Modelling of ion convection during electrochemical oxidation of aluminium

Pavel Zun¹, Andrey Svitenkov
University ITMO, Saint-Petersburg

Abstract. Mesoscopic electrically induced ionic convection in the electrolyte surrounding the anode is modelled. Dissipative particle dynamics approach is used for the modelling. Simulation shows that the relation between forming voltage and convection cell size is likely nonlinear. Interactions between this nonlinearity and modes in the oxide layer can be the cause of irregularities in the resulting structures.

1. Introduction
Anodizing of aluminium is a process that's been used in the industry for at least the last 50 years. More recently, nano-porous anodic aluminium oxide membranes have been widely used as templates in the synthesis of one-dimensional nanomaterials and quantum dot arrays [1], but some microscopic characteristics of it are not yet fully understood.

For example, there are different theories explaining the ordering of pores in the oxide layer [2, 3]. Empirically a linear dependence has been found between the inter-pore distance and the voltage applied [4]. The most common explanation involves the stress in the oxide layer [2] as the reason for pore ordering and diameter. This explanation results in a close to linear dependence for most common voltages, but it does not completely explain why the quality of structures varies dramatically for different regimes.

However, convective flow inside the electrolyte is another factor that influences pore structure. Interactions between it and the processes in the oxide layer can explain irregularities in the resulting structures. There have been few attempts to model the convective flow for this process. The only known to us attempt is [3], and it has serious drawbacks, which are discussed in more detail in the next section. The aim of this work is to clarify the influence of convective flows on inter-pore distance.

In this work the initial phase of anodic oxidation is modelled. For modelling the flows in the electrolyte a mesoscopic dissipative particle dynamics approach [5] is used.

2. Theory and related work
The process of anodizing consists of submerging an aluminium component (anode) and a cathode in water-acid solution (oxalic, sulphuric and phosphoric acids are commonly used) and applying voltage to them. This leads to electrochemical oxidation of the aluminium.

Negatively charged anions, i.e. hydroxide, acid residual and maybe oxide ions move to the anode. The electrical charge in the circuit causes positively charged aluminium ions (Al³⁺) to be generated in

¹ E-mail: pavel.zun@gmail.com
the anode and move toward the cathode. At the anode surface they react with the oxide/hydroxide ions to form aluminium oxide (in the case of the hydroxide ion, hydrogen ions are released into the solution). The following reactions are believed to occur on the anode:

\[
\begin{align*}
\text{Al} & \rightarrow \text{Al}^{3+} + 3e^- \\
2\text{Al}^{3+} & + 3\text{O}^{2-} \rightarrow \text{Al}_2\text{O}_3 \\
2\text{Al}^{2+} & + 3\text{OH}^- \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}^+
\end{align*}
\]

For which the overall equation is

\[
2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6e^-
\]

The rate of the oxidation depends on the concentration of negatively charged ions, which are brought to the surface by the electrolyte flow. Since the characteristic inter-pore distances are on the order of 100 nm, the distribution of these ions is affected by both hydrodynamic and molecular kinetic laws. Because of that, it is reasonable to use a mesoscale approach, which accounts for both of these factors. Dissipative particle dynamics (DPD) is used for the simulation.

The main driving force of the convection is the external electric field. The field and the flow is also significantly affected by the uneven distribution of positive and negative charges in the electrolyte, for example, by the anodic shielding.

There have been attempts [3] to model this process before, but the method used in [3] has severe shortcomings.

Firstly, a continual model was used, which did not account for the kinetic processes governing the charge distribution. For example, equilibrium solution of their system of equations does not lead to anodic shielding. Using their model, charge concentration drops linearly instead of exponentially.

Secondly, the convective cells took up all of the simulation area, and because of that the result was dependent upon the distance from the anode to the arbitrarily chosen upper bound of the simulation box. This upper bound does not correspond to any physical length. The model from [3] results in a linear relation between voltage and convection cell size, which is in accordance with the experiments.

Our hypothesis is that the ionic convection near the anode is an important factor for the formation of irregularities in the oxide layer. Nonlinear dependence of inter-pore distance on the applied voltage would be an indirect proof of this hypothesis, since the superposition of the effects of convection and stress in the oxide can cause the pores to distort.

3. Model, implementation and results

We implemented the model in the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) package [6]. The area directly neighbouring the anode is modelled, with periodic boundary conditions on x and y axes. In the uppermost part of the simulation box electroneutrality is enforced in the electrolyte. For short-range interactions the Coulomb forces are calculated directly and for long-range interactions a k-space PPPM solver is utilized. Long-range interactions ensure that the model is self-consistent.

For the modelling, the following parameters were used: simulation area 360×360×2 nm, temperature equal to 40° C, density of 1 g/cm³, dynamic viscosity of 0,7 mPa · s (viscosity of water at that temperature). The system was calibrated so that for the forming voltage 48 V (voltage for one of the stable modes) the cell size is equal to half experimental inter-pore distance.
Figure 1 shows a steady-state solution of the model. Red points indicate negatively charged particles, and blue points indicate positively charged ones. The anode is situated directly below the simulated area, and Debye shielding can be observed in the lower part of the area.

For our simulation we use a constantly-sized square box. Only the lower part of the electrolyte is involved in the convective flow, which guarantees independence of our results from the geometry of the simulation area. For higher voltages the whole mass of the liquid gets involved in the convection. This marks the limits of applicability of our model.

Our main point of interest is to determine whether the dependence of inter-pore distance on the applied voltage is linear or not. The distance between the opposite charged electrolyte streams is equal to half inter-pore distance. The convective cells are shown in Figure 2, where color indicates electrolyte charge density. The crosses mark the centers of two conjugate streams.

The plot of the cell size against the voltage is given in Figure 3. Lowest, highest and average cell sizes are marked. Note that the cell size (distance between two conjugate streams) is equal to half inter-pore distance.

The black line shows wavelength of the most rapidly growing mode in oxide layer as a function of the applied voltage [2].
4. Conclusions
In this work electrically induced mesoscale convection was modelled. The steady-state solution of the model shows Debye shielding. In the dynamic solution convective cells can be observed.

The dependence between the applied voltage and the cell size is likely non-linear (see Fig. 3). This is more noticeable for higher voltages, where the cell size growth rate in relation to voltage is faster than linear. This, combined with the slower than linear rate for fastest-growing mode in oxide, derived in [2], (shown in Figure 3 with the black line), can lead to instabilities and irregularities in cell structure. In the regimes where cell size and the mode wavelength match, good quality structures can be produced, and in the other regimes pores can be distorted because of interference.

Hence, this supports our hypothesis about the possibility of the interactions between ionic convection and elastic stress in the oxide layer playing a key role in the formation of irregularities in the resulting structures.

5. References
[1] Shingubara S 2003 J. Nanopart. Res. 5 17
[2] Singh G K, Golovin A A and Aranson I S 2000 Phys. Rev. B 73 205422
[3] Lu S, Su Z, Sha J and Zhou W 2009 Chem. Commun. 5639–5641
[4] Zhang F, Liu X, Pan C and Zhu J 2007 Nanotechnology 18 345302
[5] Español P and Warren P B 1995 Europhysics Letters 30(4) 191–196
[6] Plimpton S 1995 J Comp Phys 117 1-19