Cellular automata model of anodization

Łukasz Bartosik [a],[*], Janusz Stafiej [b], Dung Di Caprio [c]

[a] Institute of Physical Chemistry, Kasprzaka 44/52, Warsaw, Poland
[b] Cardinal Stefan Wyszynski University, Department of Mathematics and Natural Sciences, Wojcickiego 1/3, Warsaw, Poland
[c] PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France

ARTICLE INFO

ABSTRACT

We present a cellular automata model to simulate with a parallelized code nanostructured alumina formation during anodization. The model is based on the Field Assisted Dissolution approach for anodization. The parallel code for model simulation is run on Nvidia Tesla GPU cards. We verify that the parallel algorithm yields correct analytical results for the simple exclusion diffusion between emitting and absorbing walls in 3D. We identify the model parameters that have a strong impact on the nanostructures obtained in simulations and present the diagram of prevalence of these structures. We also simulate in our model the so called "two step anodization" and find an agreement with experimental findings.

1. Introduction

It is known for almost 100 years that several metals can be coated by the passive layer of oxides formed in an electrochemical process called anodization. It has been used extensively to increase corrosion resistance and aesthetical outlook of the surface. Anodization is a rather simple procedure that can be applied to a variety of metal surfaces, e.g., titanium [1], aluminum [2] and hafnium [3]. In the process the surface between the metal and a proper electrolyte solution is polarized by an external voltage producing metal anodic oxidation and related phenomena. The peculiarity of structures that evolve on anodized aluminum surface was first noticed in 1953. Keller et al. [4] showed with transition electron microscopy that the alumina layer displayed hexagonally ordered pores. For a considerable period of time this phenomenon attracted little attention. A renewed interest comes from its potential nanotechnological applications as scaffolds for other nanostructure synthesis [5]. Masuda and Fukuda [6] determined the experimental procedures for the preparation of regular nanoporous anodic aluminum oxide layers. Then other advancements in the problem started appearing one after another as evidenced by the works of Li et al. [7], Jessensky et al. [8] and Masuda et al. [9]. A major obstacle to obtain nicely organized pore structures is the initial state of the layer. It is fairly disorganized due to defects and initial surface roughness. It needs a thorough pre-treatment of the surface by polishing, chemical and

electrochemical etching etc. In this way the so called two step anodization is recommended by Masuda and Satoh [10]. It consists of two steps. The first step reduces the number of defects and prepares the first network of pores. The layer is then washed out but it leaves an imprint of the pore organization on the metal surface. Then the second anodization produces a better quality organized pore network grown on top of the imprints of the previous one.

The theoretical work on the phenomenon is clearly delayed and unable to describe all the aspects of the process. There are two most considered approaches to base a theoretical description on: Field Assisted Dissolution (FAD) [11] and Field Assisted Flow (FAF) [12]. Sheintuch and Smagina [13] consider the problem of stability for the Field Assisted Flow model by Singh et al. [14] and arrive at the Damped Kuramoto Sivashinsky (DKS) type equation. The model does predict a hexagonally ordered porous layer. But there are two weak points in the approach. The first point is that their analysis applies to the initial stage of the pore growth and cannot guarantee their sustained growth. The second point is that their two dimensional model can be inapplicable in three dimensions. Indeed, Gomez and Paris [15] explore the regimes of the Damped Kuramoto Sivashinsky equation and conclude that despite stable regimes of the DKS equation in a 2D space they find only chaotic regimes in three dimensions. Stable regimes for the 3D version of the equation need not exist and more research is needed to clarify this issue. In view of the above doubts on viability of 3D FAF model in this work we focus on a 3D Field Assisted Dissolution model.

In this work we design a parallel cellular automata model to simulate the 3D Field Assisted Dissolution model. We explain the rules and states of the model as well as explain our parallelization

* Corresponding author. Tel.: +48 223433268.

strategy in Section 2. We test the strategy on a simple problem of diffusion between emitting and absorbing wall. With the positive test results we pass to simulations of anodization using the verified strategies. We compare our results to theoretical predictions of the Field Assisted Dissolution model.

2. Methods

2.1. Cellular automata model

Our model is based on a probabilistic, three dimensional, asynchronous cellular automaton. We consider periodic boundary conditions along the two axes parallel to the initial surface while fixed boundary conditions are applied along the third axis. We use the 3D cubic lattice with the Moore neighborhood for a given cell. In our update scheme each lattice site is given the same chance for an update in one step of system evolution. Then one neighbor is selected from the 3D Moore neighborhood of the updated site. Each neighbor has a uniform probability of 1/26 to be selected as 26 is the coordination number for the Moore neighborhood in 3D. Let us note that the pair of sites thus selected has a double chance for selection since the neighbor and the site in another instance may change the roles. The pair thus selected is subject to an update and the rules of updates are symmetrical in that they ignore the distinction between the site and the neighbor. The pair as a whole is updated according to the formal two body reaction scheme depending on the states of the two sites.

We assume that 5 cell states describe adequately the physicochemical content of our model. These are: M – the state corresponding to the metal, OX – to the oxide, EF – the walker representation for electric field in the oxide that will be detailed further, A – to anion rich sites in the oxide S – to solvent. Let us note that the modeled oxide layer is represented by cells in one of the three states: OX, EF and A. We call them *oxide-like* states. All of these cells are considered to be filled with oxide and two of them EF and A have an additional function. States EF should be interpreted as OX electrostatic field carriers such that the average flux of these particles in a stationary state yields the magnitude of electric field. States A are considered as anion (typically superoxide O^{2-} or hydroxide OH^- ions) rich OX oxide and the anions are dragged by the electric field towards the metal anode. It is convenient often to think of states as of particles. Our update rules apply to two particles at two neighboring sites A and B where at update they can undergo a binary reaction:

$$Particle1(position\ \ A) + Particle2(position\ \ B)$$
$$= Particle3(position\ \ A) + Particle4(position\ \ B)$$

which can be selected with a given probability relative to the obvious alternative reaction channel, in which nothing is changed and leaving the selected pair of sites in their actual state:

$$Particle1(position\ \ A) + Particle2(position\ \ B)$$
$$= Particle1(position\ \ A) + Particle2(position\ \ B)$$

For example the following reaction

$$M + OX = M + EF \tag{1}$$

should be therefore read as: an M particle in site A reacts with an OX particle in site B yielding an M particle in site A and an EF particle in site B. In the above reaction, we omit an explicit notation for the sites A and B, as in the course of the simulation they correspond to a random pair of neighboring sites chosen with the algorithm detailed thereafter.

Let us note that the order in the equation is relevant and in our convention the particle at A comes before that at B:

$$M + OX = M + EF \tag{2}$$

has a different final effect than the reaction:

$$M + OX = EF + M \tag{3}$$

The difference comes from the fact that in reaction (2) the M particle stays at the site A while in reaction (3) it moves from site A to site B. As mentioned above neighboring sites A,B are equivalent to B,A. Thus reaction

$$OX + M = EF + M \tag{4}$$

is equivalent to reaction (2) and need not be duplicated.

The rules we postulate are as follows:

$$M + S = OX + OX \tag{5}$$

$$EF + S = S + S \tag{6}$$

$$EF + S = A + S \tag{7}$$

$$M + A = OX + OX \tag{8}$$

$$M + OX = M + EF \tag{9}$$

$$EF + OX = OX + EF \tag{10}$$

$$EF + A = A + EF \tag{11}$$

$$S + OX = OX + S \tag{12}$$

$$S + A = A + S \tag{13}$$

These 9 rules can be divided into three groups: reaction-like rules ((5)–(9)), diffusion-like rules ((10) and (11)) and surface reorganization ((12) and (13)). Let us emphasize that states OX, EF and A are all *oxide-like* states, containing a portion of oxide. In the following paragraphs we explain how we apply the rules in actual coding. Four of the five reaction-like rules can be viewed as descriptions of the well known electrochemical processes taking place during anodization. These are:

1. Passivation of the active metal (rule (5)).
2. Dissolution of the oxide in high electric field (rule (6)).
3. Dissociation of the solvent and anion incorporation into the oxide layer in high electric field (rule (7)).
4. Oxidation of the active metal by the incorporated anions (rule (8)).

The final reaction-like rule creates electric field walkers that we use to model the presence of electric field in the oxide layer. A detailed explanation of how we account for the electric field presence is given in the next subsection. All of the reaction-like rules have a fixed probability during simulations. Additionally the probabilities of rules (6) and (7) sum to 1.

The diffusion-like rules govern the Random Walk of electric field walkers and the movement of anions inside the oxide layer. The Random Walk is modeled by two appropriate sites swapping their positions. These rules differ from reaction-like rules in the sense that they conserve the species involved leading to their spatial redistribution. For the most part we set their probability to 1 if the correct particles encounter one another. However in all other aspects they are identical to reaction-like rules and are parallelized in the same way. In our model we assume that anion movement is mostly caused by the strong electric field present in the oxide layer. During anodization the electric field arises from the onset of the voltage between the metal and the solution. The electric field is strongest at the thinnest metal-solution separation by the oxide layer and becomes weaker as the oxide layers gets thicker. Rule (11)