

# DETERMINATION OF THE LAWS OF POLARIZATION BY COUPLING MEASUREMENTS WITH NUMERICAL TOOL

F. Druesne<sup>1</sup>, P. Paumelle<sup>1</sup> and P. Villon<sup>2</sup>

1. Technical Center, Senlis, France.
2. Compiègne Technology University (UTC), France.

## ABSTRACT

Electrochemical plating is used to give a particular property to a component. This can be a decorative aspect (silver, gilding), a physical or mechanical property different from an existing one (hard chromium), or, a protection against corrosion (nickel and chromium). On the other hand, the design of an electrochemical cell needs many experimental tests in order to lead to an optimal geometry of the electrodes, an appropriate electrolyte, and to produce a uniform deposit. The industrial cells with respect of a complex geometry can be modelled, a large gain is reached in cost. The software in three-dimensional space, simulates deposit distribution. Many industrial cells have been modelled and numerical results are in good agreement with deposit measurements.

The numerical method is based on Boundary Element Method, by coupling with a Newton-Raphson iterative technique of resolution to treat the non linearity of experimental boundary conditions.

In electroplating numerical process, boundary conditions on the cathodic and anodic electrodes are experimental polarization laws. The objective of this present work is to identify these laws, we adjust the model to be in good agreement with the experimental measurements.

**KEYWORDS:** experimental measurements, laws of polarization, numerical identification.

## 1. MATHEMATICAL MODELLING

The electrolytic domain  $\Omega$  (electric conductivity  $\sigma$ ) is limited by the bounds  $\Gamma_A \cup \Gamma_C \cup \Gamma_R$  (Figure 1), the anodic boundary  $\Gamma_A$ , the cathodic boundary  $\Gamma_C$  and the insulating part  $\Gamma_R$ ,

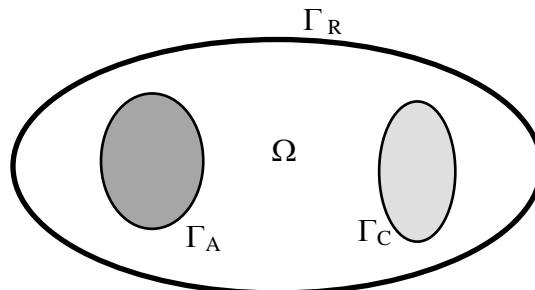


Figure 1 - General representation of an electrochemical system.

The direct problem of electrochemical plating [1] is described by:

find potential  $u(x)$  in electrolytic domain and potential difference  $\varphi$  between the two electrodes such as:

$$\left\{ \begin{array}{ll} -\nabla^2 u(x) = 0 & \text{dans } \Omega \end{array} \right. \quad (1)$$

$$\left\{ \begin{array}{ll} \sigma \frac{\partial u}{\partial n} = f(u(x)) & \text{sur } \Gamma_C \end{array} \right. \quad (2)$$

$$\left\{ \begin{array}{ll} -\sigma \frac{\partial u}{\partial n} = g(u(x) - \varphi) & \text{sur } \Gamma_A \end{array} \right. \quad (3)$$

$$\left\{ \begin{array}{ll} \sigma \frac{\partial u}{\partial n} = 0 & \text{sur } \Gamma_R \end{array} \right. \quad (4)$$

$$\left\{ \begin{array}{l} I = - \int_{\Gamma_C} \sigma \frac{\partial u}{\partial n} d\Gamma_C . \end{array} \right. \quad (5)$$

The total current  $I$  debited by the generator corresponds to the dual quantity  $\varphi$  between the two electrodes [2].

The functions  $f$  and  $g$  represents respectively cathodic and anodic polarization laws, they describes the potential gap at the electrode/solution interface. The preliminary step is the experimental measurement of this gap, after we will research numerically these functions under polynomial form,

$$\left\{ \begin{array}{l} g_\alpha(u - \varphi) = \alpha_0 + \alpha_1 \cdot u + \dots + \alpha_{ka} \cdot u^{ka} \\ f_\beta(u) = \beta_0 + \beta_1 \cdot u + \dots + \beta_{kc} \cdot u^{kc} \end{array} \right. \quad (6)$$

so we must determine the vector  $\theta^T = (\alpha, \beta)$  of polynomial behaviour laws parameters  $f$  and  $g$ .

## 2. INTEGRAL FORMULATION

The Boundary Element Method [3] [4] coupled with a Newton-Raphson iteration technique (to treat the non linearity of boundary conditions) is well adapted to the calculations of current distribution and deposit distribution. The Boundary Element Method is the most natural technique since only data on the boundaries are needed and used [5] [6] [7].

The integral formulation is described by,

$$\begin{aligned} C(x).u(x) = & - \int_{\Gamma} \frac{\partial K(x, y)}{\partial n_y} u(y) d\Gamma(y) \\ & + \int_{\Gamma_A} g_\alpha(u(y) - \varphi) K(x, y) d\Gamma_A(y) \\ & + \int_{\Gamma_C} f_\beta(u(y)) K(x, y) d\Gamma_C(y) \end{aligned} \quad (7)$$

with  $K(x,y)$  and  $\partial K(x,y)/\partial n_y$ , respectively potentials of simple and double layer, and the free term  $C(x)$  verify (8).

$$C(x) \begin{cases} = 1/2 & \text{if } x \in \Gamma \text{ continuous tangent plan at point } x \\ = 1 & \text{if } x \in \Omega \\ = 0 & \text{if } x \notin \Omega \end{cases} \quad (8)$$

The equation (7) just relates physical variables of the domain surface, they are linked by boundary conditions of the problem.

### 3. IDENTIFICATION BY OPTIMAL CONTROL THEORY

After discretisation of the integral equation (7) on the three boundaries and discretisation of (5), the non linear state equations under integral form are described by,

$$E(v,\theta) = 0 \Leftrightarrow \begin{cases} e_1(v).\theta + e_0(v) = 0 \\ e_2.v = I \end{cases} \quad (9)$$

with  $v^J=(u,\varphi)$ , these equations must be satisfied to minimize the equation (10) at the point of the measurement (interior point of the electrolyte),

$$u(x_{mes}) = \mathcal{O}v \quad (10)$$

with  $\mathcal{O}$  operator of observation at the measurement node.

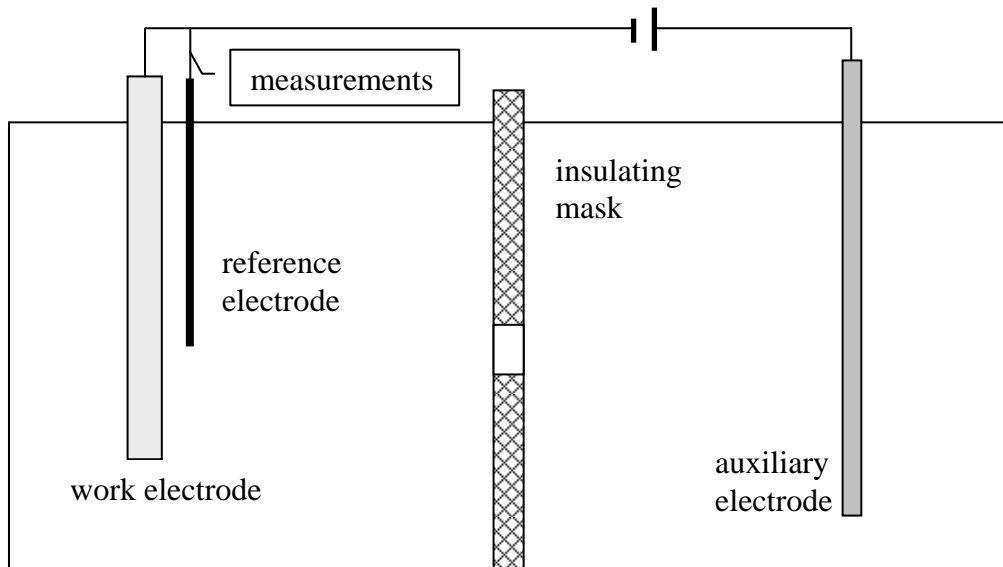


Figure 2 – experimental cell

The experiment (Figure 2) give a number of potential measurements  $Z_\eta$  at the geometric node of the measurement for different currents  $I_\eta$ . The problem consist on adjusting  $\theta$  to minimize  $|\mathcal{O}v_\eta - Z_\eta|$  for the experimental measurements  $\eta=1,\dots,M$ . The indicator  $B(\theta)$  measures

the gap between numerical potentials (10) and measured potentials  $Z_\eta$  for each experimental measurement  $\eta$ ,

$$B(\theta) = 1/2 \sum_{\eta=1}^M |o_{v_\eta} - Z_\eta|^2 + 1/2 \epsilon \theta^2. \quad (11)$$

The vector  $\theta$  of parameters for polynomial laws  $f$  and  $g$  is determined by specific minimum search algorithm based on a 2<sup>nd</sup> order descent method. At each step, the direction of research is issued from the calculation of gradient of (11) by the method of adjoint state, solution of dual equation defined by multiplier Lagrange.

#### 4. CONVERGENCE OF METHOD OF THE ADJOINT STATE

To evaluate the algorithm performance of the numerical identification, an experimental test was built.

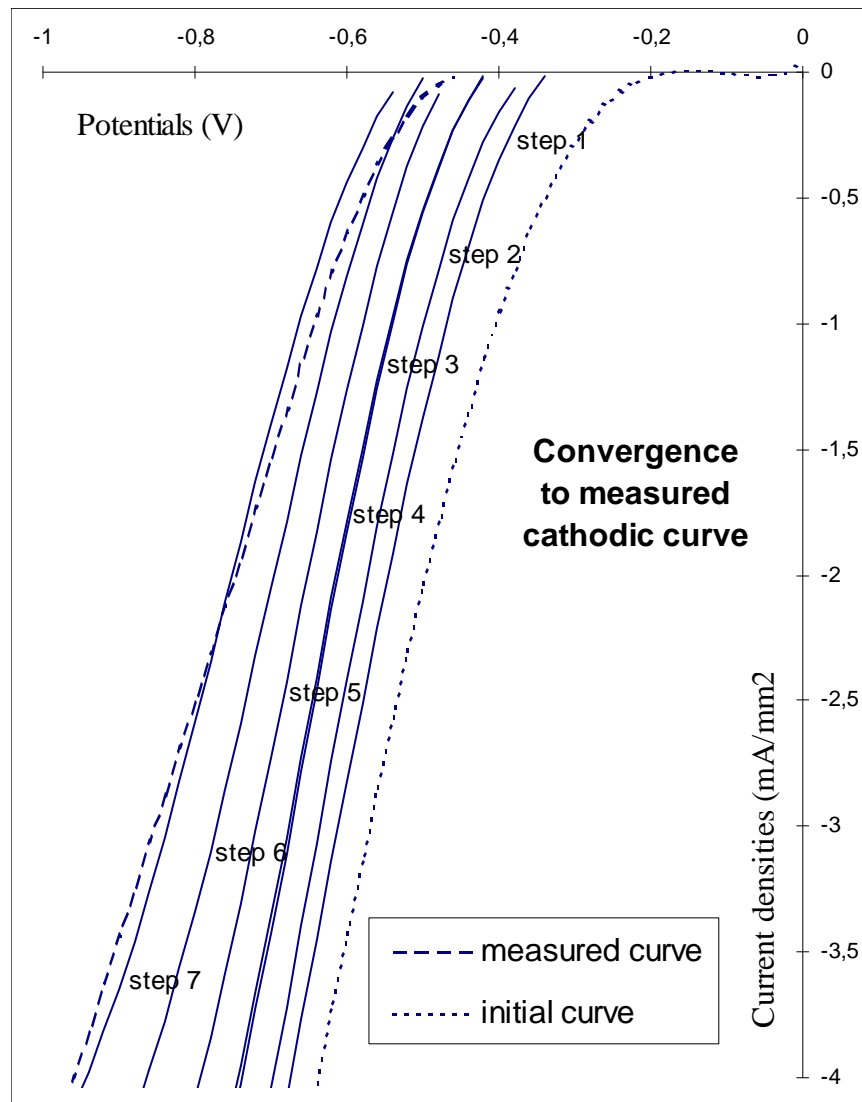


Figure 3 – Algorithm convergence

So  $Z_\eta$  are the measurements and we start the algorithm using an initial polarization curve. Figure 3 shows the convergence of the numerical polarization curve to the measurements. Another tests have been made and improve the performance of the method of adjoint state. When the measurements are reached, we can observe potentials and current densities on the electrode. These quantities constitute the real polarization curve because polarization law must be a boundary condition, and not an approximation such the measurement of a gap.

## CONCLUSIONS

The Boundary Element Method in combination with a Newton-Raphson iteration to determine current distribution is a predictive tool in applications of electrodeposition. The software used to simulate electroplating have already proved his performance, numerical results are in good agreement with experimental data.

This paper shows boundary condition on electrodes can be improved. Experimental measurements of polarization curve describe the gap between electrode and point of the measure. The method of adjoint state allows us to adjust the model to the measurements, and after convergence we access to the real polarization curve on electrode with the numerical tool.

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