The effect of sulphuric acid and oxalic acid on the formation of anodic aluminium oxide templates using two-step anodization method

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Abstract. The prevention of corrosion on the surface of aluminum by formation of a thin coating layer using anodization methods for enhanced applications is an active area of research. In this study, the fabrication of nanoporous anodic aluminum oxide (AAO) templates was performed by a two-step anodization process using aluminum with 99.98% purity in 0.3 M solution of oxalic acid or 0.1, 0.3, or 0.5 M solutions of sulfuric acid as electrolyte. Anodizing time, electrolyte solution and concentration, and current were found to be the main factors determining the pore diameter and interpore size. In addition, the voltage affected the number of pores on the AAO template. The structural features of the nanoporous templates were examined by scanning electron microscopy. The optimum conditions were determined to be 0.3 M sulfuric acid at 25 V.

Keywords: aluminum, two-step anodization, anodic aluminium oxide

1. Introduction
Aluminium, the third most abundant metal in nature after oxygen and silicon, has a variety of properties that render it useful for the easy preparation of good, economical, and corrosion-resistant heat and electrical conductors. In daily life, aluminium can be found in materials as diverse as kitchen equipment, building construction materials, or aircraft manufacturing materials. Currently, research in the field is focusing on the prevention of corrosion on the aluminium surface by forming a thin coating layer, which can occur naturally or can be induced by using anodizing methods [1].

Anodization can improve the quality of aluminium from mechanical, aesthetic, and decorative viewpoints, as well as its resistance to corrosion and abrasion on metal surfaces, through the formation of a layer of aluminium oxide (Al₂O₃) [2]. In the anodizing process, the oxide layer formation is determined by several factors, including electrolyte type and concentration, voltage, current density, temperature, distance between cathode and anode, and anodization time [3-6].

Al₂O₃ or anodic aluminium oxide (AAO) coatings can be used as templates in nanotechnology applications, such as the manufacture of carbon nanotube nanotechnology products, quantum dots, nanoporous membranes, or as templates for nanowire metal electrodeposition [7-10].

In this study, a comparative study on the formation of AAO using oxalic acid electrolyte and an electrolyte of oxalic acid and sulphuric acid (H₂SO₄) was performed. Different voltages were applied to determine the optimum pore enlargement on the aluminium surface. In addition, the AAO bandgap...
value was determined using UV–visible diffuse reflectance spectrophotometry (UV–vis DRS). The material obtained was characterized by scanning electron microscopy–energy dispersive X-ray spectrometry (SEM–EDX) and X-ray diffraction (XRD).

2. Materials and methods
For the experimental setup, the following materials were used: a Pt wire as supporting electrode, a volumetric pipette, a measuring pipette, a dropper, a measuring flask, a bulb, a weighing bottle, a glass beaker, a spatula, a stir bar, a spray bottle, a funnel, a magnetic stirrer, a power supply, and a furnace. The characterization was performed on SEM, EDX, and UV–Vis DRS instruments.

Aluminium as the main raw material was initially electropolished using a mixture of perchloric acid solution (60 wt.%) and ethanol (1:4) at 20 V and 10 °C for approximately 1 min. Then, it was washed with aquabidest and ethanol. Several electropolished aluminum plates were prepared in order to conduct the anodization using different electrolytes, i.e., 0.3 M oxalic acid (H₂C₂O₄) solution and 0.1, 0.3, and 0.5 M H₂SO₄ solutions. The electrochemical cell for the anodization was prepared by connecting the aluminum plate to the positive pole and the Pt wire to the negative pole under direct current (DC) power supply.

The anodization for the formation of the AAO film was performed in two steps. The first anodization was conducted at 25 V and ~10 ºC for 60 min. The as-prepared AAO template was then subjected to chemical etching by dipping into a mixture of chromic acid and phosphate at a temperature of ~45 ºC for 720 min. Then, the second anodization was performed for 360 min to form a new oxide layer. The AAO template was calcined for 2 h at 450 °C and then subjected to UV–vis DRS analysis to determine the bandgap value.

With the optimum electrolyte concentrations of oxalic acid and H₂SO₄, voltage variation was performed (oxalic acid at 45 V and H₂SO₄ at 15, 25, and 30 V). The structural features of the nanoporous AAO were examined by SEM, XRD, and EDX.

3. Results and discussion
For the formation of anodic alumina oxide, aluminium is used as the main raw material. The AAO layer is formed on the surface of aluminium by electrochemical process using an acidic electrolyte solution, since protons play a key role in the formation of pores in aluminium [11,12].

The aluminum plate was subjected to electropolishing in a mixture of perchloric acid and ethanol in a 1:4 ratio. The temperature was set at ~10 °C by using a cooling system to avoid excess heating during the electropolishing. A voltage of 20 V was applied for 30 s. Longer electropolishing times would cause burning on the aluminum surface, which might affect the plasticity of aluminum. The result is shown in figure 1.

We conducted a two-step anodization method for the formation of AAO films with nano-sized pores because the first anodizing process afforded irregular pores, since the steady state is not reached at this stage. The films obtained after the first anodization were subjected to chemical etching, leaving a template of molds on the aluminum surface that allowed the formation of more orderly pore arrangements in the second anodizing step (figure 2).
Table 1. SEM characterization of the AAO obtained with different electrolytes

| Electrolyte   | Pore Size (nm) | Interpore Size (nm) |
|---------------|----------------|---------------------|
| H₂C₂O₄ 0.3 M (A) | ± 31.69        | ± 25.03             |
| H₂SO₄ 0.1 M (B)   | ± 49.16        | ± 33.29             |
| H₂SO₄ 0.3 M (C)   | ± 57.72        | ± 30.52             |
| H₂SO₄ 0.5 M (D)   | ± 49.16        | ± 30.01             |

Figure 3. SEM images of the AAO obtained with different electrolytes
(a) 0.3M H₂C₂O₄ and H₂SO₄, (b) 0.1M, (c) 0.3M, (d) 0.5M

The concentrations of electrolytes are known to be important factors in the formation of AAO pores, since they affect the current generated during anodization and determine the pore diameter and the pore density. In addition, the electrolyte solution determines the pore structure and the thickness of the pore layer [3,13].

In this study, we used oxalic acid and H₂SO₄ as electrolytes to evaluate the effect of the electrolyte on the pore formation. Table 1 summarizes the pore and interpore sizes determined by SEM of the AAO films obtained using different electrolytes (A, B, C, and D) under the same conditions (25 V, ~10 °C, and 6 h for the second anodization). The corresponding SEM images are displayed in figure 3.
Table 2. SEM characterization of the AAO obtained with different voltages

| Sample | Electrolyte | Voltage (volt) | Pore Size (nm) | Interpore Size (nm) |
|--------|-------------|----------------|----------------|---------------------|
| A      | H₂C₂O₄ 0.3M | 25             | ± 31.69        | ± 25.03             |
| E      | H₂SO₄ 0.3M  | 45             | ± 97.37        | ± 30.97             |
| F      |             | 15             | ± 33.20        | ± 22.33             |
| C      | H₂SO₄ 0.3M  | 25             | ± 57.72        | ± 30.52             |
| H      |             | 30             | ± 35.79        | ± 28.45             |

Figure 4. SEM images of the AAO obtained with different voltages for oxalic acid with (a) 25 V, (b) 45 V and sulphuric acid with (c) 15 V, (d) 25 V and (e) 30 V

AAO pores were produced with the two electrolytes, but have different diameter, interpore size, and pore density. As can be seen in table 1, the use of 0.3 M oxalic acid electrolyte afforded the smallest pore size, whereas the largest pores were obtained when using 0.3 M H₂SO₄ solution. These results confirm that the formation of pores in AAO depends on the type of electrolyte and the electrolyte concentrations, with the 0.3 M H₂SO₄ electrolyte affording the optimum condition.

Voltage and current density are linearly proportional. Thus, increasing the voltage will increase the current density and vice versa. In the anodizing process using DC, the constant voltage can affect the reaction at the cathode [14]. Low concentrations and low temperatures require a higher voltage (higher current density). However, high current density is likely to result in burning. Therefore, in anodizing process, it is preferably conducted in high concentrations and high temperature so the required voltage is low [15].

We evaluated the effect of voltage using two different electrolytes, the 0.3 M oxalic acid and 0.3 M H₂SO₄. For the former, voltages of 25 and 45 V were applied, and 15, 25, and 30 V were applied for the latter. The results are detailed in table 2 and figure 4.
### Table 3. Bandgap of the AAO obtained with different electrolytes

| Electrolyte | Band Gap (eV) | Band Gap Calcination (eV) |
|-------------|---------------|--------------------------|
| H2C2O4 0.3 M (A) | 1.42          | 3.08                     |
| H2SO4 0.1 M (B) | 5.05          | 3.82                     |
| H2SO4 0.3 M (C) | 5.56          | 3.78                     |
| H2SO4 0.5 M (D) | 4.10          | 3.88                     |

### Table 4. Comparison of atomic wt.% of the AAO obtained using different electrolytes

| Atom | wt.% 3M H2C2O4 | wt.% 3M H2SO4 | Energy (keV) |
|------|---------------|---------------|--------------|
| Al   | 45.12         | 42.20         | 1.5          |
| O    | 43.75         | 43.00         | 0.5          |
| H    | 10.08         | 10.80         | 0.25         |

### Figure 5. XRD spectra of AAO templates for two different electrolytes

The result of the characterization with SEM shows that the voltage affects the pore density, pore diameter, and interpore distance. In the case of oxalic acid, the use of 25 V produced higher pore density than 45 V, most likely due to the high voltage causing the pore wall decay, which results in fewer pores and larger pore diameter.

The effect of voltage on the H2SO4 electrolyte was found to be lower than that of oxalic acid, which stems from the higher acidic strength of the former electrolyte. Higher voltages affect the thickness of the oxide layer, which can increase the stress on the anodizing process that will also affect the pore diameter and the distance between the pores.

Characterization using UV–Vis DRS was performed to determine the magnitude of the AAO bandgap obtained with the different electrolytes and also after calcination at 450 °C for 2 h.
The results displayed in table 3 show that the type of electrolyte and the calcination affect the bandgap. The bandgap difference of AAO produced by the two type electrolytes is quite large, but after the calcination process, the AAO bandgap of the two electrolytes does not differ much. The AAO bandgap after being treated with calcination was relatively not very different either using different electrolytes or different concentrations with the same electrolyte.

The AAO films obtained using the 0.3 M H2C2O4 electrolyte and the 0.3 M H2SO4 electrolyte were subjected to EDX analysis to determine the weight percent and percent of atoms present in the film. The results are shown in table 4.

The structure of the AAO samples obtained after the two-step anodization using the oxalic acid electrolyte and sulphuric acid were determined by using XRD as shown in figure 5. There are two peaks in the XRD spectra. For peak around 2θ\textdegree~64 ° (sulphuric acid) and 2θ~65 ° (oxalic acid) corresponding to the (200) plane of Al, while peaks around 2θ~76 ° (sulphuric acid) and 2θ~78 ° (oxalic acid) corresponding to (311) plane of Al as obtained by Zhao et al. [16].

4. Conclusions

The fabrication of AAO has been successfully performed by using the two-step anodizing method. The type of electrolyte, electrolyte concentration, and applied voltage produced AAO templates exhibiting diverse pore sizes and pore spacing. The voltage does not significantly affect the pore diameter and interpore size of the AAO template using sulphuric acid electrolyte compared to oxalic acid. At a lower voltage of V, the pore characteristics produced using sulphuric acid electrolyte are better than oxalic acid. The weight per cents of Al, O and H atom in the AAO template is almost the same for the two electrolyte used as well as the bandgap of the AAO templates of the two electrolytes after the calcination process is relatively not much different.

Acknowledgements

The authors would like to thank Enago (www.enago.com) for the English language review.

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