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Computational modeling of the template-assisted deposition of nanowires

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Abstract

In the present paper we developed and simulated a two-dimensional model for the electrodeposition inside the porous anodic alumina template, which deals with one only potentiostatic pulse applied to one pore. The potential distribution within the oxide is described by Laplace equation and the diffusion equation takes into account the transport of the metal ions in the solution. These equations are coupled by time-dependent boundary conditions at the deposition interface. The charge transfer process is described by a Butler–Volmer relationship. Two limit situations corresponding, respectively, to a completely insulating template and to a metallic cavity are described by the model. The first case corresponds to the ideal condition for a truly one-dimensional deposition because there is no current on the pore wall. In the second limit situation, the reacting interface is treated as an equipotential and the deposition kinetic is limited by the charge transfer process. Furthermore, in this case one has a bi-dimensional electrodeposit growth. Between these limit situations, the charge transfer process and the voltage drop inside the oxide are equally significative. In this case, the model captures the dynamic interaction between the concentration gradients and the potential distribution inside the oxide which allows us to explain several experimental observations.

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1. Introduction

Since 1994, when Masuda et al. [1] reported the honeycomb alumina structure (also called porous alumina oxide-PAO), the anodically generated nanoporous alumina has been widely studied on bulk aluminum substrates and used as a host template for the deposition of a wide variety of materials [2,3]. The aluminum anodization in two steps, under specific conditions, leads to the formation of a PAO membrane highly ordered. The structure of anodic alumina is described as a closed-packed array of auto-ordered hexagonal cells containing a central pore whose diameter changes from 20 to 400 nm [4]. Furthermore, the geometric features of the PAO membranes depend on the electrolyte, bath temperature, applied voltage or current density [5].

A fundamental problem inherent in the anodization process has not been solved yet. Under the typical conditions of anodization, an electrically insulating alumina barrier layer exists at the alumina/substrate interface rendering difficulties to directly deposit materials into the pores by the dc electrodeposition methods. Since the thickness of the barrier oxide \( b \) is proportional to the applied potential during the aluminum anodization \( b \) is about 1.2 nm V\(^{-1}\) for the anodization in oxalic and phosphoric acids [6], the thick barrier layer formed at high voltages hinders a successful subsequent electrodeposition. One common approach used to overcome this electric feature is the use of a perforated membrane which is obtained growing the porous alumina layer several microns thick and then removing the remaining aluminum metal [7–10]. The barrier layer at the pore bottom can be completely removed by selective etching with dilute \( H_3PO_4 \). Thereafter, a metal of choice, which acts as cathode during the electrodeposition, is thermally evaporated onto the base of the alumina. However, this laborious and fragile bulk alumina removal technique is not an optimal solution for template-based synthesis and is more difficult to use for subsequent processing steps due to the lack of mechanical support provided by an underlying substrate.

An alternative procedure is to reduce the thickness of the barrier layer and, in this case, the electrodeposition is directly
carried out with the aluminum/alumina ensemble as cathode. The reduction of the barrier oxide can be done by two procedures, namely chemical dissolution [11,12] or reduction of the anodization potential at the end of anodization [13,14]. The isotropic characteristic of the chemical removal leads to pores widening. An abrupt reduction of the anodization potential will lead up to the non-uniformities in the barrier layer thickness of different pores while a slow reduction can cause ramification on the pore bottom. Choi et al. [3] reported a modified electrochemical thinning process which involves two electrolytes and a gradual reduction of the anodization potential: \( \text{H}_2\text{PO}_4 \) (from 195 V down to 80 V) and \( \text{C}_2\text{H}_2\text{O}_4 \) (from 80 V down to 1 V). Although, the dc methods are more commonly employed in perforated membranes, there are reports using the thinning approach for dc electrodeposition [3]. However, in this case, it is quite unstable and, in general, a uniform pore filling is not achieved.

On the other hand, the chemical and/or electrochemical thinning processes are quite suitable for ac or pulsed dc electrodeposition. The ac deposition methods are implemented for the nanoporous alumina system due to the rectifying nature of the oxide barrier layer which does not allow the reoxidation of the deposited metal during the anodic polarization [5,14,15], the barrier layer oxide blocks the direct current because of its high resistance, which is about \( 10^{10} \) to \( 10^{12} \) \( \Omega \) cm [16]. A high value of aspect ratio (\( \lambda \)), which is defined as the ratio between the pore height and the diameter, also impairs a full and uniform filling of the pores. Sun et al. [17] reported the fabrication of highly uniform metallic arrays with low aspect ratio (\( \lambda = 0.2–7 \)) in PAO membranes. Whereas Gerein and Haber [18] reported the Cu deposition in pores with height of 24 \( \mu \)m in which they obtained a nearly full filling on a depth of 15 \( \mu \)m from the pore bottom, but the full-filled pore fraction down to 50% on the surface. In addition, the presence of side reactions must be considered, that is hydrogen evolution (\( 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2 \)) and the aluminum oxide-hydroxide dissolution (\( \text{AlOOH} + \text{e}^- \rightarrow \text{AlO}_2^- + (1/2)\text{H}_2 \)). According to Sun et al. [17] this last side reaction is responsible for the template degradation during longer polarizations. The approach of using non-aqueous solutions to overcome these undesirable reactions was reported by Yin et al. [19]. Finding out the most suitable condition for the deposition based solely on an empirical approach is a formidable task owing to the several experimental sets which can be employed and the particularities of each system.

The drawbacks listed above are directly or indirectly related to the current distribution, which is intimately connected to mass transport inside the pores. These factors determine the extent and uniformity of the pore filling, that is, the height reached by the deposit in each pore and the fraction of pores which is completely filled. These aspects are related since a more filled pore becomes a less resistive pathway to the electric current inhibiting further deposition into other pores. The influence of the concentration gradients on the current distribution is largely recognized, which justifies the use of pulsed techniques to restore the ion concentration inside the pore during the open circuit time.

For a suitable description of the current distribution during the electrodeposition in porous alumina, one must consider the particularities of its electric behaviour. It is well established that the anodic aluminum oxide, owing to the rectifying property, conducts preferentially under cathodic polarization. The amorphous and hydrated alumina which compose the outer porous and barrier oxide is not a perfect insulator [20]. Furthermore, the porous oxide conductivity is six times bigger than barrier oxide [21]. Therefore, once the electrons flow by the barrier layer, according to the relative solution and oxide resistivities, the electric current can flow through the pore walls. The electronic transport through the pore walls has been disregarded in the literature and the experimental facts are being analyzed on the strength of diffusional gradients.

In the current paper, we propose a model which calculates the concentration distribution in the solution and the potential distribution inside the oxide. The full set of the model equations is outlined and discussed in the next section. In order to determine the characteristic behaviours, a wide range of physical chemistry and geometric parameters were explored. Representative simulations are presented in Section 3 to assess the consistency and applicability of the model.

2. The model

The computational modeling of the electrodeposition is quite complex due to two features. Firstly, we have two relevant processes: the mass and charge transport in the solution which can be treated by continuous equations and, the growth and nucleus coalescence which involves intrinsically a complex and discontinuous geometry. In addition, the deposit growth changes the system geometry, displacing the deposition surface. In the mathematical literature this is termed a moving boundary problem or Stefan problem. In this kind of problem the boundary of the domain is not known in advance and must be determined as a part of the solution [22]. An additional complication is the spatial domain considered, since the deposition occurs inside a pore not in a flat surface.

We set the time extent of the computational experiments in the time order of a single potentiostatic pulse applied to one pore in a pulsed deposition. Consequently, the volume of the deposited metal is negligible compared to the pore volume. Furthermore, if between each pulse there is an open circuit time long enough for restoring the concentration homogeneity, each one will start on the same initial and boundary conditions. Obviously, the only difference will be the displacement of the deposition surface due to the deposit formation in the previous pulse. Then, we can separate the moving boundary problem in two independent steps: (a) the concentration and potential distribution during a single pulse are calculated considering an unchanged geometry and (b) after a complete pulse and before start the new one, the position of the reacting interface is updated assuming a continuous model in which the interface displacement in each point is normal to the surface and proportional to the deposited charge in the earlier step:
\[ \delta_s = \frac{M_m}{d_m z F} \int i \, dt \quad (1) \]

where \( \delta_s \) stands for the deposition surface displacement, \( M_m \) the molar mass and \( d_m \) the density of deposited metal, \( i \) is the deposition current, \( z \) is the electroactive specie valence and \( F \) the Faraday constant. In the present paper we restrict ourselves to the analysis of the first step, presenting results for a single pulse applied to one single pore. Results for several pulses and several pores will be presented in a forthcoming paper.

Additional assumptions were made (i) double electric layer achieves a steady state fast compared to the polarization time of a pulse. This is because the interfacial capacitance is of the order of microfarads \( (0.39 \mu \text{F cm}^{-2} \text{[5]}) \) while solution resistance is of the order of ohms. Therefore, the characteristic time decay of capacitive current is of the order of \( 10^{-5} \) s, much lower than the pulse time \( (10^{-3} \) s); (ii) we are disregarding any side reactions, so only the deposition reaction is present; (iii) the solution and deposited metal resistances are negligible in relation to other resistances in the system; (iv) there is an excess of support electrolyte in the deposition bath, so that migration of the electroactive species in solution can be disregarded.

Fig. 1 schematically depicts the spatial domain of the problem in Cartesian coordinates discretized by a triangular finite element mesh. The domain, which is limited in a rectangular area of dimensions \( l_x \) and \( l_y \), is subdivided in two distinct regions: one composed by solution and another by template. We assumed a rectangular pore centered at the origin of the \( x \)-axis. The aluminum/oxide interface is on the rectangle base and the origin of the coordinates system is located at its middle point. The relevant geometrical quantities are defined as follows: \( b \) stands for the barrier layer thickness, \( 2r \) and \( h \) stand for the diameter and the height of the pore, respectively.

A non-dimensional model was written in terms of the non-dimensional variables and parameters defined in Table 1. In this table \( c \), \( i \) and \( \phi \) stand, respectively, for the electroactive specie concentration, deposition current density and electric potential, all of them depend on the position and time. A characteristic

<table>
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<tr>
<th>Table 1</th>
<th>Definitions of the independent and dependent variables and parameters</th>
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<td>Equations</td>
<td>Dimensional</td>
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<tr>
<td><strong>Independent variables</strong></td>
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<tr>
<td>( x )</td>
<td>( X = \frac{x}{h} )</td>
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<tr>
<td>( y )</td>
<td>( Y = \frac{y}{h} )</td>
</tr>
<tr>
<td>( t )</td>
<td>( T = \frac{t}{\tau} )</td>
</tr>
<tr>
<td><strong>Dependent variables</strong></td>
<td></td>
</tr>
<tr>
<td>( c )</td>
<td>( C = \frac{c}{c_\infty} )</td>
</tr>
<tr>
<td>( i )</td>
<td>( I = \frac{i}{i_0} )</td>
</tr>
<tr>
<td>( \phi )</td>
<td>( \phi = \alpha \phi )</td>
</tr>
<tr>
<td>( \eta_{\text{st}} )</td>
<td>( \Gamma_{\text{st}} = \alpha \eta_{\text{st}} )</td>
</tr>
<tr>
<td><strong>Parameters</strong></td>
<td>( D, \rho, \alpha, \eta, f, z, c_\infty, h, 2r, b )</td>
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Fig. 1. Spatial domain of the physical problem: (a) schematic and (b) discretized by a triangular finite element mesh.
time \( (\tau) \), defined in terms of the pore height \( (h) \) and electroactive specie diffusion coefficient \( (D) \) was used in the definition of the non-dimensional time \( (T) \). The non-dimensional spatial coordinates \( (X, Y) \) are relative to the pore height while the non-dimensional concentration \( (C) \) is relative to the bulk concentration of the electroactive specie \( (c_\infty) \), and non-dimensional current density \( (I) \) is relative to the exchange current density \( (i_0) \). The non-dimensional potential \( (\Phi) \) is defined in terms of the transfer coefficient \( (\alpha) \) and \( f = F/RT \), where \( F \) is the Faraday constant, \( R \) the universal gas constant and \( T \) the absolute temperature, assumed to be 298.15 K. The non-dimensional model contains five parameters: \( \chi, \psi_o, \Gamma, B \) and \( \lambda \) all of them were written in terms of the dimensional parameters, which were defined early, the applied overpotential \( (\eta) \) and the oxide electric resistivity \( (\rho_o) \).

The non-dimensional electric potential \( (\Phi) \) is calculated solving the following equation inside the template:

\[
\nabla \cdot \left( -\frac{\nabla \Phi}{\psi_o} \right) = 0
\]  

(2)

If several pulses are considered, we must take into account the formation of the conductive metallic phase, in contact with the oxide, which will change the whole potential distribution. This could be accounted for solving Eq. (2) simultaneously in the oxide and the metal phases which requires the definition of the oxide electric resistivity \( (\rho_o) \). The electric flux normal to the deposition surface is expressed as a function of the deposition current following Eq. (3):

\[
\tilde{n} \cdot \nabla \Phi = -\psi_o I \quad \text{on the reacting interface}
\]  

(3)

where \( \tilde{n} \) stands for a unitary vector normal to the considered surface. We must distinguish between an oxide/solution interface and a metal/solution interface, replacing \( \psi_o \) by \( \psi_m \) accordingly. In this paper we present results for the first pulse of the deposition, so that only the oxide/solution interface is present.

Choosing an appropriate reference potential, the electric potential of the oxide at the aluminum/oxide interface is

\[ \Phi = 0 \]  

(4)

at the aluminum/oxide interface

No flux conditions at the side boundaries, which correspond to the non-conductive non-hydrated oxide, complete the set of boundary conditions [20,21]:

\[ \tilde{n} \cdot \nabla \Phi = 0 \]  

(5)

on the insulating boundaries

Owing to Eq. (4), the drop voltage inside the template is numerically equal to the electric potential at the reacting interface. Writing the charge transfer overpotential \( (\Gamma_{ct}) \) as the difference between the applied overpotential and the ohmic voltage drop and inserting it into the Butler–Volmer equation, the deposition current density at the reacting interface can be expressed by

\[
I = -(\exp(\Gamma + \Phi) - C^* \exp(-\Gamma + \Phi))
\]  

(6)

where \( C^* \) stands for non-dimensional interfacial concentration of the electroactive specie. It is important to note that we solve the non-dimensional Laplace equation with the above time dependent boundary condition. Thus we implicitly assume that the electric potential adjust itself to any boundary condition with a characteristic time constant much lower than any other process in the system.

In order to access the interfacial concentration we must solve the diffusion equation:

\[
\frac{\partial C}{\partial T} = \nabla^2 C
\]  

(7)

Eq. (7) is solved under the following initial condition:

\[
C = 1 \quad \text{for} \quad T = 0
\]  

(8)

One boundary condition is obtained considering the charge transfer through the reacting interface:

\[
\tilde{n} \cdot \nabla c = -\chi I \quad \text{on the deposition surface}
\]  

(9)

The second boundary condition is provided by the semi-infinite diffusion condition:

\[
C = 1 \quad \text{for} \quad y \to \infty
\]  

(10)

In some simulations we assume a perfect stirred solution, replacing the semi-infinite diffusion by a constant concentration at the pore mouth:

\[
C = 1 \quad \text{at the pore mouth}
\]  

(11)

These equations are numerically and simultaneously solved by finite element method (FEM), although the finite element is extensively employed in engineering, it is not so a widespread tool for solving electrochemical problems. More details about the implementation of the FEM in electrochemical systems can be found in a paper presented by Nann and Heinze [23], where they show how to apply the FEM to mathematical equations and how to introduce the boundary conditions often used in electrochemistry. The equations, which make up the model presented in the current paper, were solved by FEM through a professional version of the commercial solver FlexPDE. It performs the calculation with an adaptive mesh and automatic time step refinement. The initial mesh is very dense inside and around the pore, as shown in Fig. 1b, due to the fast change in the potential and concentration immediately after the polarization.

3. Results and discussion

Before discussing the potential distribution inside the template, it is instructive to analyze two limit situations: (i) the membrane is perforated and template resistivity is assumed to be infinite, thereby deposition could occur only at the pore depth (ii) template resistivity is null and the pore wall forms an equipotential surface and consequently deposition could occur at the entire oxide/solution interface. For both situations the potential distribution is constant and the evolution of the system depends only on the concentration gradient.
3.1. Case 1: absence of current density on the pore wall

We are going to analyze the limit situation, where the $\psi$ is infinite, which holds the ideal condition for a truly one-dimensional deposition, that is, a perforated membrane ($B = 0$) and the absence of any current on the pore wall. Fig. 2a and b shows the contour plots of the concentration and some flux lines which come from outside the pore towards the pore inner, on the end of polarization ($T = 3$). We compared two pores with different aspect ratios keeping the other parameters unchanged.

In Fig. 2a, we are going to deal with a low value of aspect ratio ($\lambda = 5$). The contour plots inside the pore are equally spaced lines parallel to the pore bottom and emerge from pore mouth as semi-circles. The flux lines radially converge to the pore mouth, following perpendicularly to the pore bottom. In another extreme of the aspect ratio ($\lambda = 500$), Fig. 2b, we also observed the uniformity of contour plots inside the pore and the depletion layer is confined inside the pore keeping the concentration of the outer solution practically unchanged. In both cases, the diffusional process inside the pore is one-dimensional leading to a one-dimensional deposition. As we set up a boundary condition of semi-infinite diffusion, the system will reach a situation close to steady state in which $\partial^2 C / \partial Y^2 = 0$ and the current density decreases asymptotically, as the depletion layer goes along. When we are dealing with high aspect ratio (Fig. 2b), the depletion layer does not go along to the solution out of the pore, accomplishing a steady state in which we can define a limiting current. For a one-dimensional diffusional process, the limiting current can be defined as $i_l = zFDc_\infty/h$ and, from this definition, the parameter $\chi$ as $i_0/i_l$. This expression provides a physical meaning for the parameter $\chi$, which corresponds to the ratio between the interfacial process rate and the maximum rate possible for a given mass transfer condition. Although this interpretation is not strictly valid for a 2D case, it still provides a qualitative physical interpretation for the parameter.

3.2. Case 2: uniform current density distribution along the reacting interface

In the second limit condition, one has a metallic cavity, since the template resistivity is null, thereby the entire interface behaves as an equipotential surface.

Fig. 3 shows the temporal evolution of the contour plots and flux lines for one typical situation. It is clear that in these conditions we have a two-dimensional diffusional process and there is deposition along the pore wall. Then, the nearly steady state is expressed by $\varphi^2 C = 0$ which does not mean uniformity of the concentration gradients and, consequently, of the flux. In fact, it can be observed in Fig. 3 that the streamlines concentrate near the pore mouth leading to a non-uniform distribution of the current and deposition rate. The consequence of this non-uniformity of current is the reduction of the pore mouth’s width, which restricts increasingly the diffusion. The full pore filling is limited by this situation and not by the depletion of electroactive species inside the pore. In this case, differently from the earlier case (Fig. 2a and b), the aspect ratio has remarkable influence.
Fig. 3. Contour plots of the concentration (heavy lines) and flux lines inside the pores at different times: (a) \( T = 0.0045 \); (b) \( T = 0.029 \); (c) \( T = 0.212 \) and (d) \( T = 3 \). Non-dimensional concentration values are indicated by numbers over the contour lines. Simulation performed with the following parameters: \( B = 0 \); \( \chi = 1 \); \( \Gamma = -0.25 \) and \( \lambda = 2.5 \).

In Fig. 4, two simulations carried out with different aspect ratios and values to parameter \( \chi \) are presented. In this figure, the contour plots of the concentration inside the pore are shown, where the gray scale indicates the concentration value. When the aspect ratio is high enough (Fig. 4b), the depletion layer lies confined within the pore inner and a steady state is achieved. The concentration gradients evolve along the time in the same way presented in Fig. 3. Nevertheless, the depletion layers from the walls move quickly towards and overlapped each other, so that the concentration becomes constant in a given pore height. This uniformity of concentration parallel to the pore bottom was hypothetically assumed by West in his theoretical model [24]. Consistently with the theoretical prediction of the last author, our simulation show that, for high aspect ratios, the deposit growth will develop from the pore walls resulting in a narrower pore or eventually in the complete closure of the pore mouth with void
We studied the influence of the aspect ratio in the time evolution of the average current density ($I_{\text{avg}}$) inside the pore. $I_{\text{avg}}$ was calculated integrating the local current over the internal pore surface and dividing by the respective surface area:

$$I_{\text{avg}} = \frac{\int_\sigma I \, ds}{\int_\sigma ds}$$

where $\sigma$ denotes the entire deposition surface internal to the pore. We have noted that the variation of the average current density with time can be perfectly fitted by a second order exponential decay which is defined by

$$I = I_0 + I_1 \exp(-TT_1) + I_2 \exp(-TT_2),$$

where $I_0$, $I_1$, $I_2$, $T_1$ and $T_2$ are adjustable parameters. This fact indicates that the average current density decay is determined by two processes with different characteristic times. Interestingly, as the aspect ratio rises, the second order exponential decay collapses into a first order exponential decay, that is, when a second order exponential fitting is tried, what is actually obtained is $T_1 = T_2$. Furthermore, if the semi-infinite diffusion condition (Eq. (10)) is replaced by Eq. (11), a first order exponential decay with characteristic time decay equal to the $T_1$ in the previous case is obtained. These results are summarized in Table 2. The first characteristic time ($T_1$) can be associated to the transport internal of the pore and the second characteristic time ($T_2$) can be associated to the transport from the outer solution to the pore inner. For low values of the aspect ratio ($\lambda < 20$) the transport inside the pore overlaps with that one out of the pore and the second order exponential decay does not fit the average current density decay. For intermediate aspect ratio ($20 < \lambda < 1500$) the two phenomena are separated in the time domain and the second order exponential fit results in two distinct characteristic time constants. When the aspect ratio is high enough to maintain the concentration gradients inside the pore (see Fig. 4b), or when this condition is assumed by Eq. (11), the second characteristic time ($T_2$) disappears. The relevance of this insight resides in the fact that the analysis presented above can be used as a diagnostic criterion for determining if the diffusion is restricted to the pore inner.

The results presented in the last figures represent the simplest cases and delimit our physical problem, since a more interesting situation is between these cases. The first case, in which $\psi \rightarrow \infty$, corresponds to the ideal condition for a truly one-dimensional deposition. In the second limit situation, where $\psi \rightarrow 0$, the reacting interface is treated as an equipotential. Now we are going to analyze the potential distribution and, consequently, the current distribution inside the template for an intermediate situation.

![Fig. 4. Contour plots of the concentration for different aspect ratios: (a) $\lambda = 25$ and $\chi = 1$; (b) $\lambda = 300$ and $\chi = 0.005$, both at the end of the polarization ($T = 3$). Gray levels represent non-dimensional concentrations ranging from 0.36 to 1 on the left and from 0.48 to 1 on the right. Numbers over the contour lines indicate non-dimensional concentrations. For both cases $\Gamma = -0.5$ and $B = 0$.](image)

Table 2

<table>
<thead>
<tr>
<th>Characteristic times from exponential fitting of the current plots</th>
<th>Semi-infinite diffusion</th>
<th>Constant concentration at the pore mouth</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>$T_1$</td>
<td>$T_2$</td>
</tr>
<tr>
<td>25</td>
<td>0.01</td>
<td>0.45</td>
</tr>
<tr>
<td>250</td>
<td>0.0015</td>
<td>0.33</td>
</tr>
<tr>
<td>2500</td>
<td>0.00015</td>
<td>–</td>
</tr>
</tbody>
</table>
3.3. The potential distribution inside the template

In the beginning of the polarization, when there are no concentration gradients, the relationship between the voltage drop inside the template and the transfer charge overpotential, at each point of the interface, depends exclusively on the relationship between \( i_0 \) and \( \rho_o \), which is expressed in our model by parameter \( \psi \). The latter, defined as \( \alpha \rho_o h i_0 \), can be interpreted as the ratio between two resistances: (i) charge transfer resistance \( (1/\alpha h i_0 S) \) and (ii) template resistance \( (\rho_o h / S) \), where \( S \) is the area of the template/solution interface.

In order to investigate the influence of the parameter \( \psi \) on the relative magnitude of those overpotentials, we simulated the beginning of the process when there are not concentration gradients. Considering that the overpotential throughout the oxide is a spatially distribute variable which is numerically equal to the electric potential at the reacting interface, we took the potential values at a fixed position on the interface (far from the pore mouth). Owing to the discrete nature of the calculus, the initial overpotential distribution is obtained only after the first interaction time, that is, in \( T \sim 10^{-6} \) and not in \( T=0 \), which does not invalidate the arguments above. Fig. 5a shows the relative voltage drop inside the oxide, \( \Gamma / \Omega \), as a function of the parameter \( \psi \), keeping the other parameters unchanged. The curve in Fig. 5a could be divided in three regions (1–3), for which the corresponding current distributions are represented in Fig. 5b.

In this figure, the non-dimensional current density is plotted as a function of a generalized distance \( 2 \lambda X - Y \) when \( X < 0 \) and \( 2 \lambda X + Y \) when \( X > 0 \) which allows to represent the entire interface in one single axis. The intervals corresponding to the pore walls ([−2, −1] and [1, 2]) and the pore bottom ([−1, 1]) are indicated in the figure.

The results shown in Fig. 5a and b are summarized as follows. Once we assumed \( B = 0 \), the pore bottom is in direct contact with a metallic phase and consequently its potential and also the current density throughout it are uniform and independent of the \( \psi \). For high values of \( \psi \), the voltage drop inside the film approaches asymptotically to the applied overpotential indicating that the deposition kinetic is limited by the PAO resistivity (the limiting condition discussed in Section 3.1), thereby no current density flows through the pore walls.

For low values of \( \psi \), the voltage drop inside the film vanishes indicating that the deposition kinetic is controlled by charge transfer at the reacting interface (the limiting condition discussed in Section 3.2). In this case, the initial current density is uniform along the entire pore wall and does not differ from it at the pore bottom. Between these limiting conditions, \( 0.01 < \psi < 100 \), both the charge transfer kinetics and the voltage drop inside the PAO contribute significantly.

It is important to emphasize that the initial distribution of the current density and potential presented in Fig. 5a and b will be changed as concentration gradients appear and will be different in an unperforated membrane. Fig. 6a and b presents some electric field lines inside the oxide in the beginning and in the end of the simulations, respectively. The gray scale indicates the concentration of the electroactive species inside the pore.

When there are not concentration gradients, the field lines converge to the pore bottom (Fig. 6a), following the path of lower resistance. Obviously, this behaviour depends on \( \psi \) and the lower its value, the more uniform the electric field and current density distribution will be. The reduction of \( i_0 \) as well as \( \rho \) leads to the decrease of \( \psi \), allowing the bi-dimensional growth, as described early. Hence, there will be specific growth conditions to each system, since \( i_0 \) can range over many magnitude orders and that \( \rho \) depends on the preparation conditions of the template. For example, the reduction of \( i_0 \) by cation complexation [26] will cause also the reduction of \( \psi \), which can lead to appearing of current at the pore walls.

The current density distribution presented in Fig. 6a corresponds to the initial stages of the deposition when the concentration gradients are not very intense and consequently the mass transfer resistance is not so significative. However, as the pore solution becomes more depleted, that current density configuration will not maintain itself and the mass transfer resistance lead to a potential rearrangement over the template. Fig. 6b presents the field lines distribution in the end of the polarization.
Fig. 6. Contour plots of the cation concentration and some field lines at the (a) beginning and (b) end of the computational experiment. Gray scale represents non-dimensional concentrations gradients from 0 to 1. Simulations carried out with the following parameters: $\Gamma = -0.5$; $\chi = 1$; $\lambda = 500$; $\Psi = 200$ and $B = 0$.

showing the rearrangement induced by the concentration gradients. As the concentration gradients appear, the field lines drove towards the template surface. The most important consequence of this field lines configuration is the undesirable deposition on the pore surface before the full pore filing. This phenomenon is called by top deposition. The simulations capture the top deposition, showing that it results from the dynamic interaction between the electric field and the concentration gradients.

Furthermore, our computational results corroborate the catch up theory, firstly proposed by Sauer et al. [27] to explain the uniform pore filling obtained. The authors, based on fact that the electrochemical thinning always leads to changes in the barrier layer thickness, have proposed that, in pores with a thinner barrier layer, the metal ions will be depleted before than in pores with slightly thicker barrier layer. This behaviour would result in a slower reduction of the current flow in these pores, allowing them to catch up. When simulations with the same parameters, but different barrier layer thickness are compared, this behaviour is revealed.

Fig. 7 shows the current density at the pore bottom for three barrier layer thicknesses in two values of $\chi$ during the potentiostatic pulse. For low value of $\chi$, fastly the system achieves a constant current density according to the barrier layer thickness. On other hand, when the parameter $\chi$ is high, although the current densities are different at the beginning of the computational experiment, the three curves arrive at the same current density distribution in the end of the pulse. As the concentration gradients are formed, the higher mass transfer resistance compensates the lower ohmic voltage drop and the three simulations arrive at the same current density distribution in the time of a single pulse.

4. Conclusions

A simple mathematical model, which allows us to analyze separately each potentiostatic pulse applied to one pore, in a pulsed deposition was proposed. The potential and current density distributions throughout the template were calculated by the simultaneous solution of the Laplace and diffusion equations, which are coupled by a time-dependent boundary condition, defined by the kinetic of the charge transfer at the reacting interface. Two limit situations were explored: $\psi \to \infty$ and $\psi \to 0$. The first case corresponds to the ideal condition for a
one-dimensional growth. On the other hand, when $\psi \to 0$, a two-dimensional growth takes place and the complete pore filling is not possible since the deposition is faster at the pore mouth. The computational simulations capture the interaction between the concentration gradients and the electric field distribution inside the template. The electric field dynamically adjusts to new boundary conditions driven by the concentration gradients. This dynamic process explains the top deposition and is consistent with catch up theory. According to our numerical results, the diffusional gradients have two important and opposite roles. On one hand, they are important for a uniform pore filling during the electrodeposition in a membrane with pores which present differences in barrier layer thickness. In this case, the diffusional gradients equalize the pore filling throughout the membrane via the catch up effect. On the other hand, the diffusional gradients are responsible for the rearrangement of the potential distribution leading to the undesirable surface deposition. In spite of the relative simplicity of the proposed model, since we focused on a single potentiostatic pulse applied to one pore, it captures important events decisive for the electrodeposition growth which are defined in the beginning of the electrodeposition.

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**Appendix A. Nomenclature**

$b$ and $B$ dimensional and non-dimensional barrier layer thickness

c and $C$ dimensional and non-dimensional electroactive specie concentration

$c_\infty$ and $c^*$ bulk and interfacial electroactive specie concentration

$D$ electroactive specie diffusion coefficient

$F$ Faraday constant

$h$ and $2r$ pore height and diameter

$i$ and $I$ dimensional and non-dimensional current density

$\Gamma_{\infty}$ and $i_0$ exchange current density

$M_m$ and $d_m$ molar mass and density of the deposited metal

$R$ universal gas constant

$z$ electroactive specie valence

**Greek letters**

$\eta$ and $\Gamma$ dimensional and non-dimensional applied overpotential

$\eta_l$ and $\Gamma_l$ dimensional and non-dimensional overpotential at the reacting interface

$\eta_{\Omega\Omega}$ and $\Gamma_{\Omega\Omega}$ dimensional and non-dimensional ohmic drop voltage

$\lambda$ pore aspect ratio

$\rho_m$ and $\rho_0$ deposited metal and oxide resistivity

$\phi$ and $\Phi$ dimensional and non-dimensional electric potential

$\chi$ and $\psi$ non-dimensional model parameters

**References**


