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Author(s)	Nakajima, Daiki; Kikuchi, Tatsuya; Natsui, Shungo et al.
Citation	Applied Surface Science, 321, 364-370 https://doi.org/10.1016/j.apsusc.2014.10.014
Issue Date	2014-12-01
Doc URL	https://hdl.handle.net/2115/57114
Type	journal article
File Information	Ketoglutaric.pdf



Growth behavior of anodic oxide formed by aluminum anodizing in glutaric and its derivative acid electrolytes

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Abstract

The growth behavior of anodic oxide films formed via anodizing in glutaric and its derivative acid solutions was investigated based on the acid dissociation constants of electrolytes. High-purity aluminum foils were anodized in glutaric, ketoglutaric, and acetonedicarboxylic acid solutions under various electrochemical conditions. A thin barrier anodic oxide film grew uniformly on the aluminum substrate by glutaric acid anodizing, and further anodizing caused the film to breakdown due to a high electric field. In contrast, an anodic porous alumina film with a submicrometer-scale cell diameter was successfully formed by ketoglutaric acid anodizing at 293 K. However, the increase and decrease in the temperature of the ketoglutaric acid resulted in non-uniform oxide growth and localized pitting corrosion of the aluminum substrate. An anodic porous alumina film could also be fabricated by acetonedicarboxylic acid anodizing due to the relatively low dissociation constants associated with the acid. Acid dissociation constants are an important factor for the fabrication of anodic porous alumina films.

Keywords: Aluminum; Anodizing; Glutaric Acid; Ketoglutaric Acid; Acetonedicarboxylic Acid

1. Introduction

Anodic porous alumina with numerous vertical, nano-scale pores can easily be fabricated via aluminum anodizing in several types of acidic aqueous solutions and has been widely applied in the fields of corrosion protection and electronic applications[1-6]. In particular, the development of highly ordered anodic porous alumina, which is fabricated via self-ordering and two-step anodizing under appropriate electrochemical conditions, has expanded the applicability of porous alumina[7]. Accordingly, plasmonic devices[8], antireflection polymer structures[9], optical devices[10], and high-density recording media[11] have been successfully fabricated through the combination of methods for developing highly ordered anodic porous alumina and other nanostructure fabrication techniques.

The electrolyte species used for anodic porous alumina fabrication can be specifically classified into the following three groups: inorganic, organic cyclic oxocarbonic, and organic carboxylic acids. It is a well-known experimental fact that anodic porous alumina can be formed by anodizing in these acidic electrolytes, which provide low acid dissociation constants. To date, sulfuric[12-16], selenic[17,18], phosphoric[19,20], and chromic[21] acids have been reported as useful inorganic electrolytes for fabricating anodic porous alumina. The ideal cell arrangement of porous alumina can be achieved via sulfuric, selenic, and phosphoric acid anodizing, whereas poorly ordered porous alumina is fabricated via chromic acid anodizing[22,23]. Cyclic oxocarbonic acids such as squaric[24], croconic, and rhodizonic[25] acid were very recently determined to be suitable organic electrolytes for fabricating porous alumina, although the details of the growth behavior are still unknown. Carboxylic acids can also be employed as suitable electrolytes for fabricating porous alumina, including oxalic[26,27], malonic[28,29], citric[30,31], malic[32], acetylenedicarboxylic[33], tartaric[34,35], tartronic[36], glycolic[37], and formic[38] acid. Because the nanostructural features and chemical properties of anodic porous alumina are determined and limited by the electrolyte used[39], the discovery of a new suitable electrolyte would expand the applicability of porous alumina.

Typical dicarboxylic acids and their corresponding acid dissociation constants, pK_{a1} and pK_{a2} , are summarized in Table 1[40-42]. Oxalic acid has low pK_a values of 1.04 and 3.82 and is widely used for the fabrication of highly ordered anodic porous alumina with a cell size on the order of 100 nm. Malonic acid also has low pK_a values of 2.60 and 5.29, and anodic porous alumina can also be formed via malonic acid anodizing. In contrast, dicarboxylic acids with a long-main-chain structure, including succinic, glutaric, and adipic acid, have relatively high dissociation constants. Therefore, studies have shown that anodic porous alumina cannot be obtained via anodizing aluminum in these solutions; however, the electrochemical behavior and nanostructural features of anodized specimens during anodizing have not been described in such studies[43,44]. Additionally, α -ketoglutaric acid (usually called “ketoglutaric acid”, $\text{HOOC-CO-(CH}_2\text{)}_2\text{-COOH}$) is one of the derivatives of glutaric acid with a ketone

group and has low pKa values of 1.90 and 4.56. Therefore, unlike glutaric acid, it is strongly believed that ketoglutaric acid has the potential to behave as a suitable electrolyte for fabricating anodic porous alumina.

Herein, we report the growth behavior of anodic oxide fabricated via anodizing in glutaric and ketoglutaric acid solutions. A barrier anodic oxide film is formed on an aluminum substrate by glutaric acid anodizing, and further anodizing causes “breakdown” and gives rise to sparking phenomena. In addition, anodic porous alumina formed above 200 V can be successfully obtained by ketoglutaric acid anodizing. The growth behavior of porous alumina during ketoglutaric acid anodizing under various electrochemical conditions is reported in detail. Moreover, in this study, a new electrolyte for fabricating anodic porous alumina was discovered based on an analysis of acid dissociation constants and the experimental results that were obtained.

2. Experimental

High-purity aluminum foils (99.99 wt%, 110 μm thick, 20 mm $\times$ 20 mm with a handle, Showa Aluminum Co., Japan) were used as the anodizing specimens. The aluminum foils were ultrasonically degreased in an ethanol solution for 10 min, and then silicone resin was coated on the bottom of the handle to avoid contact between the handle and the acidic solution used. After drying the coated silicone resin, the specimens were immersed in anodizing solutions and then anodized for up to 60 min. For the anodizing procedure, the following acidic solutions were prepared: a) 0.3 M glutaric acid ($T = 293\text{ K}$, Kanto Chemical Co., Japan) and b) 0.1-2.0 M ketoglutaric acid ($T = 273\text{-}333\text{ K}$, Tokyo Chemical Industry Co., Japan). These acidic solutions were vigorously stirred with a magnetic stirrer during anodizing, and the temperature of the solutions was maintained at a constant value using a water bath (UCT-1000, AS ONE, Japan). The specimens were anodized at constant current densities of $i = 20\text{-}100\text{ Am}^{-2}$, and a platinum plate was used as the counter electrode. The corresponding voltage during constant current anodizing was recorded by a PC-controlled direct current power supply (PWR-400H, Kikusui, Japan). The pH of the solution was measured with a digital pH meter (SevenMulti, Mettler Toledo, Switzerland).

After anodizing, the specimens were immersed in a 0.20 M CrO_3 /0.51 M H_3PO_4 solution ($T = 353\text{ K}$) for up to 20 min to selectively dissolve the anodic oxide. The growth plane of the anodic oxide was exposed to the surface by selective oxide dissolution. Thus, a nanodimple array corresponding to the shape of the bottom of the anodic oxide film could be observed. The nanomorphologies of the specimens anodized in glutaric and ketoglutaric acid solutions were examined by scanning electron microscopy (SEM, JIB-4600F/HKD and JSM-6500F, JEOL, TM-1000, Hitachi) and atomic force microscopy (AFM, Nanocute, SII Nano Technology). To facilitate the observation of the anodic oxide, a thin platinum conductive layer was coated on the oxide by a sputter coater (MSP-1S, Vacuum Device, Japan).

3. Results and Discussion

3.1 Constant current anodizing in glutaric acid and nanomorphologies of resulting films

Figure 1 shows the changes in anodizing voltage, V , with time, t , in a 0.3 M glutaric acid solution ($T = 293\text{ K}$) at different constant current densities, $i = 20, 50$, and 100 Am^{-2} . The pH of the solution was measured to be 2.40 at room temperature. At $i = 100\text{ Am}^{-2}$, the anodizing voltage increased linearly up to approximately 500 V during the initial stage of anodizing. The rapid increase ceased at approximately 2.5 min, and the voltage increased slightly with time during subsequent anodizing for up to 60 min. The gradual change in voltage showed a tendency similar to that of the decrease in current density ($i = 50$ and 20 Am^{-2}), but the rate of linear increase during the initial stage and the subsequent plateau voltage decreased with increasing current density. The slopes of the linear relationships were measured to be 50 Vmin^{-1} at 20 Am^{-2} , 130 Vmin^{-1} at 50 Am^{-2} , and 250 Vmin^{-1} at 100 Am^{-2} , which were proportional to the current density. The insert of Figure 1 shows the surface appearance of the aluminum specimen during anodizing at 50 Am^{-2} , and the images were obtained over the plateau voltage under light and dark conditions. Numerous sparking phenomena, indicated by white circles on dark condition, were observed during anodizing, and intense oxygen gas evolution was also observed for the aluminum specimen. This electrochemical behavior and the corresponding sparking phenomena are typically observed during the formation of barrier anodic oxide films on aluminum and the subsequent breakdown of the anodic oxide[1].

Figure 2a shows an SEM image of the surface of the aluminum specimen anodized in 0.3 M glutaric acid solution at 50 Am^{-2} for 60 min. The anodic oxide shows a very rough surface in the figure, and there are numerous micropores and cracks on the oxide film due to breakdown during high voltage anodizing. Based on the observation of a fracture cross-section of the anodized specimen, disregarding defect regions (Fig. 2b), an anodic oxide film measuring approximately 700 nm in thickness was formed on the aluminum substrate, and the film consisted of a thin compact anodic oxide without any type of nanopore, as indicated by high-magnification SEM observation (insert figure). Thus, the anodic oxide film formed by glutaric acid anodizing was a barrier anodic oxide film.

In general, a barrier anodic oxide film is obtained by constant current anodizing in neutral solutions such as borate and adipate and consists of a thin, compact, amorphous oxide. Subsequent anodizing causes an increase in voltage and film thickening, and a linear relation, with a proportional constant of approximately $1.2\text{--}1.3\text{ nmV}^{-1}$, between the anodizing voltage and the thickness of the barrier oxide under constant current anodizing has been reported[1,45]. The growth of the barrier oxide film then stops abruptly due to dielectric breakdown, with visible sparking on the specimen. The thickness of the barrier oxide obtained by glutaric acid anodizing (700 nm, $V = 530\text{ V}$) is in good agreement with the proportional constant indicated above. An anodic porous alumina could not be formed on the aluminum substrate by glutaric acid

anodizing, as shown in Figs. 1 and 2, and such barrier anodic oxide formation may result in high dissociation constants and accordingly high pH levels of the glutaric acid solution used.

3.2 Constant current anodizing in ketoglutaric acid and nanomorphologies of resulting films

Figure 3 shows the variation in the anodizing voltage with time in a 0.3 M ketoglutaric acid solution ($T = 293\text{ K}$) at different constant current densities, $i = 20, 50$, and 100 Am^{-2} . The pH of the ketoglutaric acid solution at room temperature was measured to be 1.37, which is significantly lower than that of the 0.3 M glutaric acid solution. The voltages increased linearly with anodizing time at each current density, and the slope increased with current density, as observed during glutaric acid anodizing. The voltages, however, showed peak values of approximately 200-225 V and increased gradually with anodizing time after reaching the peak values. This electrochemical behavior, characterized by a peak in voltage, is clearly different from that observed during glutaric acid anodizing for barrier anodic oxide formation, as shown in Fig. 1. More importantly, this electrochemical behavior demonstrated voltage-time transients similar to those obtained by anodizing for the formation of anodic porous alumina[1]. Neither a sparking phenomenon nor oxygen gas evolution was observed on the aluminum specimen during ketoglutaric acid anodizing. On the other hand, a non-uniform anodic oxide with light-and dark-gray coloring was observed on the specimen anodized at 100 Am^{-2} . In this specimen, the anodizing was carried out under high current density, and a corresponding non-steady voltage increase was observed during anodizing, as shown in Fig. 3. Therefore, further investigations by AFM and SEM were carried out below 50 Am^{-2} . It was expected that steady growth of the anodic oxide would occur under these electrochemical conditions.

To observe the oxide growth behavior at the interface between the anodic oxide layer and the aluminum substrate, the anodized specimens were immersed in a $\text{CrO}_3/\text{H}_3\text{PO}_4$ solution to selectively dissolve the anodic oxide. Figure 4 shows three-dimensional AFM images of an exposed aluminum substrate anodized at 50 A m^{-2} for a) 1 min, b) 3 min 45 s, and c) 20 min. During the initial stage of anodizing, up to 1 min, the anodizing voltage increased linearly (Fig. 3), and a stripe pattern from the upper left to the lower right was observed on the aluminum substrate (Fig. 4a). This stripe pattern can be observed on the surface of the as-received aluminum, and corresponds to the marks formed by the rolling of the aluminum foil. The anodizing voltage showed a peak value of 220 V at 3 min 45 s, at which time numerous nanodimples measuring several 100 nm in diameter could be observed on the aluminum substrate (Fig. 4b). It is believed that these nanodimples correspond to the shape of the bottom of the anodic porous alumina film. As the anodizing time was increased to 20 min (Fig. 4c), a greater number of deeper nanodimples were clearly observed on the substrate due to the steady state growth of the anodic oxide.

Figure 5a shows an SEM image of the surface of the aluminum specimen anodized in a 0.3 M ketoglutaric acid solution at 50 Am^{-2} for 60 min. The stripe pattern also corresponds to the marks formed by the rolling process. Numerous nanopores measuring approximately 55-85 nm in diameter are clearly observed on the entire surface of the anodic oxide. An SEM image of a fracture cross-section of the anodized specimen is shown in Figure 5b, which demonstrates that a thick anodic porous alumina film with porous and barrier layers was clearly formed on the aluminum substrate. The nanopores in the porous layer were arranged perpendicularly from the top surface to bottom interface and were separated from the aluminum substrate by a thin barrier layer measuring approximately 200 nm in thickness (insert figure). Based on the above-mentioned results obtained for constant current anodizing (Figs. 3-5), ketoglutaric acid anodizing results in the formation of anodic porous alumina, unlike glutaric acid anodizing.

Figure 6a shows the changes in the anodizing voltage, V , with time, t , during ketoglutaric acid anodizing at 50 Am^{-2} in different electrolyte concentrations, $C = 0.1 \text{ M}$, 0.3 M , and 2.0 M at 293 K. The pH levels of the solutions at room temperature were measured to be 1.64, 1.37, and 0.80, respectively. The plateau anodizing voltage, which corresponded to the steady-state growth of anodic porous alumina, decreased with the increase in the electrolyte concentration. Accordingly, the average cell diameter of the porous alumina measured by SEM observations became smaller with the increase in electrolyte concentration: 650 nm at 260 V in 0.1 M (Fig. 6b) and 540 nm at 200 V in 2.0 M (Fig. 6c). Typically, there is a linear relationship between cell diameter and anodizing voltage for anodic porous alumina, and this relation is described as follows[4,39]:

$$D = 2.5 V [\text{nm}] \quad (1)$$

where D is cell diameter. The cell size obtained by ketoglutaric acid anodizing is in fair agreement with this linear relationship. During ketoglutaric acid anodizing, the barrier layer at the bottom of porous oxide may become thinner with increasing electrolyte concentration because the barrier oxide can easily dissolve into the electrolyte solution under low-pH conditions. Therefore, the anodizing voltage under steady-state oxide growth decreases with the increase in the electrolyte concentration (Fig. 6a), and the cell diameter also decreases.

Figure 7a shows the anodizing voltage-time transients obtained during anodizing in a 0.3 M ketoglutaric acid solution at 50 Am^{-2} at different temperatures of $T = 273$, 293 , and 333 K . At a high temperature of 333 K , a rough voltage-time curve with small oscillations was obtained due to the “burning” phenomenon, which refers to the local thickening of the anodic oxide. Conversely, the anodizing voltage suddenly decreased to approximately 40 V during the initial stage of anodizing at $T = 273 \text{ K}$. Many micropores measuring 100-200 μm in diameter were formed on the aluminum substrate at this temperature due to the pitting corrosion of aluminum (Fig. 7b). Therefore, increases and decreases in temperature during ketoglutaric acid anodizing have a

negative effect on anodic porous alumina fabrication. Highly ordered anodic porous alumina could not be obtained via ketoglutaric acid anodizing under any electrochemical conditions applied.

3.3 Possibility of discovering new electrolyte

As described in Sections 3.1 and 3.2, thin barrier anodic oxide film was formed on aluminum via glutaric acid anodizing, whereas a thick anodic porous alumina film could be successfully formed via ketoglutaric acid anodizing. Based on these experimental results, it is expected that the formation of anodic porous alumina is strongly affected by the pKa values of the electrolyte used. Namely, ketoglutaric acid, with low pKa values ($\text{pKa}_1 = 1.90$ and $\text{pKa}_2 = 4.56$), allows for porous alumina formation as observed for oxalic and malonic acid. Conversely, glutaric acid, with relatively high pKa values ($\text{pKa}_1 = 4.13$ and $\text{pKa}_2 = 5.03$), results in barrier oxide formation due to the low solubility of aluminum oxide in this acid. Typically, the carbonyl on the carbon chain of ketoglutaric acid is a powerful electron-withdrawing group and increases the acidity of the electrolyte[46]. Therefore, ketoglutaric acid possesses low pKa values, especially a low pKa_1 , the first dissociation constant. Based on these considerations, additional electrolytes for anodic porous alumina fabrication may be easily found by examining acid dissociation constants. For example, acetonedicarboxylic acid (β -ketoglutaric acid, $\text{HOOC-CH}_2\text{-CO-CH}_2\text{-COOH}$) is a well-known derivative of glutaric acid with a ketone group at its center and possesses dissociation constants of $\text{pKa}_1 = 3.23$ and $\text{pKa}_2 = 4.27$, as shown in Table 1. Because these pKa values are lower than those of glutaric acid and similar to those of malonic acid, it is believed that acetonedicarboxylic acid also has the potential to serve as a suitable electrolyte for anodic porous alumina formation.

Figure 8 shows an SEM image of a fracture cross-section of the specimen anodized in a 0.3 M acetonedicarboxylic acid at 50 Am^{-2} and 293 K for 15 min. An anodic porous alumina film measuring approximately $2.5 \mu\text{m}$ in thickness was successfully formed on the aluminum substrate. Although the porous alumina was not ordered, numerous nanopores were clearly observed on the anodic oxide. Therefore, acetonedicarboxylic acid can also serve as an electrolyte for anodic porous alumina fabrication, although further investigation of acetonedicarboxylic acid anodizing will be required to understand the growth behavior of porous alumina in this electrolyte.

The nanomorphological properties of anodic porous alumina films, including anodizing voltage, cell diameter, and order, are limited by the narrow variety of suitable anodizing electrolytes. The discovery of an additional electrolyte is very important for the applicability of anodic porous alumina in optical and electronic devices. Therefore, the discovery of new electrolytes such as ketoglutaric and acetonedicarboxylic acid based on acid dissociation constants is very useful for the expansion of porous alumina nanotechnologies.

4. Conclusions

We reported the growth behavior of anodic oxide formed by anodizing in glutaric, ketoglutaric, and acetonedicarboxylic acid solutions under constant-current-density conditions. A thin barrier anodic oxide was formed on an aluminum substrate by glutaric acid anodizing, whereas a thick anodic porous alumina film with numerous nanopores was formed by ketoglutaric acid anodizing because of the electrolyte's relatively low acid dissociation constants. We observed that anodizing in acetonedicarboxylic acid, which possesses similarly low dissociation constants, also allows for the formation of anodic porous alumina. The acid dissociation constants of the anodizing electrolyte employed are an important factor for anodic porous alumina fabrication.

Acknowledgments

This research was conducted at Hokkaido University and was supported by the "Nanotechnology Platform" Program of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan. The work was financially supported by the Japan Society for the Promotion of Science (JSPS) "KAKENHI" and Toyota Physical & Chemical Research Institute Scholars.

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Captions

Table 1. Summary of dicarboxylic acids, corresponding chemical formulas, and acid dissociation constants pK_{a1} and pK_{a2} .

Fig. 1. Changes in anodizing voltage, V , with time, t , in a 0.3 M glutaric acid solution at 293 K and constant current density of $i = 20, 50$, and 100 Am^{-2} . The insert figure shows video images of the aluminum surface during glutaric acid anodizing at 50 Am^{-2} under light- and dark-field conditions.

Fig. 2. SEM images of the a) surface and b) fracture cross-section of the specimens anodized in a 0.3 M glutaric acid solution at 50 Am^{-2} for 60 min. Each insert figure shows a high-magnification SEM image of the surface and cross-section surrounded by a yellow square.

Fig. 3. Changes in anodizing voltage, V , with time, t , in a 0.3 M ketoglutaric acid solution at 293 K and constant current density of $i = 20, 50$, and 100 Am^{-2} .

Fig. 4. AFM images of the interface between the anodic oxide and the aluminum substrate. The specimens were anodized in a 0.3 M ketoglutaric acid solution at 50 Am^{-2} for a) 1 min, b) 3 min 45 s, and c) 20 min and then were immersed in a $\text{CrO}_3/\text{H}_3\text{PO}_4$ solution at 353 K to expose the interface.

Fig. 5. SEM images of the a) surface and b) fracture cross-section of the specimens anodized in a 0.3 M ketoglutaric acid solution at 50 Am^{-2} for 60 min.

Fig. 6. a) Changes in anodizing voltage, V , with time, t , in 0.1, 0.3, and 2.0 M ketoglutaric acid solution at 293 K at a constant current density of 50 Am^{-2} . b), c) SEM images of the surface of the nanodimples formed by anodizing in 0.1 M and 2.0 M ketoglutaric acid.

Fig. 7. a) Changes in anodizing voltage, V , with time, t , in a 0.3 M ketoglutaric acid solution at 273, 293, and 333 K and constant current density of 50 Am^{-2} . b) SEM image of the surface of the specimen anodized by ketoglutaric acid anodizing at 273 K.

Fig. 8. SEM image of the fracture cross-section of the specimen anodized in a 0.3 M acetonedicarboxylic acid solution at 50 Am^{-2} for 15 min.

Table 1

Electrolyte	Chemical formula	pKa ₁	pKa ₂	Porous alumina
Oxalic acid	HOOC-COOH	1.04	3.82	Yes
Malonic acid	HOOC-CH ₂ -COOH	2.60	5.29	Yes
Succinic acid	HOOC-(CH ₂) ₂ -COOH	3.99	5.20	No
Glutaric acid	HOOC-(CH ₂) ₃ -COOH	4.13	5.03	No
Adipic acid	HOOC-(CH ₂) ₄ -COOH	4.26	5.03	No
α -ketoglutaric acid	HOOC-CO-(CH ₂) ₂ -COOH	1.90	4.56	?
Acetonedicarboxylic acid (β -ketoglutaric acid)	HOOC-CH ₂ -CO-CH ₂ -COOH	3.23	4.27	?

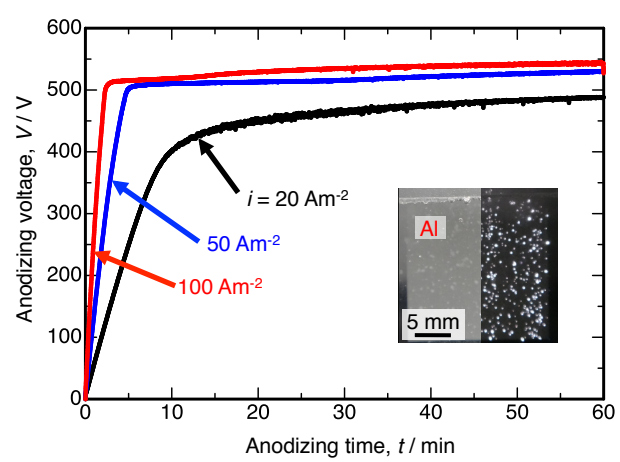
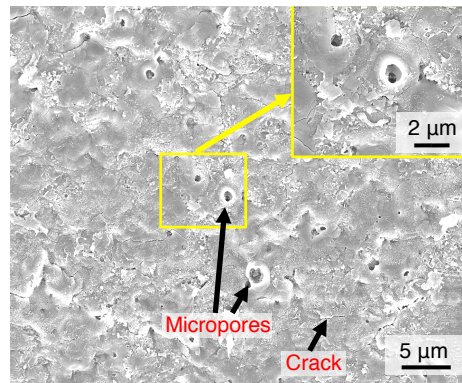


Fig. 1

a) Surface



b) Cross-section

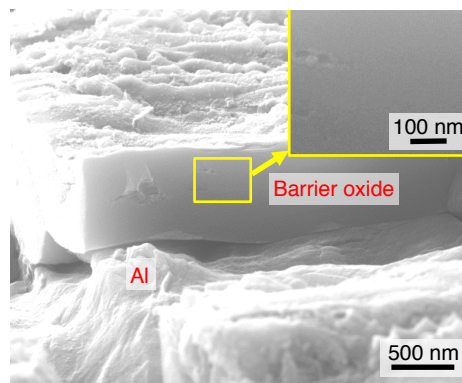


Fig. 2

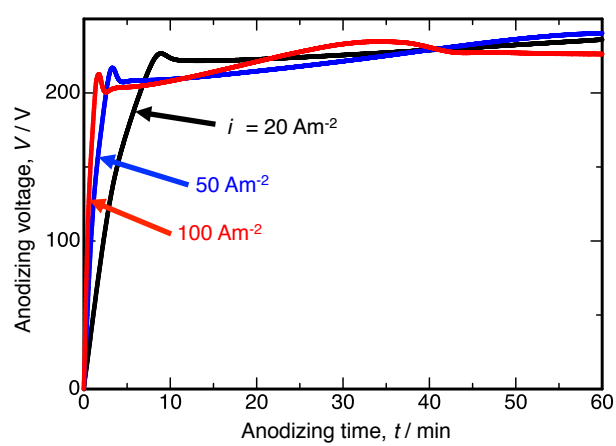


Fig. 3

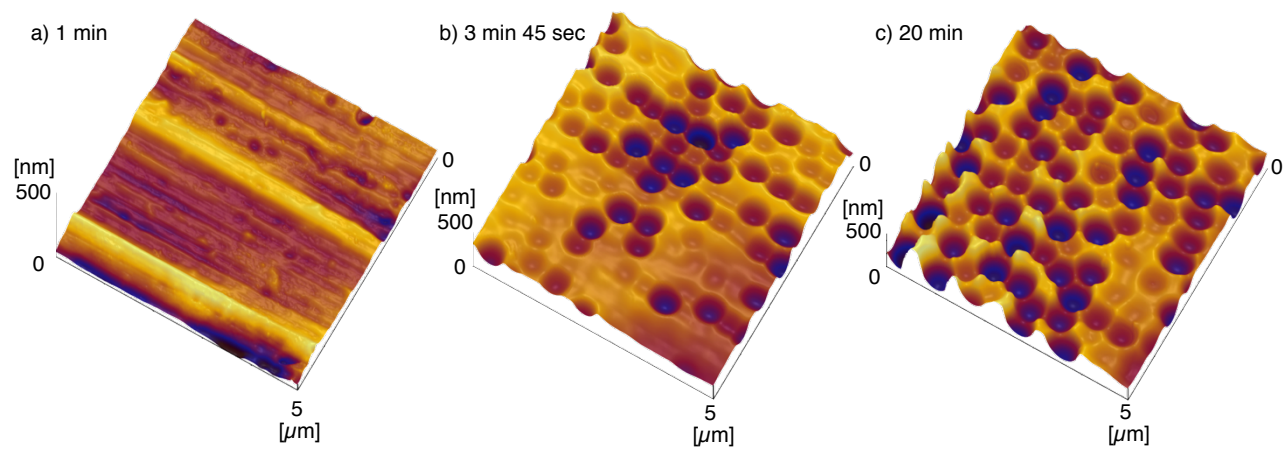


Fig. 4

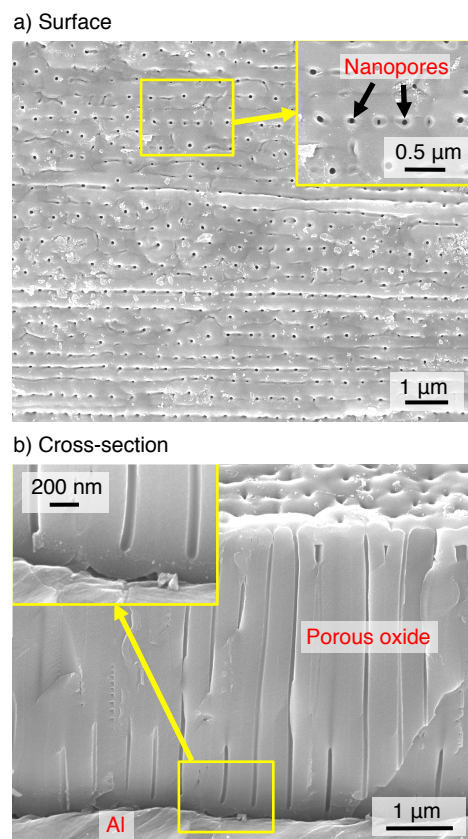


Fig. 5

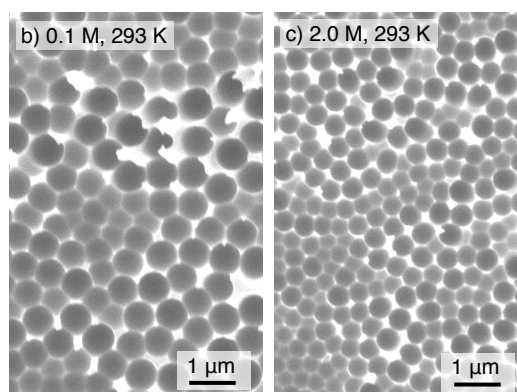
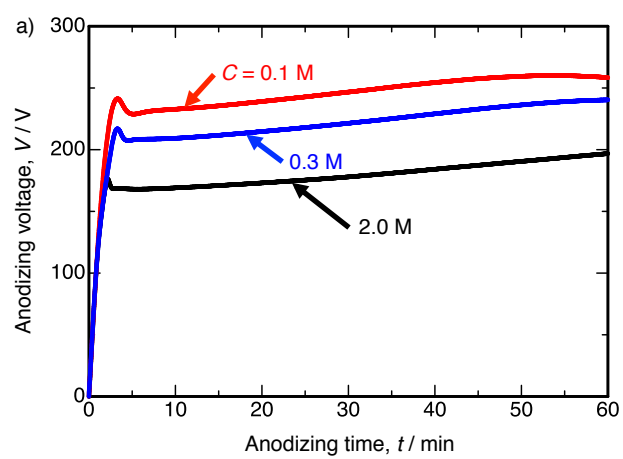


Fig. 6

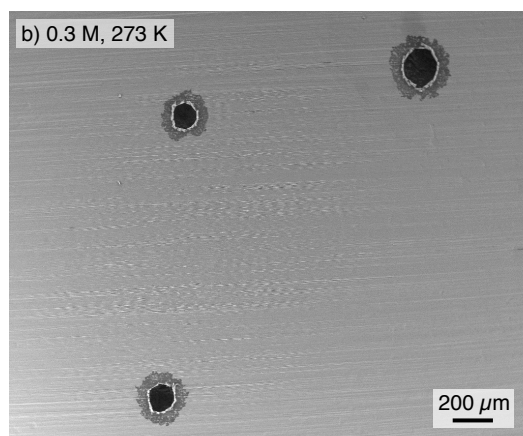
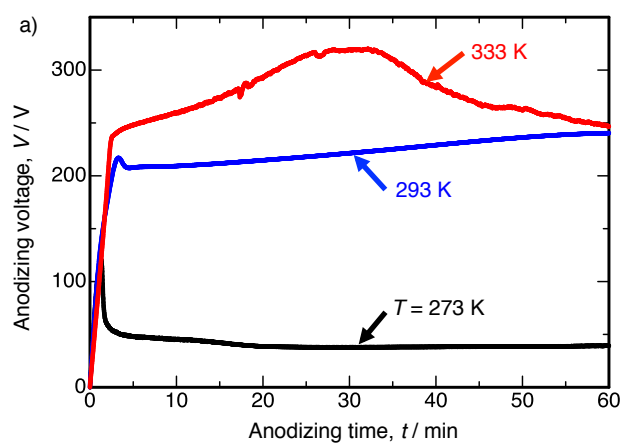


Fig. 7

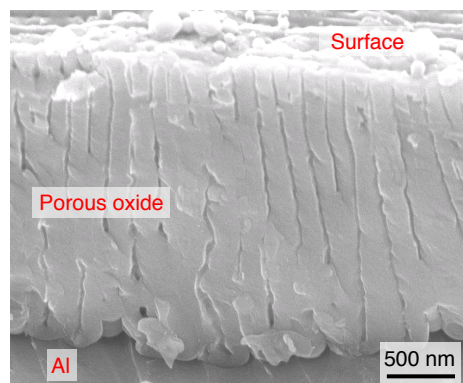


Fig. 8