Nanopore formation and growth in phosphoric acid Al anodization

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This work describes the pore formation mechanism for anodizations of aluminum foils in phosphoric acid (pore diameters \(\sim 100 \text{ nm}\)). A detailed study of the four major anodization regimes in phosphoric acid is presented comparing scanning electron microscopy (SEM) cross-sectional views with the respective current density transients. The comparison of the anodization process in phosphoric acid with that using sulfuric and oxalic acid electrolytes is accurately performed through the normalization of the current transients to the characteristic times and current densities of the process.

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1. Introduction

Nanoporous alumina membranes have gained much importance in the last years due to their potential industrial and technological applications for nanometric device fabrication. Current nanolithographic techniques (e-beam, X-ray, focused ion beam) are expensive and have a low throughput, thus new assembling methods are required for large scale inexpensive production of nanodevices. Anodic nanoporous alumina templates, which can be readily obtained by common electrochemical processes, may be one such method for achieving the required nanodimensions.

The self-organized growth of these templates using a two step anodization process\textsuperscript{[1]} allows us to easily obtain well ordered hexagonal arrays of nanopores ranging in diameter from 2 to 900 nm (with pore widening) and interpore distances from 35 to 980 nm\textsuperscript{[2]}. Due to the ordered hexagonal arrays of nanopores and their easy method of fabrication, these templates are also extremely valuable for well ordered growth of nanowires, nanotubes, nanorods and nanodots\textsuperscript{[3,4]}, providing a whole new range of applications in areas such as medicine\textsuperscript{[5]} (biosensors, photocatalysts), electronics (ultrahigh-density magnetic memories, optoelectronic devices), energy storage (solar cells).

The pore formation during the anodization process varies with the electrolyte type, concentration, temperature and applied anodizing potential. Depending on the combination of these parameters, different pore sizes and interpore distances can be achieved. However, to obtain long-range ordered nanopores, specific conditions are required such as sulfuric acid at 25 V, oxalic acid at 40 V and phosphoric acid at 195 V\textsuperscript{[6,7]}, giving 65, 100 and 500 nm interpore distances, respectively. Studies carried out with other acids showed that the interpore distance is linearly proportional to the anodizing potential, irrespective of the electrolyte type. This distribution indicates that each acid allows the formation of a certain range of self-organized structures. Interpore distances between 300 and 500 nm can only be obtained using phosphoric acid. Since high anodizing potentials (160–195 V) and consequently high current densities are required for this type of acid, a pre-anodization process has to be made to avoid the aluminum rupture\textsuperscript{[8]}. This work shows that the pre-anodization does not affect the pore formation mechanism in the subsequent anodization in phosphoric acid. It presents a comparison of the phosphoric current density transient with the ones obtained in sulfuric and oxalic acids and a detailed study of the pore formation in phosphoric acid using scanning electron microscopy (SEM).

2. Experimental procedure

Nanoporous alumina films were obtained by electrochemical anodization of high-purity (99.997\%) aluminum foils, 0.25 mm thick, with a home-made anodization cell. The anodization area was a circle of diameter around 0.6 mm. Before anodizing, aluminum foils were degreased with acetone and ethanol, followed by soft chemical polishing in aqueous sodium hydroxide solution (1 M). The last treatment removes the native oxide layer and
performs a smooth chemical etching of the surface, which was then rinsed with deionized water [9].

The anodization processes were performed at constant temperature (6 ± 1 °C), in a vigorously stirred bath solution using three different electrolytes: sulfuric acid (0.3 M), oxalic acid (0.3 M) and phosphoric acid (0.1 M) at 25, 40 and 195 V, respectively. To suppress breakdown effects and to enable uniform oxide film growth at high voltage (195 V in phosphoric acid) a pre-anodization in 0.3 M oxalic acid at 40 V was performed for 8 min [8].

The current density transients \( j(t) \) were monitored during the anodization process using a Keithley 2400 Sourcemeter. Morphology characterization of the nanoporous alumina was done using FEI Quanta 400 FEG SEM.

### 3. Results and discussion

According to Parkhutik et al. [10] the equations governing pore formation are invariant under the \( V = CV \) and \( t = Ct \) transformations. Having this in mind, we normalized the obtained current density transients using \( t' = t/t_{\text{max}} \) and \( j' = j/j_{\text{max}} \), where \( t_{\text{max}} \) and \( j_{\text{max}} \) are the time and current density maximum values, respectively, in each electrolyte and \( t' \) and \( j' \) the adimensional parameters associated with each variable. When anodizing in sulfuric acid, the current density reaches its maximum value of about 1.1 mA/cm² after approximately 4.9 min. In oxalic acid, it takes around 2.2 min to reach \( j_{\text{max}} \approx 3.2 \text{ mA/cm}^2 \). However, anodizations in phosphoric acid are much longer taking about 80.2 min to reach \( j_{\text{max}} \approx 2.5 \text{ mA/cm}^2 \). Since larger pore structures are formed (diameters of 100 nm, compared with 15 and 30 nm obtained in sulfuric and oxalic acids, respectively, and interpore distances of 500 nm, compared with 65 and 100 nm in sulfuric and oxalic acids, respectively) longer times are required for the self-organization process to be completed. Fig. 1 shows the normalized current density transients obtained for anodizations using the three different electrolytes [sulfuric (square), oxalic (triangle) and phosphoric (star)], revealing a good correspondence between the curves, as predicted by the Parkhutik et al. model [10]. The slight differences detected can be assigned to the approximation used which does not consider important physical-chemical effects (such as space charge accumulation or double layer formation at the interfaces). In Fig. 1 we identify the following differences:

(i) The minimum \( j' \) value in phosphoric acid is lower than that of the other acids, possibly due to the oxide layer present at the beginning of the anodization process (performed after a pre-anodization step). This leads to a decrease in the current density needed to initiate pore formation.

(ii) The anodization in oxalic acid is a faster process, meaning that pores start to nucleate sooner than in the other acids. Being oxalic an organic acid, its negative ions are barely incorporated into the alumina. The low concentration of these ions in the alumina makes the electric field higher than in the other cases allowing the pores to nucleate earlier.

When anodizing in phosphoric acid at high applied potentials (195 V) we use a pre-anodization process in oxalic acid [8]. This forms a protective nanoporous alumina layer (~550 nm thick) with pore diameters around 30 nm (Fig. 2(a)), avoiding the burnt of the sample when subsequently applying the desired high potential (195 V).

The current density transient observed for the pre-anodization in oxalic acid (Fig. 1) allowed us to verify the four major regimes, typical of the pore formation in a first anodization (see below) [10]. We found that, even after a pre-anodization process, the current density transient observed for the subsequent anodization in phosphoric acid also exhibits four major regimes (Fig. 1). The main difference is that instead of anodization times of around 5 min, we need about 2 h to observe all four regimes. Since the alumina barrier formed at the bottom of the pores is thicker for anodizations in phosphoric acid (~200 nm thick instead of 30 or 50 nm in sulfuric

![Fig. 1. Normalized current density transients for anodization processes in sulfuric (25 V), oxalic (40 V) and phosphoric acids (195 V after pre-anodization process). Both axis were normalized using \( t' = t/t_{\text{max}} \) and \( j' = j/j_{\text{max}} \), where \( t_{\text{max}} \) and \( j_{\text{max}} \) are the time (min) and current density (mA/cm²) maximum values, respectively. For each electrolyte we have different \( t_{\text{max}}; j_{\text{max}} \) values: (1.1; 4.9) in sulfuric, (2.2; 3.2) in oxalic and (80.2; 2.5) in phosphoric acid. The inset shows the curve in phosphoric acid without normalization.](image)

![Fig. 2. SEM cross-sectional views of the pore formation mechanism. A pre-anodization process in 0.3 M oxalic acid (40 V) was performed for 8 min (a), followed by the anodization process in 0.1 M phosphoric acid (195 V) for 50 min (b), 80 min (c) and 4 h (d).](image)
or oxalic acids, respectively), longer times are needed to form the complete barrier. Moreover, the pore structures grown in phosphoric acid are larger than in sulfuric and oxalic acids. Therefore, the nucleation and self-organization of pores is a much slower process.

SEM cross-sectional images of each regime were taken and analyzed in detail allowing a better understanding of the pore formation mechanism. Fig. 2(a) shows the nanoporous alumina membrane formed during the pre-anodization process. The image emphasizes the existence of a protective (non-conductive) layer (~550 nm thick) just before the application of high anodizing potentials in phosphoric acid. After the application of 195 V, in phosphoric acid, the four major regimes (see inset Fig. 1) could be distinguished:

(i) Regime 1 corresponds to the quick initial drop of the current density, taking usually 6–20 s (in phosphoric acid) to reach its minimum value. In this case the minimum value (~0.5 mA/cm²) was reached at about 15 s, corresponding to the formation of an oxide barrier (non-conductive) film.

(ii) Then the current density remains approximately constant for about 50 min (regime 2). During this period the oxide barrier is formed and partially solubilized at the same time resulting in a continuous barrier-type alumina film (Fig. 2(b)) [10]. The thickness obtained for this barrier (~200 nm) is the one expected if a pre-anodization process had not been done.

(iii) At this phase, the increase of the electric field at convex fluctuations of the surface promotes field-enhanced oxide dissolution and, consequently, pores begin to grow (Fig. 2(c)), leading to a rapid increase (lasting about 30 min) of the current density to around 2.5 mA/cm² (regime 3).

(iv) At the end of regime 3, some pores merge, leading to an improved organization and inducing a slight decrease of the current density, reaching approximately 2.3 mA/cm². Finally, the repulsive forces between the pores make them grow downwards at a constant rate leading to organized structures at the bottom (Fig. 2(d)). This corresponds to regime 4, where the current density maintains a constant value due to the equilibrium reached between the oxide dissolution (at the oxide/electrolyte interface) and its formation (at the metal/oxide interface).

4. Conclusions

The normalization of the current density transients obtained during the anodization processes in sulfuric, oxalic and phosphoric acids emphasized a good correspondence between them and allowed us to compare more accurately the pore formation mechanism in different electrolytes. The four regimes of the pore growth, expected by direct observation of these curves, were also confirmed by analysis of the SEM cross-sectional views. During the first and second regimes only an alumina barrier is formed. In the third regime, pores begin to nucleate. The fourth regime simply corresponds to the continuous growth of the pores. The protective layer formed during the pre-anodization in oxalic acid prevented the aluminum rupture without affecting the pore formation in the subsequent anodization step in phosphoric acid.

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