0.778$ V between the cathode and anode. The same physicochemical input parameters as in [2] and [7] are used. For these parameters the potential model (PM) and the electrochemical problem can be approached by the Laplace equation (1) with non-linear boundary conditions (3).

3.2. THREE-DIMENSIONAL RESULTS

The computational domain is meshed using in 32 714 triangular elements and 10 660 points (Fig. 3 right). Around the singularity the mesh is highly refined in order to capture the edge effects. On the other zones the mesh size is further coarsened. This enables to perform calculations on a normal PC with 8GB RAM and 2.4GHz CPU within about 10 minutes for one time step. The calculated deposition time $T = 86.9$ hours is divided into 25 constant time steps, $\Delta t = 209$ minutes (12 540 *s*).

The governing Laplace equation is solved using the 3D BEM, which yields the normal current density distribution at the electrode surface. In a second step using the equation (10), the nodal points are displaced proportional with the normal current density. The process is repeated until the total process time is achieved. The high non-uniform current density due to the edge effects on electrode surfaces near to the insulating substrate, transfers to a pronounced non-uniform deposition layer. Successive simulated layer thickness deposition profiles on the cathode, together with photography of the final copper deposition are presented in Fig. 4.

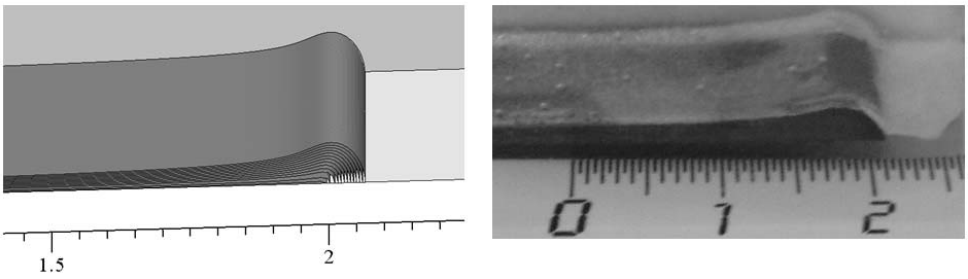

Fig. 4 – Simulation of the 3D deposition profile (left) and the experimental result in [2] (right).

The comparison between the simulated and experimental electrode profiles in (Fig. 5) shows a good agreement [2, 7]. The maximum relative deviation, between the 3D simulations and measurements is 17% at the peak of the growth. The maximum relative deviation, between the 3D and 2D simulations in [2, 7] is about 8%. The deviation between the 3D and 2D simulation results can be due a better accuracy of the 2D BEM solver versus the 3D BEM solver. Another source of errors for both 2D and 3D models versus the experimental results is that the

underlying potential model does consider the mass transfer phenomena that occur in the diffusion layer near the electrode. These phenomena are more pronounced for the higher variations in the gradient of the field, *e.g.* at the neighbourhood of the cathode and insulator substrate.

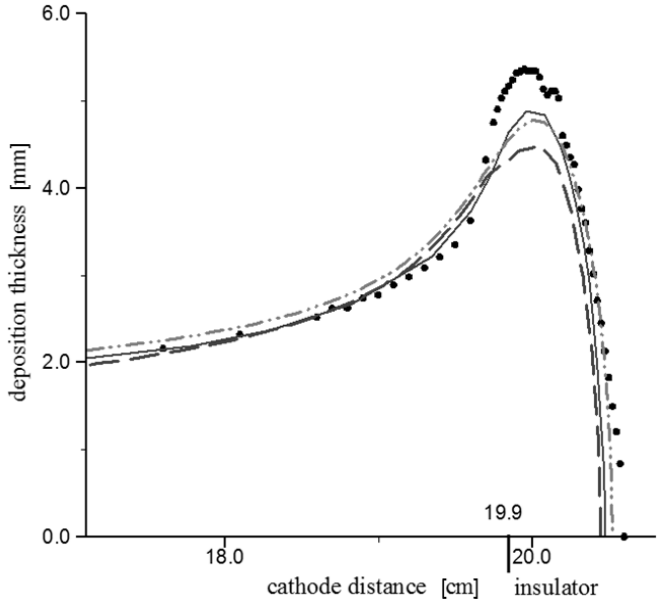

Fig. 5 – Deformed plot representation of the numerical and experimental results: measured (•) [2], simulated 2D NDM (—) [2], simulated 2D LSM (••—••) [7], simulated 3D NDM (— —).

4. **CONCLUSIONS**

The principles of 3D electrode shape change simulations in electroplating calculations have been presented. The simulation tool is based on the potential model solved with a standard 3D BEM approach for calculation the current density distribution at the electrode and nodal displacement method to find the electrode growth profile. In order to reveal the method, an example dealing with the 3D simulation of electroplating near an insulator (singularity) is presented and compared with measurements and two-dimensional (2D) simulations from literature. The 3D and 2D results match very well. Differences can be considered as resulting from numerical inaccuracies developed by both the 2D and 3D approaches. Another source of errors is that the potential model cannot take into account the mass transfer phenomena that occur in the diffusion layer. The use of the 3D simulation tool allows calculating different set-ups in a fast and cheap way.

The methodology developed here proved its robustness when dealing with and combining distinctive stages in the electrode growth simulations process such as current density computation and nodal displacement.

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