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Porous Aluminum Oxide Formed by Anodizing in Various Electrolyte Species

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Abstract

Anodizing of aluminum and its alloys is widely investigated and used for corrosion protection, electronic devices, and micro-/nanostructure fabrication. Anodizing of aluminum in acidic solutions causes formation of porous aluminum oxide films, which consists of numerous hexagonal cells perpendicular to the aluminum substrate, and each cell has nanoscale pores at its center. Recently, highly ordered porous aluminum oxide has been widely investigated for various novel nanoapplications. In this review article, we introduce the fundamentals of anodic oxide films including barrier and porous oxides. Then, we summarize the electrolyte species used so far for porous oxide fabrication and describe the self-ordering conditions during anodizing in these electrolyte solutions. Fabrication of highly ordered porous oxides through the vertical section can be achieved by a two-step anodizing and nanoimprint technique. Various nanoapplications based on the ordered porous oxide are also introduced.

Key words: Aluminum; Anodizing; Electrolyte; Anodic oxide film; Porous aluminum oxide; Self-ordering

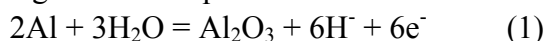
1. Introduction

Anodizing (anodization) is one of the most important electrochemical processes of aluminum and its alloys and has been widely used for the surface finishing for a very long time. Aluminum anodizing is typically achieved by electrochemical anodic oxidation using various aqueous solutions involving electrolyte species. Anodic oxide films including barrier and porous oxide films can be formed uniformly on the aluminum substrate through a simple anodizing process without any special equipment. Because anodic aluminum oxide film has a wide variety of physical and chemical properties including corrosion resistance, hardness, wettability, adhesion, insulation, dielectric, and luminescence, the anodizing process is extremely useful in various applications of industrial aluminum and its alloys for aircraft, automobiles, buildings, and electronics. Notably, characteristically ordered nanoporous features of anodic oxide film have very recently attracted attention for various micro- and nanostructure fabrication techniques in the fields of chemical, physical, environmental, and biological sciences. Moreover, anodizing techniques can easily be applied to other valve metals such as titanium, zirconium, hafnium, niobium, tantalum, and tungsten, and various valve metal oxides with nanoporous/nanotubular features can easily be fabricated via anodizing.

In the present review article, we introduce the fundamentals of anodizing science and technology, especially focused on the electrolyte species used. We describe the two types of anodizing oxide films: barrier and porous oxides, typical electrolyte species used for porous oxide formation. In addition, fabrication of self-ordered porous oxide by anodizing under appropriate electrochemical conditions will be discussed, and we briefly explain the latest novel applications using ordered porous aluminum oxides.

2. Barrier and porous oxide films formed by aluminum anodizing

Anodizing is an electrochemical anodic oxidation process, used especially to form an oxide film on the electrode substrate. Figure 1 shows a schematic model of a typical anodizing setup, including an electrochemical cell, an aluminum anode, and a cathode, and the setup is very simple. The anodizing solution is generally stirred with a magnetic stirrer during anodizing. When aluminum is anodized in aqueous electrolyte solutions, two different aluminum oxide films are typically formed on the aluminum substrate: barrier and porous oxide films [1-3]. Figure 2 shows schematic models of these two types of anodic oxide films formed on the aluminum substrate and corresponding electrochemical transients during constant current and voltage anodizing. Aluminum anodizing in neutral solutions including borate [4-7], adipate [8,9], and phosphate [10,11] electrolytes causes the formation of barrier anodic oxide film (Fig. 2a) according to the following chemical equation:



Barrier oxide film consists of a dense, compact thin amorphous oxide layer with a maximum thickness of approximately 1 μm . The thickness of the barrier oxide, δ (nm), is proportional to the electrochemical potential (nearly equal to applied voltage), E (V), applied to the aluminum specimen during anodizing and can be calculated using the

following equation:

$$\delta = kE \text{ [nm]} \quad (2)$$

where k is a proportionality constant, generally calculated to be approximately $1.5 \text{ (V nm}^{-1}\text{)}$. This constant is obtained from detailed observations of the vertical cross-section of the anodized specimens by transmission electron microscopy [10]. Constant current anodizing in neutral solutions causes a linear increase with anodizing time, and then the linear oxide formation stops abruptly at high potential, called the “breakdown potential” [12,13]. For example, the breakdown of the barrier oxide occurs at approximately 420 V in the 0.5 M H_3BO_3 /0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ typical borate solution. The breakdown potential depends on the type and concentration of the electrolyte used [4]. In the case of constant voltage anodizing in neutral solutions, the current density increases drastically just after the voltage is applied and then gradually decreases with anodizing time. This current transient corresponds to the formation of a barrier oxide film in the initial stage with subsequent repair of defects in the barrier oxide. The barrier anodic oxide films have been investigated in great detail by many researchers and are used mainly for electrolytic capacitor applications due to their high dielectric property [14-19].

Aluminum anodizing in acidic electrolyte solutions causes the formation of a porous anodic oxide film on the aluminum substrate (Fig. 2b) [1-3,20-23]. Porous oxide film is also known as anodic aluminum oxide (AAO), porous anodic alumina (PAA), anodic porous alumina, porous anodic aluminum oxide (PAOX), etc., and these names correspond to the same “porous oxide film” fabricated by anodizing in acidic solutions. Porous oxide film possesses a characteristic honeycomb structure with nanopores, as described in Fig. 2b. This honeycomb structure was first reported by Keller et al. in 1953 (Keller-Hunter-Robinson model) [24]. The porous oxide film consists of numerous nanoscale hexagonal cells perpendicular to the aluminum substrate, and each cell has a nanopore at the center. These pores are separated from the aluminum substrate by a thin hemispherical barrier oxide. Therefore, the porous oxide film consists of two layers, including an upper “porous layer” and a lower “barrier layer”. Constant current aluminum anodizing in acidic solutions exhibits the characteristic voltage-time transient, namely, a) linear increase of the voltage in the initial stage, b) slightly decreasing, and c) steady, as shown in Fig. 2b. These changes correspond to a) barrier oxide film growth on the aluminum substrate, b) porous layer formation by selective dissolution of the barrier oxide into the acidic solution, and c) steady-state growth of the porous oxide film with balanced oxide formation and dissolution during anodizing. The current-time transient obtained by constant voltage anodizing in acidic solutions also corresponds to the growth behavior of the porous oxide film.

The cell diameter (meaning identical to interpore distance) of the porous oxide film formed by anodizing in acidic solutions increases with the anodizing voltage [25]. Thus, high-voltage anodizing provides porous oxide films with larger cell diameters. The electrolyte species used by anodizing is strongly affected by the maximum voltage that can be applied. The use of an inappropriate electrolyte species during high voltage anodizing causes the formation of non-uniform oxides by a phenomenon called “burning”. It is therefore important to choose the appropriate electrolyte and voltage for

uniform growth of a porous oxide film.

The growth behavior of porous anodic oxide films has also been reported by many research groups using high resolution transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Several review articles are very useful for further understanding of the growth mechanism of a porous oxide film [1-3].

3. The electrolyte species for porous aluminum oxide formation

The nanomorphology and chemical and physical properties of a porous oxide film depend strongly on the electrolyte species that is used. Porous oxide film is known to be formed by acidic electrolytes, which provide low acid dissociation constants (pK_a). Figure 3 summarizes the useful electrolytes that have been reported to date for the fabrication of porous oxide films on aluminum. These electrolytes can be classified into the following three groups: inorganic acids, organic carboxylic acids, and organic cyclic oxocarbonic acids. The anodizing behaviors of aluminum in these electrolyte solutions will now be discussed.

3.1 Inorganic acid electrolytes

Sulfuric acid (H_2SO_4) anodizing was patented by Gower et al. in 1927 for the surface finishing and corrosion protection of aluminum and its alloys [26]. Since then, sulfuric acid is one of the most popular electrolytes for the formation of porous oxide films on aluminum, from laboratory level basic research to industrial applications because of the low cost of the anodizing electrolyte. The porous oxide obtained by sulfuric acid anodizing is a colorless transparent film. Sulfuric acid anodizing works effectively at relatively low voltage measured at 15-40 V [27-34], and these voltage values are the smallest in the major acidic electrolyte species. The corresponding cell diameter of the porous oxide film formed by sulfuric acid anodizing is also the smallest and is measured to be below 100 nm. Therefore, sulfuric acid is the most suitable electrolyte to fabricate the nanoscale small pore in the porous oxide films. Moreover, an ultra-narrow hexagonal cell could be obtained successfully by sulfuric acid anodizing at less than 15 V under the improved experimental conditions [35-37]. Sulfuric acid anodizing is also used for a “hard anodizing process” in the fields of various industrial components. Hard anodizing operates in sulfuric acid at low temperatures, typically 273 K or below, and causes the formation of a hard porous oxide film with a large Vickers hardness [38]. Therefore, the mechanical properties of the aluminum and its alloys covered by the hard oxide films are greatly improved.

Selenic acid (H_2SeO_4) anodizing was first reported by us in 2013 as a new electrolyte for porous oxide fabrication [39,40]. The chemical structure of selenic acid is very similar to the chemical structure of sulfuric acid, and selenic acid is a strong diacid with dissociation constants of $pK_{a1} = -3.0$ and $pK_{a2} = 1.7$, the same as the dissociation constants of sulfuric acid. Importantly, selenic acid is easily soluble in water and can be used as the anodizing solution. Selenic acid anodizing typically works at approximately 25-50 V. This voltage range is a little larger than the voltage range for sulfuric acid

anodizing, and the corresponding cell diameters are larger, 60-110 nm. During selenic acid anodizing, reddish selenium is cathodically deposited on the counter electrode because of the reduction of selenate ions with hydrogen gas evolution. Selenic acid anodizing produces a colorless transparent porous oxide film, as does sulfuric acid anodizing. Because a) selenic acid is a relatively expensive electrolyte, b) anodizing voltage and the corresponding cell diameter of the porous oxide are similar to the anodizing voltage and cell diameter obtained by anodizing in sulfuric and oxalic acid, and c) selenate electrolyte is decomposed at the cathode during anodizing, selenic acid anodizing may not be available for industrial anodizing applications. However, the comparison of the growth behavior and the corresponding nanofeatures of the porous oxide films formed in sulfuric and selenic acid may be useful for understanding the mechanism of porous oxide growth.

Chromic acid (H_2CrO_4) anodizing was patented by Bengough et al. in 1923 [41] and is one of the oldest anodizing processes. The porous oxide film formed by chromic acid anodizing has a grayish color and was widely used for surface finishing of aluminum and its alloys in industrial applications for a very long time due to its high corrosion resistance. However, chromic acid anodizing recently has a tendency to be avoided because of the toxicity of hexavalent chromium (Cr^{6+}) when chromic acid is used as the electrolyte solution. Chromic acid anodizing typically operates at 20-50 V, and the porous oxide film that is obtained possesses a pore branching colonial structure [42-46] different from the porous oxide obtained by anodizing in other electrolyte solutions. Therefore, the ideal hexagonal cell structure described in Fig. 2b cannot be fabricated by chromic acid anodizing, and chromic acid anodizing cannot be applied to nanofabrication with the ordered porous structures.

Anodizing via phosphoric acid (H_3PO_4) was reported by Taylor et al. in 1945 [47]. Phosphoric acid anodizing typically operates at relatively high voltages, 60-195 V [48-53], and the porous oxide film with large cell diameter measuring up to 500 nm can be formed on the aluminum substrate. The oxide film formed by phosphoric acid anodizing exhibits a light blue appearance. Because phosphoric acid anodizing easily causes formation of sub-micrometer-scale large cells, phosphoric acid anodizing has been widely used for the fabrication of various periodic nanostructures with similar sub-micrometer periods in the field of nanotechnology.

Sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$) anodizing was first reported by Piontelli in 1941, but the growth behavior and nanostructural features of the porous oxide formed by sulfamic acid anodizing are still unknown [54-56]. Recently, sulfamic acid anodizing was also reported by several researchers for mainly luminescence applications. Porous oxide films with irregular cell arrangement can be formed in sulfamic acid at the relatively low anodizing voltage of 5-35 V.

Yokovleva et al. worked on aluminum anodizing in concentrated nitric acid (HNO_3) solution and reported the possibility of porous oxide film formation by nitric acid anodizing [57]. However, extremely nonuniform oxides with little porous structures were observed in SEM images, and these oxides may be different from typical porous oxides obtained by anodizing in other acidic solutions.

3.2 Organic carboxylic electrolytes

Oxalic acid (HOOC-COOH) anodizing was patented by Kujirai et al. in 1923 [58]. Oxalic acid is the simplest dicarboxylic acid with a short chain and low dissociation constants, and oxalic acid anodizing has been widely investigated by many research groups [59-66]. Although oxalic acid is relatively expensive compared with sulfuric acid, oxalic acid anodizing is also widely used for industrial applications. Oxalic acid anodizing is typically performed at 20-65 V, and these anodizing voltages correspond to the middle range between sulfuric acid anodizing and phosphoric acid anodizing. The porous oxide film formed by oxalic acid anodizing exhibits a yellowish color, and the cells with diameters larger and smaller than 100 nm are arranged in the oxide film.

Malonic acid ($\text{HOOC-CH}_2\text{-COOH}$) is also a useful electrolyte for the fabrication of porous oxide films, and several research groups have reported on the growth behavior of the anodic oxide during malonic acid anodizing [67-72]. Malonic acid anodizing works effectively at approximately 80-140 V, and porous oxide films with relatively large cells compared with oxalic acid anodizing, measuring approximately 200-300 nm in diameter, can be formed on the aluminum substrate. Generally, the anodizing voltage for porous oxide formation may increase with the size of the chemical structure of the electrolyte used. Porous aluminum oxide films can be fabricated by anodizing in dicarboxylic acids such as oxalic (C2) and malonic acid (C3) electrolytes, as described above. However, dicarboxylic acids with a long main-chain structure, including succinic (C4), glutaric (C5), adipic (C6), pimelic (C7), suberic (C8), azelaic (C9), and sebacic acid (C10) cannot provide the porous oxide films because of their relatively high dissociation constants [73,74].

Citric acid ($\text{HOOC-CH}_2\text{-C(OH)(COOH)-CH}_2\text{-COOH}$) is very useful for fabrication of porous oxide films with large cell diameters [75-78]. Citric acid anodizing is typically performed at the high voltage of 200-370 V, and porous oxide films with cells above 500 nm in diameter are obtained. Malic acid ($\text{HOOC-CH(OH)-CH}_2\text{-COOH}$) anodizing is also known as a high voltage anodizing electrolyte and operates at 200-450 V [75,79,80]. However, this high voltage anodizing in citric and malic acids easily causes the formation of a non-uniform anodic oxide with a black burned oxide film during anodizing.

Several other useful electrolyte species for porous oxide film formation have been reported to date: tartaric acid ($\text{HOOC(CHOH)}_2\text{COOH}$) at 195-240 V [72,75,81,82], glycolic acid ($\text{CH}_2\text{OH-COOH}$) at 60-150 V [75], formic acid (H-COOH) at 18-30 V [83], tartronic acid (HOOC-C(OH)-COOH) at 26 V [84], acetylenedicarboxylic acid ($\text{HOOC-C}\equiv\text{C-COOH}$) at 88-95 V [85], ketoglutaric acid ($\text{HOOC-CO-(CH}_2)_2\text{-COOH}$) at 170-260 V [86], and acetonedicarboxylic acid ($\text{HOOC-CH}_2\text{-CO-CH}_2\text{-COOH}$) at 150 V [86]. Because the formation of porous oxide films on aluminum is strongly affected by the acid dissociation constants of the electrolyte used, additional carboxylic electrolytes for porous oxide formation may be still found by examining dissociation constants in further research work [86].

3.3 organic cyclic oxocarbonic electrolytes

Cyclic oxocarbonic acids including squaric acid with a four-membered ring, croconic acid with a five-membered ring, and rhodizonic acid with a six-membered ring have recently been reported as useful electrolytes for the formation of porous oxide films [87,88]. The porous oxide films can be obtained under the following electrochemical conditions: squaric acid at 100-120 V, croconic acid at 90-125 V, and rhodizonic acid at 80-160 V. The growth behavior of the porous oxide formed using these oxocarbonic acids is still unknown, and it is interesting to understand the growth behavior for the formation mechanism of porous oxides, although these organic electrolytes are expensive and not suitable for industrial applications. Typical anodizing voltages and the corresponding electrolytes are schematically summarized in Fig. 4.

3.4 Other electrolytes

Several anodizing research groups have reported the really interesting results about the growth behavior of anodic oxides during anodizing with other electrolytes. Takahashi et al. reported that porous aluminum oxide films could be formed by anodizing in neutral borate solution ($\text{H}_3\text{BO}_3/\text{Na}_2\text{B}_4\text{O}_7$) at a high temperature [89]. Baron-Wiechec et al. reported aluminum anodizing in a borax ($\text{Na}_2\text{B}_4\text{O}_7$) solution at 333 K and successfully fabricated a porous oxide film [90]. Neutral electrolyte anodizing at a high temperature causes the formation of porous aluminum oxide film by active dissolution of aluminum oxide during anodizing. Noguchi et al. investigated the anodizing behavior via aluminum anodizing in alkaline solutions containing ammonium fluoride, ammonium tartrate, ammonium carbonate, and ammonium tetraborate, and porous oxide films with nanopores measuring 10-150 nm in diameter were successfully formed on the aluminum substrate [91]. However, it is difficult to obtain a well-ordered porous oxide film by anodizing in these neutral and alkaline electrolyte solutions, but the growth behavior of the anodic oxides is very interesting for novel porous oxide fabrication.

The mixture of the electrolyte species is also a useful approach to control the anodizing voltage and corresponding cell diameter. Sulfuric/oxalic [92-94] and oxalic/phosphoric [95] acid mixtures were recently reported for the porous oxide formation. The oxide films formed by these mixed electrolytes exhibit intermediate properties of the electrolytes used.

4. Fabrication of highly ordered porous aluminum oxide

Porous oxide films anodized in several appropriate electrolyte solutions under the appropriate experimental conditions, including concentrations, temperatures, and voltages, are self-ordered during anodizing, and highly ordered porous oxide can be fabricated. In the pioneering work of Masuda et al., they first found that long period oxalic acid anodizing at 40 V at appropriate concentrations and solution temperatures greatly improved the regularity of the cell arrangement and produced an ideally arranged honeycomb porous structure [96]. Such self-ordering behavior of the porous oxide is also found via anodizing in the several following specific electrolyte solutions

[97,98]: sulfuric acid at 19-25 V [30,98], oxalic acid at 40 V [66,96,98-100], selenic acid at 42-48 V [39,40], malonic acid at 120 V [72], phosphoric acid at 160-195 V [48,97], and tartaric acid at 195 V [72]. Figure 5 demonstrates the cell arrangement of the porous oxide films formed by 3.0 M selenic acid anodizing at 273 K for 3 h. The oxide-aluminum interfaces are shown in the SEM images. Disordered arrays are distributed on the aluminum substrate at 37 V. In contrast, the regularity is greatly improved by anodizing at 46 V, and ideal cell arrangements can successfully be obtained. Figure 6 summarizes the self-ordering anodizing voltage and the corresponding cell diameter of the porous oxide via the various ordering electrolytes described above. The cell diameter increases linearly with the ordering voltage, described as follows:

$$D = 2.5 V [\text{nm}] \quad (3)$$

where D corresponds to the cell diameter and V corresponds to the ordering voltage. Very recently, we found that etidronic acid (1-hydroxyethane-1,1-diphosphonic acid) anodizing at the high anodizing voltage of 210 to 270 V causes the formation of a self-ordered porous oxide with a cell diameter measuring 530-670 nm, as described in Fig. 6 [101]. This novel electrolyte is very useful for the fabrication of a highly ordered porous oxide with large cell diameters above 500 nm. As described in Fig. 6, the self-ordering voltages are still limited to several voltage regions by a few acidic electrolytes, and there are many vacant regions in the figure (namely, no appropriate electrolyte and also no self-ordering voltage). Therefore, the discovery of additional electrolytes is very important for self-ordered porous oxides with complete control of cell diameters, and several research groups at this time are investigating to find novel electrolytes for porous oxide fabrication.

In the typical anodizing using a simple anodizing electrochemical setup, higher electric fields cause the formation of nonuniform burnt oxide on the aluminum substrate [72,77,102,103]. To extend the self-ordering voltage and perform the higher voltage anodizing without burning, it is important to remove the Joule's heat generated from the anodizing specimen effectively. This approach is generally called "hard anodizing" (note that the original meaning of the hard anodizing is a formation process of a hard porous oxide film with large Vickers hardness). Figure 7 shows the schematic model of the electrochemical cell in the hard anodizing. The Joule's heat generated from the specimen during hard anodizing is effectively removed using a heat sink on the back side of the specimen. The hard anodizing allows the fabrication of a self-ordered porous oxide with various cell diameters under high voltage conditions: sulfuric acid at 27-80 V to 72-145 nm [104], oxalic acid at 120-150 V to 220-300 nm [105], and phosphoric acid at 195 V to 320-380 nm [106]. In addition, several research groups have reported using the advanced hard anodizing technique to further extend the self-ordering voltage and the corresponding cell diameters [107-111]. Noh et al. have reported the fabrication of highly ordered nanotubular aluminum oxide by hard anodizing [112]. Although the anodizing area is limited to one side (surface) of the specimen during anodizing, hard anodizing is an effective process to fabricate the self-ordered porous oxide with various nanofeatures.

Another approach to extending the self-ordering voltage and also to avoid burning during high voltage anodizing is the use of organic solvents such as ethylene glycol and glycerol. These organic solvent solutions including the electrolyte allow ultra-high voltage anodizing without burning, different from aqueous solutions. Fabrication of ordered porous alumina with higher than 500 nm and micrometer-scale cell diameters is successfully achieved via anodizing in organic solvents, including citric acid electrolyte [113-116].

Figure 8a shows the schematic models of the vertical cross-section of the anodic porous oxide films formed by self-ordering anodizing. Generally, the aluminum specimen is electropolished in a solution of a mixture of $\text{HClO}_4/\text{CH}_3\text{COOH}$ or $\text{HClO}_4/\text{C}_2\text{H}_5\text{OH}$ before the anodizing [117-118]. During subsequent self-ordering anodizing, the nanopores are formed in a disorderly fashion in the oxide film in the initial stages, and then well-ordered nanopore structures are formed at the interface between the anodic oxide and the aluminum substrate [119]. Therefore, highly ordered anodic porous oxides through the top surface to the bottom interface cannot be obtained via a simple anodizing method. The quantitative arrangement analysis of the porous oxide can be achieved by fast Fourier transform of the microscope images [44,45,64,65,120-124]. To produce a highly ordered porous oxide with whole vertical regions, the following two-step anodizing method is available: a) first anodizing, b) selective dissolution of the anodic oxide in a $\text{CrO}_3/\text{H}_3\text{PO}_4$ solution at a high temperature, and c) second anodizing using the well-ordered template aluminum, fabricated by steps a) and b), as described in Fig. 8b and 8c [96,125,126]. Although the cell arrangement of the anodic oxide in a large area is affected by the crystal grains of the aluminum substrate [127,128], near-perfect ordered porous aluminum oxide can easily be obtained via two-step and long anodizing. Another possible technique for the highly ordered porous oxide is achieved by combination of anodizing with a nanoimprint method (Fig. 8d) [129-133]. A perfectly ordered porous oxide can be fabricated by the imprinting process using a perfectly ordered stamp and subsequent anodizing under appropriate self-ordering conditions, although an expensive imprinting stamp is needed.

5. Various nanoapplications based on the porous aluminum oxide

As described above, highly ordered porous aluminum oxide with a high aspect ratio and controllable nanoscale cell diameter can easily be fabricated via aluminum anodizing. Although periodic nanostructures can also be obtained by other nanostructure fabrication techniques represented by photolithography, the ease of anodizing without any expensive equipment is very important for various nanotechnology researchers. Using characteristic nanostructural features, anodic porous aluminum oxide has been widely investigated for many nanoapplications: antireflection structures [134-139], reflectors [140-142], diodes [143-145], plasmonic devices [146-149], sensors [150-152], containers [153,154], catalyst supports [155-157], masks [158-160], emulsification filters [161,162], magnetic recording media [163-165], memory devices [166-168], photovoltaic devices [169], nanomeshes [170], etc. Greatly wide-ranging applications of anodic porous oxides have been reported to date.

6. Summary

We introduce the fundamentals of porous aluminum oxide films fabricated by anodizing in this review. It is important to choose an appropriate electrolyte and anodizing conditions for ordered porous aluminum oxide fabrication. Recently, porous oxide technology including nanotube structures extends not only to aluminum but also to other metals such as titanium [171,172], zirconium [173], hafnium [174], niobium [175], tantalum [176], and tungsten [177]. Moreover, a third generation anodic oxide, different from barrier and porous oxide, anodic alumina nanofibers fabricated by novel anodizing has been investigated by us. In this investigation, ultra-high-density single nanometer scale alumina nanofibers grow on the aluminum substrate during anodizing [178]. Anodizing science and technology will continue to evolve in the future.

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Captions

Figure 1. Schematic representation of the typical anodizing setup.

Figure 2. Barrier and porous anodic oxide films on aluminum formed by anodizing.

Figure 3. Summary of the anodizing electrolytes used for porous oxide fabrication.

Figure 4. Summary of the anodizing electrolytes and corresponding anodizing voltages.

Figure 5. Surface images of the anodized specimens in 3.0 H₂SeO₄ solution for 3 h at 273 K and a) 37 V and b) 46 V. The oxide films were selectively removed by chemical etching to observe the growth plane of the porous oxide.

Figure 6. The relationship between the cell diameter, D , and the self-ordering voltage, V , for porous oxide formed in various acidic electrolytes.

Figure 7. Schematic representation of the hard anodizing setup.

Figure 8. Fabrication of a highly ordered porous oxide film by a two-step anodizing and nanoimprint technique.

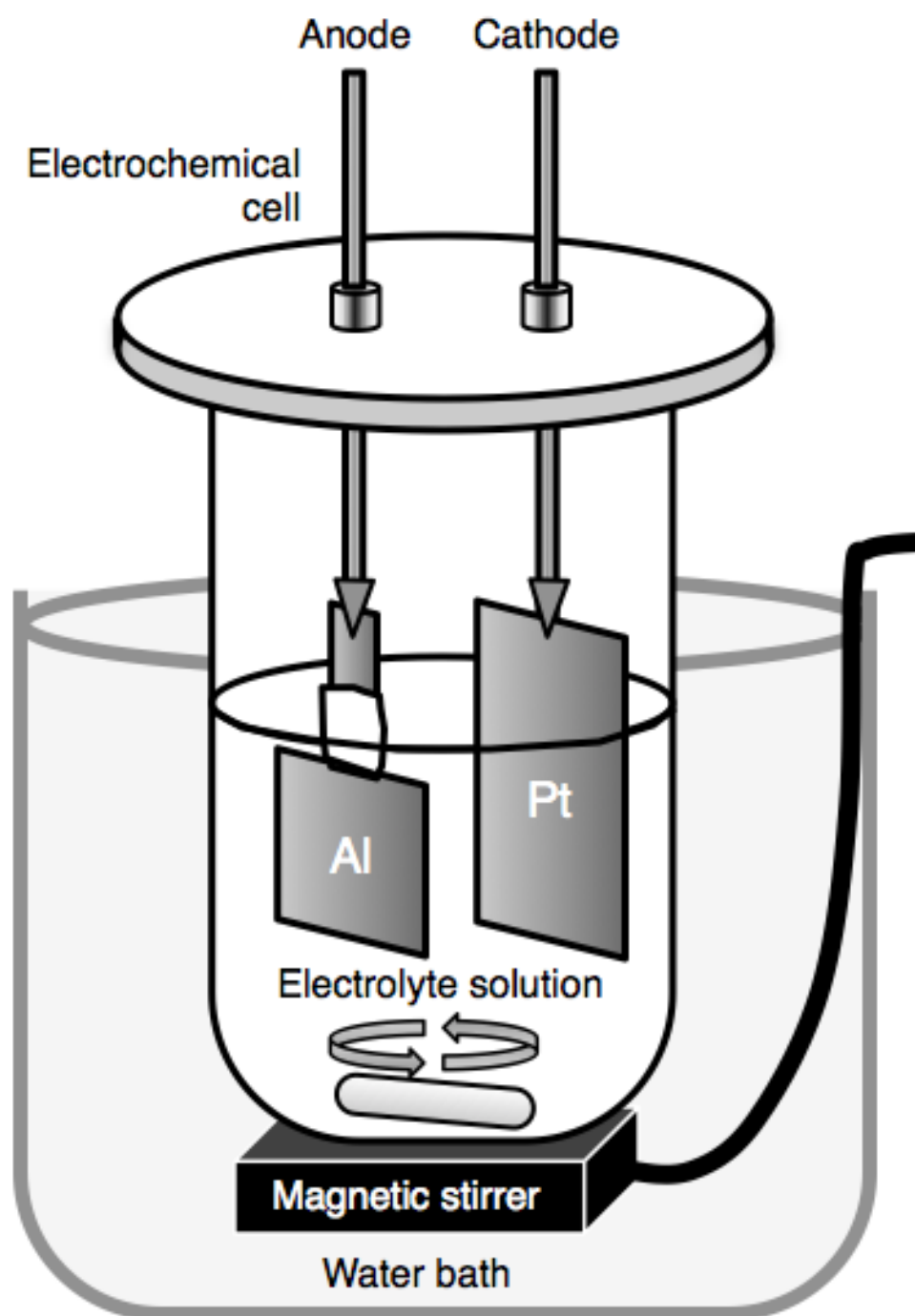
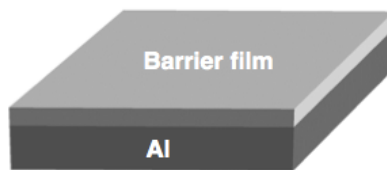
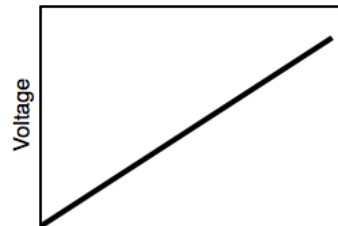


Figure 1.

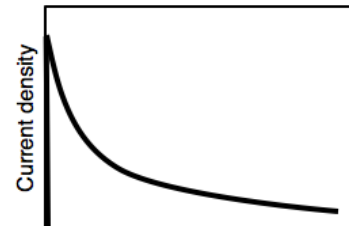
a) Barrier oxide film



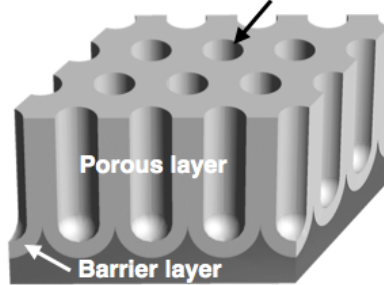
Constant current anodizing



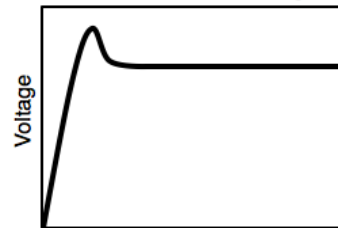
Constant voltage anodizing



b) Porous oxide film



Constant current anodizing



Constant voltage anodizing

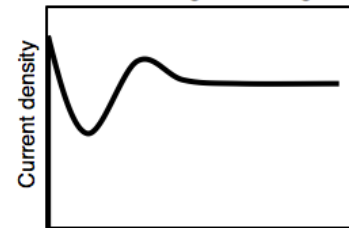


Figure 2.

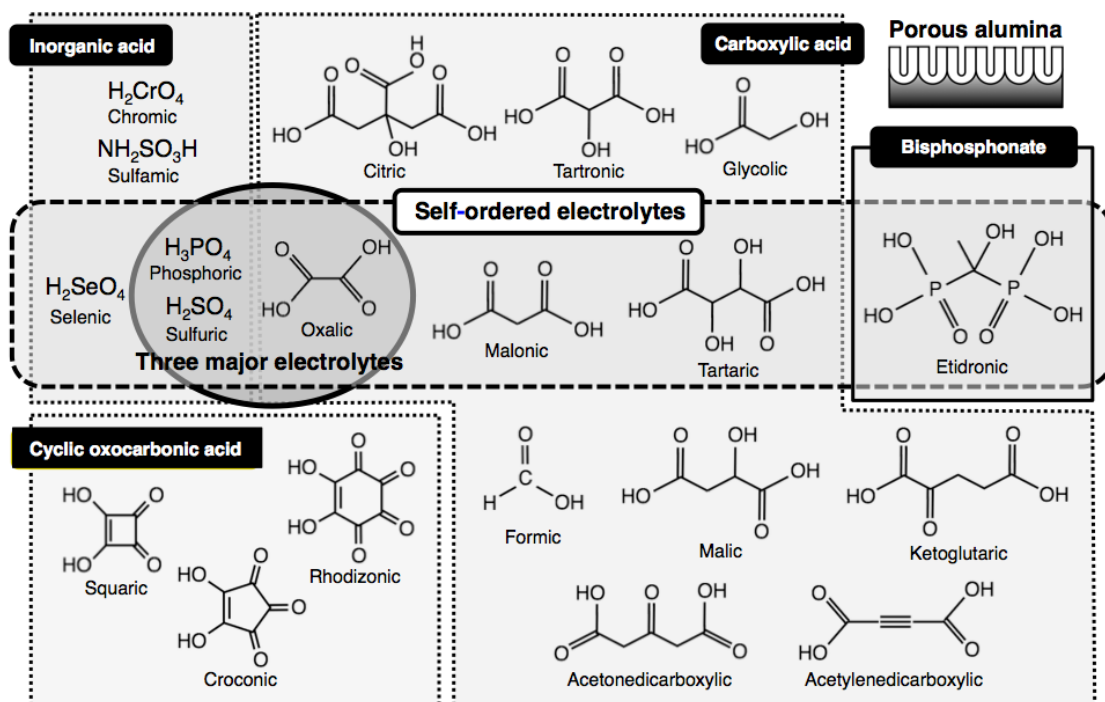


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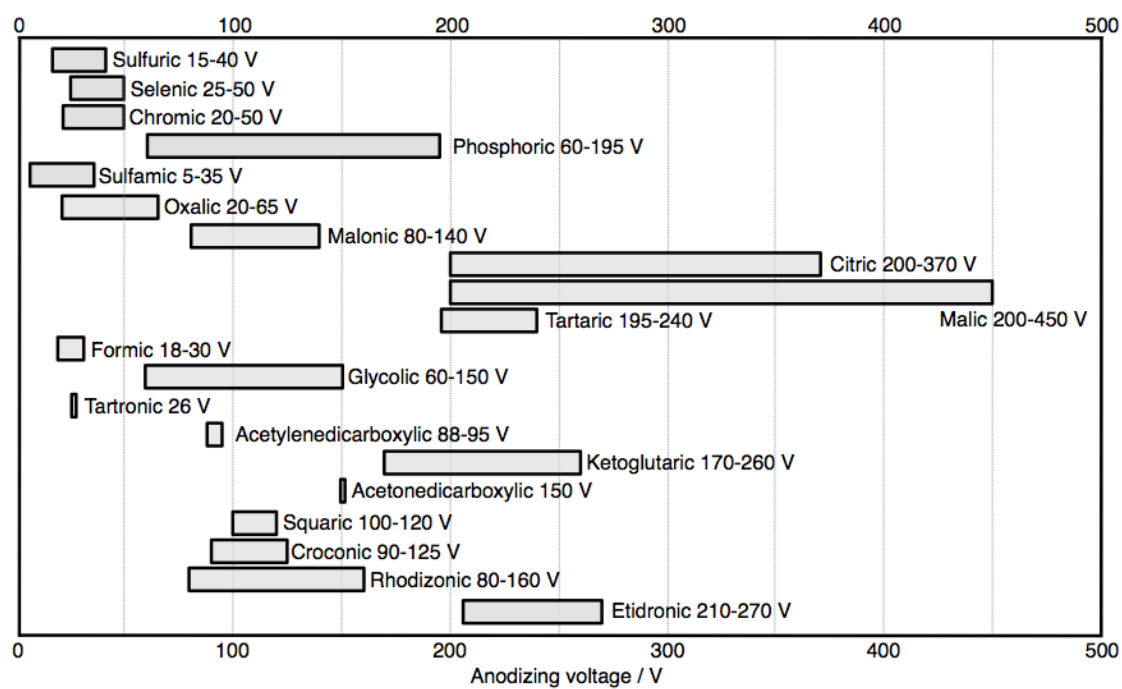


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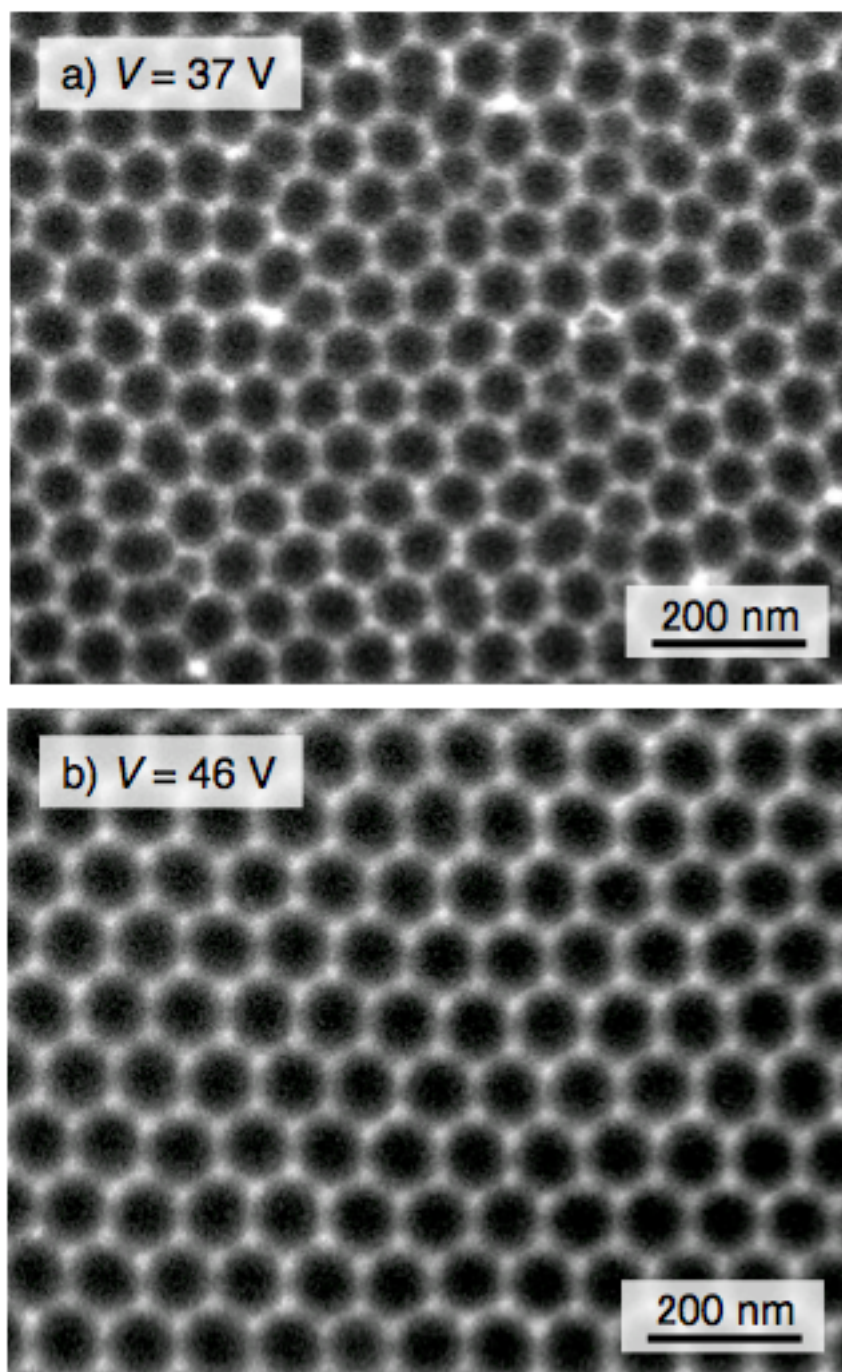


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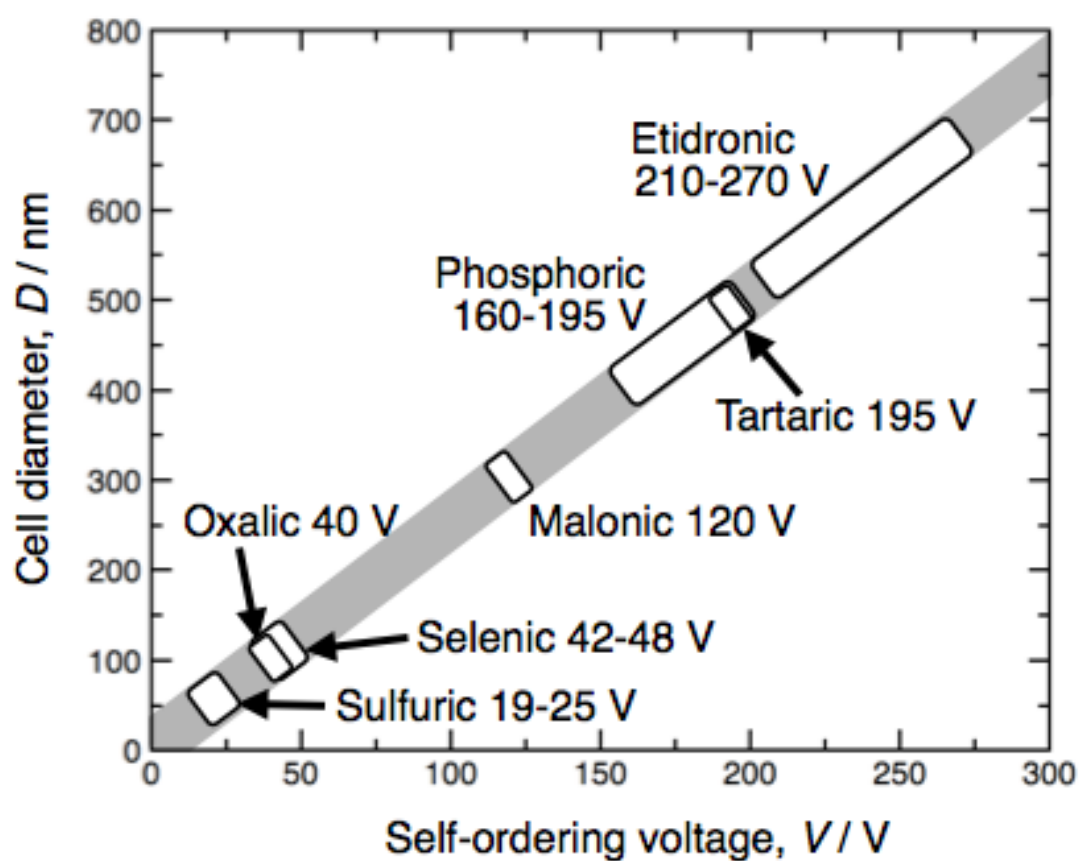


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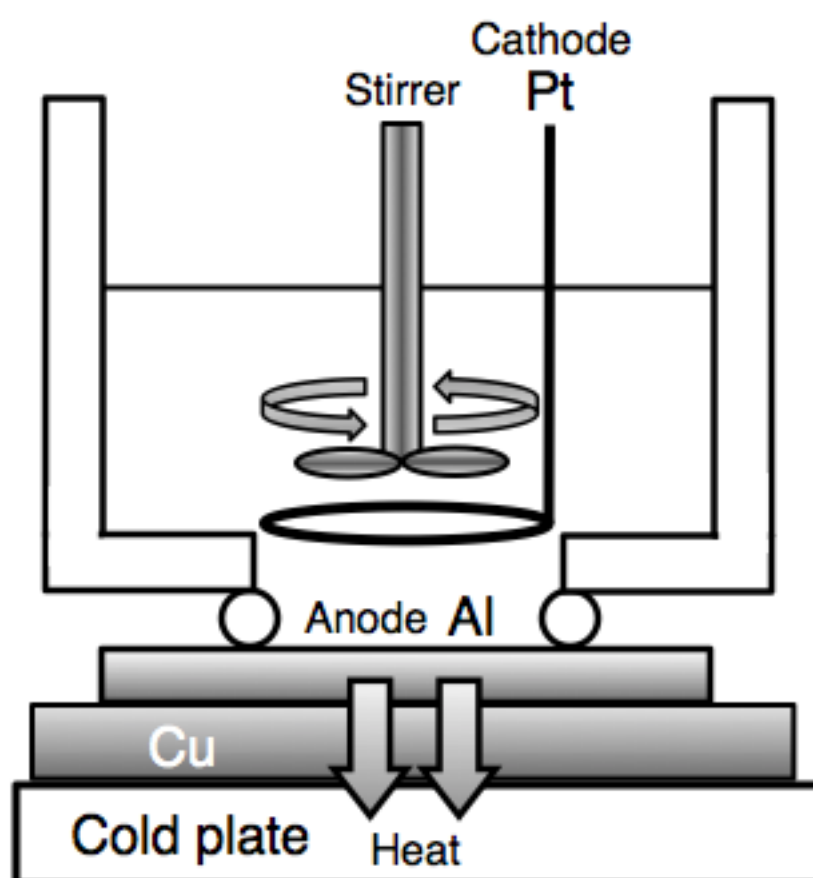


Figure 7.

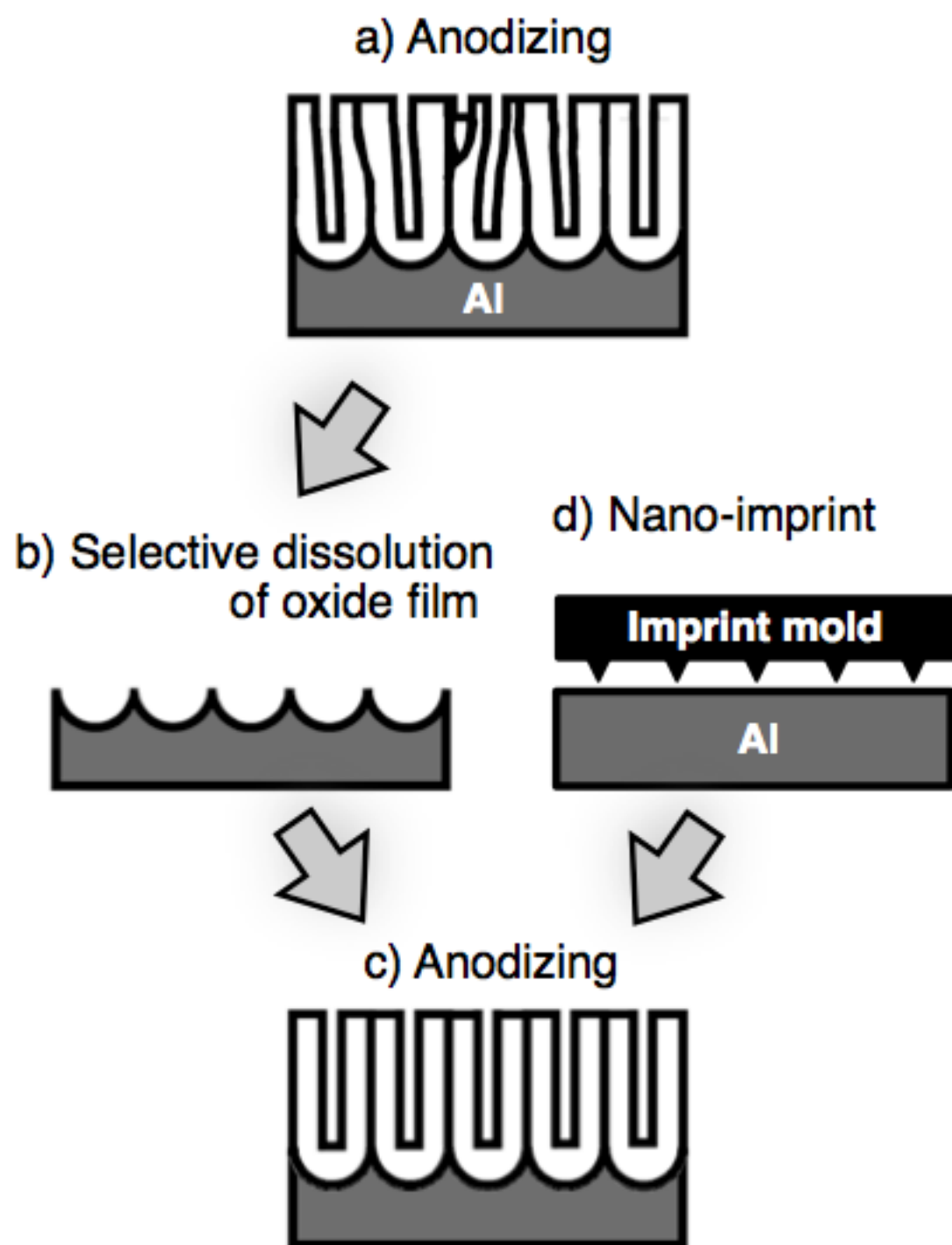


Figure 8.