# Effect of Two-Step Oxidation Conditions on Pores in Anodic Aluminum Oxide (Postprint)

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## Abstract

Porous anodic aluminum oxide (AAO) was prepared in oxalic acid solution via a two-step anodization method, and the influences of voltage, anodization time, and oxalic acid concentration on the pore characteristics of AAO were systematically investigated. The results demonstrate that during the first anodization step, the interpore distance increases with increasing anodization voltage, whereas the anodization time and oxalic acid concentration exert negligible effects; during the second anodization step, time, voltage, and oxalic acid concentration essentially have no influence on the interpore distance, yet the pore diameter of AAO increases markedly with increasing anodization voltage, with pores arranged in a hexagonal array. Moreover, as the second anodization voltage increases, the pore morphology transitions from circular to elongated and subsequently to hexagonal; when the oxalic acid concentration in the second anodization is increased to 0.4 mol/L, adjacent pores in the fabricated AAO exhibit penetration along specific orientations, and even dissolution, while the overall ordering of the pore distribution remains largely unaffected.

## Full Text

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## Effects of Dual Oxidation Conditions on the Pores of Anodic Aluminum Oxide

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**Abstract**

Aluminum foil was anodized via a two-step process in oxalic acid solutions. The influence of processing parameters—including voltage, time, and solution concentration—on the pore characteristics of anodic aluminum oxide (AAO) films was investigated for both the first and second anodization steps. Results show that during the first anodization, pore spacing increases with rising voltage, while anodization time and oxalic acid concentration have minimal influence. During the second anodization, pore spacing remains essentially unchanged when varying voltage, time, or solution concentration. However, pore diameter increases significantly with rising voltage, and the pores exhibit a well-ordered hexagonal array arrangement. Furthermore, as the second-step oxidation voltage increases, pore shape evolves from circular to elongated, and then to hexagonal. When the oxalic acid concentration for the second oxidation increases to 0.4 mol/L, adjacent pores in the resulting AAO exhibit oriented piercing along specific directions, and even dissolution occurs, while the overall pore distribution orderliness remains largely unaffected.

**Keywords:** inorganic non-metallic materials, porous anodic aluminum oxide, two-step anodization, oxalic acid solution, pore characteristics

## Introduction

In the 1950s, Keller et al. [1] discovered that aluminum oxide coatings prepared by anodization in sulfuric acid, phosphoric acid, and oxalic acid exhibited distinct microporous structures with vertical channels and uniform, ordered array distributions. In recent years, porous anodic aluminum oxide (AAO) has been widely used for fabricating nanomaterials such as nanorods [2] and nanotubes [3], with applications in biosensors [4], protein separation [5], magnetic material preparation [6], and other fields. The ordered arrangement and pore size of AAO significantly influence its performance and have remained a key research focus. The primary processing parameters affecting AAO properties include oxidation temperature and time [7, 8], oxidation voltage, and electrolyte type and concentration [9]. While increasing the number of anodization cycles [10, 11] can improve pore ordering, this approach is complex and time-consuming. Consequently, the most widely used AAO preparation method remains the two-step anodization process proposed by Masuda et al. in 1995 [12].

Gösele et al. [13] investigated the influence of electrolyte type on AAO pore size, while Meng et al. [14] used a voltage reduction method to control the step amplitude of oxidation voltage, producing AAO membranes with controllable branch numbers and studying the effects of different oxidation voltages on pore morphology. AAO prepared in oxalic acid exhibits uniform pore size and ordered arrangement. Therefore, this study employs the two-step anodization method in oxalic acid solution to systematically investigate the effects of both first-step and second-step oxidation parameters on AAO pore characteristics.

## 1. Experimental Methods

AAO was prepared using a two-step anodization process. To study the influence of first-step oxidation parameters, these were varied while keeping second-step parameters constant. Prior to oxidation, high-purity aluminum foil (99.999% purity, 0.5 mm thickness) was annealed in a muffle furnace at 500°C for 1 hour to eliminate structural defects and residual stress. The annealed foil was then ultrasonically cleaned in acetone and anhydrous ethanol. Electrochemical polishing was performed using the foil as the anode and a platinum mesh as the cathode (6 cm separation) in a mixed solution of perchloric acid and ethanol (volume ratio 1:4) at 18 V for 2 minutes, producing a bright, smooth surface. After ultrasonic cleaning in deionized water for 10 minutes, the polished foil was anodized for the first time in oxalic acid solution at 15°C using platinum mesh as the cathode (11 cm separation). The first-step oxidation parameters are listed in . This produced a yellowish surface film. The samples were ultrasonically cleaned in deionized water for 10 minutes, then the first oxide layer was removed by etching in a mixed solution of chromic acid (1.8 wt%) and phosphoric acid (6 wt%) at 60°C for 6 hours. After ultrasonic cleaning for 10 minutes, the resulting bright white aluminum foil was subjected to second-step anodization in oxalic acid solution. The second-step oxidation parameters were fixed at: oxalic acid concentration (CB) 0.3 mol/L, temperature (T) 15°C, oxidation voltage (U) 50 V, and time (t) 4 h.

To investigate the effects of second-step oxidation parameters, the first-step parameters were fixed at CB 0.3 mol/L, T 15°C, and U 50 V, t 4 h, while second-step parameters were varied as shown in .

The microstructure of samples was examined using a Quanta 600 FEG field emission scanning electron microscope (SEM) to analyze variations in pore diameter, wall thickness, spacing, and distribution orderliness with processing parameters. For quantitative analysis, random regions were selected in SEM images, and all pore diameters, spacings, and wall thicknesses within these regions were measured and averaged to minimize errors from pore shape variations and imaging artifacts.

## 2. Results and Discussion

### 2.1 Effects of First-Step Oxidation Parameters

SEM images of samples after first-step oxidation and after removal of the first oxide layer [Figure 1: see original paper] reveal disordered, irregular pores following the first oxidation, with only rough pits remaining after layer removal. These cannot accurately reflect the influence of first-step parameters. Therefore, the effects of first-step oxidation were evaluated by varying these parameters while keeping second-step conditions constant.

Varying first-step oxidation time (parameters 1# in ) while maintaining other parameters yielded the morphologies shown in [Figure 2: see original paper]. For oxidation times of 2 h, 4 h, and 8 h, the average pore diameters were 41 nm, 40 nm, and 42 nm, respectively; average wall thicknesses were 85 nm, 91 nm, and 91 nm; and average pore spacings were 125 nm, 131 nm, and 133 nm. The AAO surface exhibited dense, smooth structures with pores arranged in a regular two-dimensional hexagonal lattice. Under identical second-step conditions, varying the first-step oxidation time produced no significant or systematic changes in pore diameter, wall thickness, or spacing, indicating that first-step oxidation time has minimal influence on AAO properties.

Varying first-step oxidation voltage (parameters 2# in ) produced the morphologies shown in [Figure 3: see original paper]. At voltages of 40 V, 50 V, and 60 V, average pore diameters were 30 nm, 40 nm, and 55 nm; wall thicknesses were 78 nm, 91 nm, and 81 nm; and pore spacings were 108 nm, 131 nm, and 136 nm. The AAO surfaces were dense and flat, though pore ordering decreased at higher voltages (e.g., 60 V). Both pore diameter and spacing increased with voltage, while wall thickness showed no clear trend and varied only slightly.

Varying first-step oxalic acid concentration (parameters 3# in ) yielded the morphologies shown in [Figure 4: see original paper]. At concentrations of 0.2, 0.3, and 0.4 mol/L, average pore diameters were 45 nm, 40 nm, and 42 nm; wall thicknesses were 82 nm, 91 nm, and 80 nm; and pore spacings were 127 nm, 131 nm, and 122 nm. Under constant second-step conditions, increasing electrolyte concentration produced no systematic changes in pore diameter, wall thickness, or spacing, and pore shape and arrangement remained essentially unchanged.

### 2.2 Effects of Second-Step Oxidation Parameters

While keeping first-step parameters constant, varying second-step oxidation time (parameters 1# in ) produced the morphologies shown in [Figure 5: see original paper]. For second-step times of 2 h, 4 h, and 8 h, average pore diameters were 44 nm, 51 nm, and 55 nm; wall thicknesses were 85 nm, 73 nm, and 71 nm; and pore spacings were 127 nm, 124 nm, and 127 nm. The AAO surface exhibited dense, smooth structures with pores ordered in a two-dimensional hexagonal array. Increasing second-step time led to slight increases in pore diameter and minor decreases in wall thickness, while spacing showed no clear trend, indicating that second-step oxidation time has limited influence on AAO properties.

Varying second-step oxidation voltage (parameters 2# in ) while maintaining first-step parameters produced the microstructures shown in [Figure 6: see original paper]. At second-step voltages of 40 V, 50 V, and 60 V, average pore diameters were 43 nm, 51 nm, and 83 nm; wall thicknesses were 83 nm, 73 nm, and 39 nm; and pore spacings were 127 nm, 124 nm, and 123 nm. As second-step voltage increased, pore diameter increased significantly, wall thickness decreased, and spacing remained essentially constant, with pores maintaining hexagonal ordering. Pore shape evolved from circular to elongated, and then to hexagonal.

AAO prepared with varying second-step oxalic acid concentration (parameters 3# in ) is shown in [Figure 7: see original paper]. At concentrations of 0.2, 0.3, and 0.4 mol/L, average pore diameters were 41 nm, 51 nm, and 56 nm; wall thicknesses were 79 nm, 73 nm, and 68 nm; and average spacings were 124 nm, 124 nm, and 126 nm. Increasing second-step oxalic acid concentration led to larger pore diameters and thinner walls, while spacing remained essentially unchanged. However, at higher concentrations (e.g., 0.4 mol/L), oriented piercing of adjacent pores occurred along parallel, specific directions, as indicated by lines I, II, and III in [Figure 7c: see original paper]. Additionally, large-area dissolution was observed in region of [Figure 7c: see original paper].

### 2.3 Discussion

To further investigate the effects of the two-step oxidation parameters, [Figure 8: see original paper] presents the variation trends of AAO pore characteristics. During first-step oxidation, voltage exerts the dominant influence. As first-step voltage increases, pore spacing increases significantly [Figure 8b: see original paper], accompanied by a moderate increase in pore diameter [Figure 8a: see original paper], while wall thickness shows minimal change [Figure 8c: see original paper]. Oxidation time and oxalic acid concentration have relatively minor effects. During second-step oxidation, voltage also plays the primary role, while time and concentration have minimal impact on spacing. However, excessive oxalic acid concentration during the second step causes intense reactions that lead to oriented pore piercing and even dissolution of the AAO layer [Figure 7c: see original paper]. As second-step voltage increases, pore diameter increases dramatically [Figure 8a: see original paper], wall thickness decreases [Figure 8c: see original paper], and pore spacing remains essentially constant [Figure 8b: see original paper]. Comparing the pore diameter variation curves in [Figure 8a: see original paper] reveals that the pore-widening effect of second-step voltage is significantly greater than that of first-step voltage. In contrast, [Figure 8b: see original paper] shows that increasing first-step voltage is more effective for enlarging pore spacing.

Masuda et al. [15] proposed that after removal of the first oxide layer, pits remain on the aluminum substrate surface. These pits induce a non-uniform electric field distribution during the second oxidation, resulting in higher current density at the pit locations where anodization proceeds more readily, forming nanopores. The nanopores subsequently expand within these pits [16, 17], eventually developing into larger pores. Therefore, the diameter of the first oxide layer and the resulting pits directly influences the pore spacing of the final AAO structure, with larger pits producing greater pore spacing. This suggests that during first-step oxidation, increasing voltage enlarges the pit diameter, thereby increasing AAO pore spacing.

The relationship between pore diameter and oxidation voltage has been widely reported, though no universally accepted theoretical model currently explains this phenomenon. According to the electric field-assisted dissolution model [18] and the stable pore growth model [19], oxide layer formation and field-assisted dissolution compete during the initial anodization stage until stable AAO pores form. At this point, the electric field becomes confined to the pore bottom, where oxide generation and dissolution continue while side walls cease dissolving, maintaining a constant thickness. Consequently, in both first- and second-step oxidations, pore diameter and spacing show minimal variation with oxidation time, while oxide layer thickness and pore depth increase with extended second-step time. This suggests that higher second-step voltage requires longer side-wall dissolution time before the electric field becomes confined to the pore bottom in stable, larger pores. However, if the anodization reaction becomes too intense (e.g., at very high voltage or excessive oxalic acid concentration), the AAO oxide layer may dissolve completely.

## 3. Conclusions

Using the two-step anodization method to prepare AAO, oxidation voltage exerts the strongest influence on pore characteristics. Increasing first-step voltage significantly enlarges pore spacing, while increasing second-step voltage substantially increases pore diameter. During both oxidation steps, oxidation time and oxalic acid concentration have relatively minor effects. However, when oxalic acid concentration is too high (0.4 mol/L), the intense anodization reaction causes oriented piercing of adjacent pores and even dissolution of the oxide layer.

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