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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 (bis about  $1.2 \text{ nm V}^{-1}$  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<sub>3</sub>PO<sub>4</sub>. 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

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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: H<sub>3</sub>PO<sub>4</sub> (from 195 V down to 80 V) and  $C_2H_2O_4$  (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 µm 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  $(2H_2O + 2e^- \rightarrow 2OH^- + H_2)$  and the aluminum oxidehydroxide dissolution (AlOOH +  $e^- \rightarrow AlO_2^- + (1/2)H_2$ ). 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 composes 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:

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