

The Anodization of Aluminum for Nanotechnology Applications

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In light of the ever-increasing demand for the development of an effective, inexpensive and technologically simple method, a naturally occurring self-organization of oxide nanopores during the anodization of aluminum has recently attracted a vast amount of research attention in the field of nanotechnology. This article gives a brief overview on some of the recent advances in the anodization of aluminum, focusing on the fabrication of highly ordered nanoporous anodic aluminum oxide. Conventional anodization, newly developed hard anodization, pulse anodization process, and generic approaches for the fabrication of three-dimensional pore structures with periodically modulated diameters are discussed.

INTRODUCTION

Anodization is an electrochemical oxidation process employed to increase the thickness of the native oxide layer on the surface of metals (e.g., Al, Ti, Hf, W, Nb, Sn, Zr, etc.) or semiconductors (e.g., Si, InP, GaAs, etc.) (Figure 1a).¹⁻³ Among anodizable materials, aluminum has been of particular interest due to its many profitable engineering properties. In general, anodization of aluminum can result in two different types of anodic oxide depending on the nature of an electrolyte used; a compact and non-porous barrier-type oxide from neutral electrolytes and a porous-type oxide from acidic electrolytes (Figure 1b).³ Over the last several decades, the process, particularly porous-type anodization, has raised substantial technological interest in the industry.^{4,5} Many desirable properties such as higher thickness, hardness, good corrosion resistance, higher abrasive and wear resistance over the native

oxide can be imparted to the aluminum or its alloys by subjecting the metal

to anodic oxidation. The anodic process also provides a suitable surface or base for subsequent electroplating, painting and decorative coloration by incorporation of pigments followed by sealing of the anodized materials.

This electrochemical process has recently drawn a renewed attention in academic research, especially in the field of nanotechnology. An idealized structure of nanoporous anodic aluminum oxide (AAO) is schematically shown in Figure 1c. Anodic aluminum oxide formed by porous-type anodization under a controlled electrochemical condition is characterized by a large number of non-interconnecting parallel pores extending through the film to the oxide/metal interfaces, where each cylindrical nanopore is closed by a thin barrier oxide layer with hemispherical geometry. Each pore and the region surrounding it comprise a hexagonal cell. These cells are self-organized in the form of a hexagonally close-packed structure, like a honeycomb.⁶ Based on the recent development, self-ordered nanoporous AAOs with a uniform pore diameter in the range of 20–400 nm and with a pore density in the range of 10^8 – 10^{10} pores/cm² can conveniently be prepared by anodization of aluminum. The depth of straight nanopores can easily be controlled in the range of a few tens of nanometers to more than several hundred micrometers by varying the anodization time. Due to the unique structural feature of nanoporous AAO and also to the tailoring capability of its structural parameters, the anodization process has attracted scientific attention in the use of the resulting AAO not only as template for fabricating structurally well-defined nanostructures (e.g., arrays of nanodots, nanotubes, and nanowires) in a large quantity,⁷⁻¹² but

How would you...

...describe the overall significance of this paper?

This article conveys some of the latest advances in anodization of aluminum, which has long been an indispensable process in the surface finishing industry, but now becomes one of the most important processes in nanotechnology for developing advanced nanodevices.

...describe this work to a materials science and engineering professional with no experience in your technical specialty?

This article is an introduction to anodization of aluminum, which is a subject of electrochemistry. Anodization of aluminum under a controlled electrochemical condition yields ordered porous alumina with a close-packed hexagonal array of cylindrical nanochannels. The diameter, density, and aspect ratio of pores can be tightly controlled by varying the anodization condition, which makes the porous anodic alumina an important platform in nanotechnology for developing various functional nanostructures.

...describe this work to a layperson?

Anodization of aluminum, an electrochemical oxidation of aluminum, can produce a honeycomb-like nanoporous oxide film. The process was developed for the protection of seaplane parts from corrosive seawater in 1923. The products of the process can be found everywhere around us, for example in cookware, architectural items, vehicles, and machine parts. Now nanotechnology scientists are paying attention to this nearly century-old process for developing various functional nanostructures. This article gives a brief overview on the recent progress in the anodization of aluminum.

as a starting material for developing high-performance sensor, biomedical, photonic, energy harvesting, and memory devices.¹³⁻¹⁷

MILD ANODIZATION

Over the past several decades, studies on aluminum anodization have been driven by the aluminum industry, and thus mostly devoted to the improvement of technical quality of the anodic films for various commercial applications and also to the production at an efficient rate and cost. Although a wide variety of anodization processes and proprietaries have continued to be developed in industry, the spatial ordering and the uniformity of pores in anodic oxide films have not been a matter of concern. Anodic oxide films produced by a typical industrial process, which is represented by hard anodization (HA), are characterized by non-uniform pore structures with numerous micrometer-sized cracks. Thus, they are not suitable for nanotechnology applications.

In 1995, Masuda and Fukuda

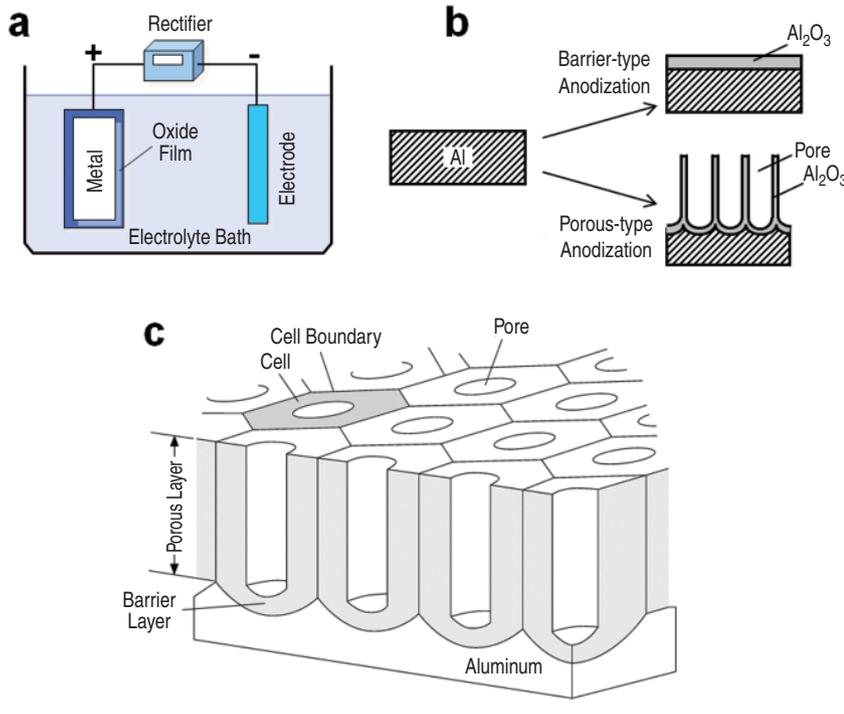


Figure 1. Schematic illustrations showing (a) a simplified anodization setup, (b) two different types of aluminum anodization, and (c) an idealized structure of anodic aluminum oxide (AAO) produced by a porous-type anodization.

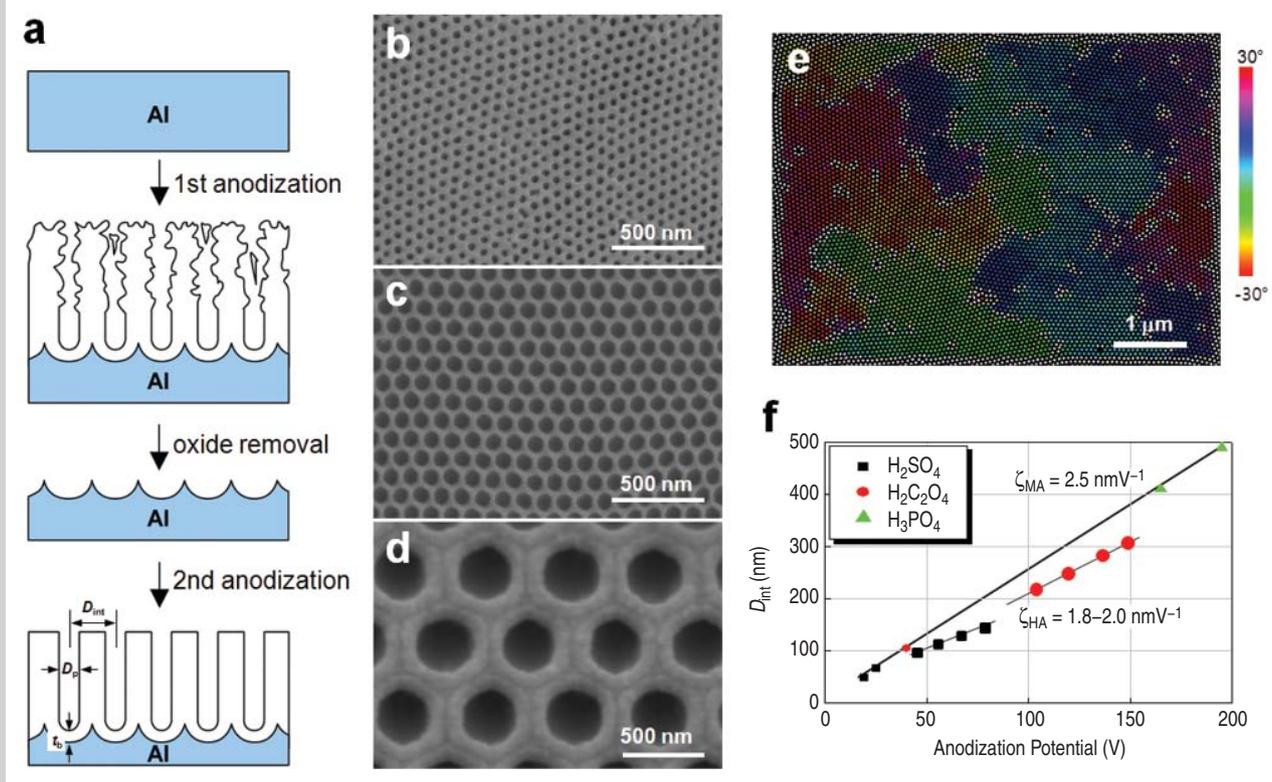


Figure 2. (a) A schematic procedure of a conventional two-step mild anodization (MA) for self-ordered anodic aluminum oxide (AAO). (b-d) Representative SEM micrographs of self-ordered AAOs produced by MA using (b) 0.3 M H_2SO_4 at 25 V, (c) 0.3 M $H_2C_2O_4$ at 40 V, and (d) 1 wt.% H_3PO_4 at 195 V. (e) A color-coded SEM image of AAO formed by two-step MA using 0.3M H_2SO_4 at 25 V, showing a poly-domain structure (Reprinted with permission from Reference 44 © 2008 American Chemical Society). An area with the same color consists of a domain. Pores that have no apparent hexagonal coordination (i.e., defect pores) are marked white. (f) Summary of self-ordering potentials and the corresponding inter-pore distance (D_{int}) in mild anodization (MA) and hard anodization (HA).

found that AAO formed by long-term anodization ($t \sim 160$ h) under a potentiostatic condition ($U = 40$ V) using 0.3 M oxalic acid exhibits a self-ordered cell configuration at the bottom part of AAO as a consequence of gradual rearrangement of the cells initially in a random configuration.¹⁸ They reported that the size of the defect-free domain, in which pores are almost ideally arranged forming a honeycomb structure, increases with the anodization time but is limited to several micrometers.¹⁸ This experimental observation led to the development of the ‘two-step anodization’ process, by which nanoporous AAO with highly ordered arrangement of uniform nanopores can be obtained (Figure 2a).¹⁹ Since then, anodization of aluminum has drawn renewed attention, particularly in the field of nanotechnology research for the application of highly ordered AAO to the development of various functional nanostructures. Many studies have been carried out in an attempt to improve the regularity of the pore arrangement, to control the size and position of the pores, and to understand the development of nanopores and their self-organizing process during anodization of aluminum. Much research effort has focused on the exploration of optimum ordering conditions for the electrolyte systems (i.e., sulfuric, oxalic, phosphoric, and chromic acid) that were investigated by Keller et al. in the early 1950s.⁶

Ordered AAOs that are suitable for nanotechnology applications have been fabricated by mild anodization (MA) of aluminum in a limited processing window, known as ‘self-ordering regime,’ under which self-organized growth of ordered nanopores occurs (Figure 2b–d): (i) sulfuric acid (H_2SO_4) at 25 V for an interpore distance (D_{int}) = 63 nm,^{20,21} (ii) oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) at 40 V for $D_{\text{int}} = 100$ nm,^{18,20,21} and (iii) phosphoric acid (H_3PO_4) at 195 V for $D_{\text{int}} = 500$ nm.²³ Many morphological investigations revealed that structural parameters (e.g., the pore diameter (D_p), interpore distance (D_{int}), barrier layer thickness (t_b)) of AAOs formed under self-ordering regimes depend primarily on anodization potential (U),^{21,24,25} which is in line with the earlier reports.^{6,26–29} The interpore distance (D_{int}) and the barrier layer thickness (t_b) are linearly

dependent on the applied potential (U) with proportionality constants $\zeta = 2.5$ nmV⁻¹ for D_{int} and $\eta = 1.2$ nmV⁻¹ for t_b (Figure 2f).^{6,21,24,28} Pore diameter (D_p) has also been known to increase at a rate of *ca.* 1.3 nmV⁻¹.²⁶ But the potential dependence of D_p is not as sensitive as the interplay between the current density and the temperature, concentration and nature of the electrolyte used.^{30–32} For the self-ordered AAO formed under MA conditions, Nielsch et al. proposed an empirical rule that self-ordering of porous alumina requires a porosity (P) of about 10% irrespective of the anodizing potential and composition of electrolyte and anodization conditions; $P(\%) = \text{the surface area ratio of pores to the whole oxide film} = (\pi/2\sqrt{3})(D_p/D_{\text{int}})^2 \times 100$.²⁴ But there are some reports that self-ordered AAOs can be attained at other porosity (P) values ranging from 10% to 30% depending on MA conditions.^{31,33}

Anodization of aluminum has been extensively studied over the last several decades. But there is still much work to do in order to fully understand the

self-organized formation of oxide nanopores. For self-organized growth of AAOs, mechanical stress at the metal/oxide interface that is associated with volume expansion during oxidation of aluminum was proposed as a main driving force for the close-packed hexagonal arrangement of oxide nanopores.^{21,34} It is generally accepted for steady-state film growth that oxide nanopores are generated as results of a dynamic equilibrium between the rate of field-assisted oxide dissolution at the electrolyte/oxide (e/o) interface and the rate of oxide formation at the metal/oxide (m/o) interface, which keeps the thickness of the barrier layer constant.^{22,26,30,35,36} However, this dissolution-based pore formation mechanism has been disputed many experiments. Oxygen isotope (¹⁸O) studies indicated that the pore formation does not take place through a simple oxide dissolution process, and suggested that pore formation consists of some kind of oxide decomposition through the direct ejection of Al^{3+} into the solution and the oxide formation

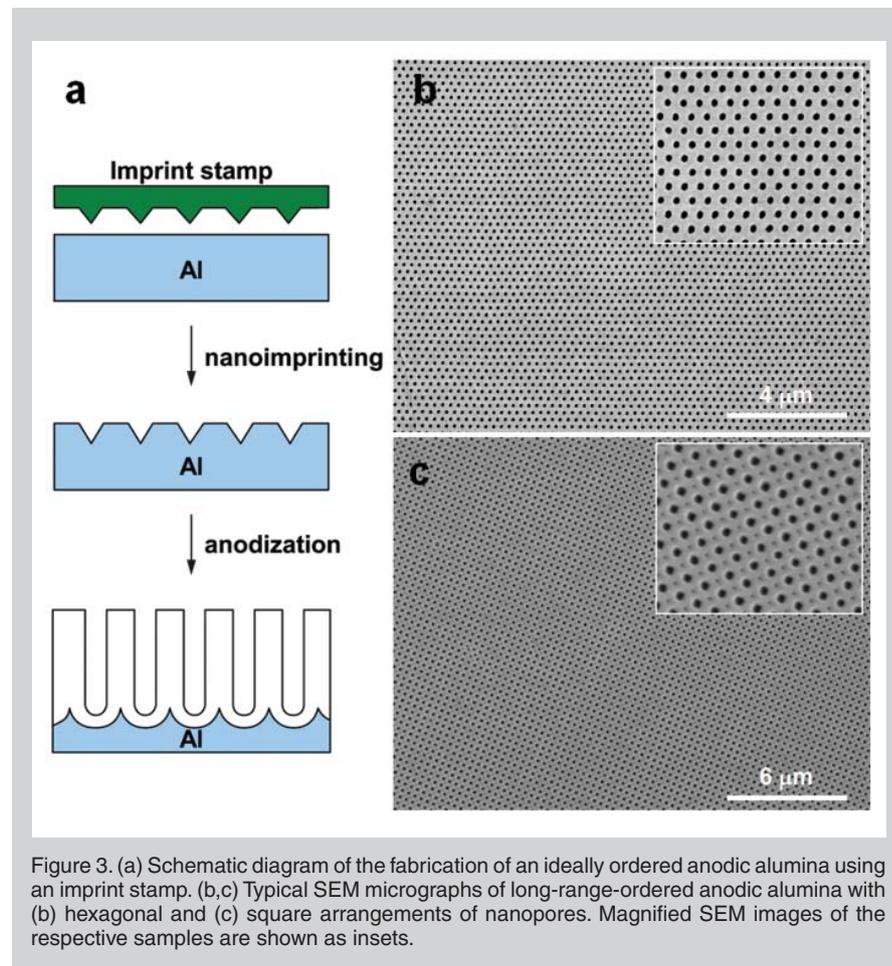


Figure 3. (a) Schematic diagram of the fabrication of an ideally ordered anodic alumina using an imprint stamp. (b,c) Typical SEM micrographs of long-range-ordered anodic alumina with (b) hexagonal and (c) square arrangements of nanopores. Magnified SEM images of the respective samples are shown as insets.

at the *m/o* interface through oxygen transport.^{37,38} Other experiments revealed that the field-assisted oxide dissolution at the pore base is virtually negligible.^{39,40} In line with these results, recent tungsten tracer studies indicate that flow of oxide materials has a major role in forming pores, contrary to expectations of a dissolution model of pore development.^{41,42} The flow of the oxide was suggested to arise from the field-assisted plastic flow of oxide materials from pore base toward the cell boundary and the generation of stress due to electrostriction and the oxidation of aluminum. This flow-based pore formation mechanism has been further supported by theoretical study.⁴³

Anodic aluminum oxide formed by two-step anodization under the self-ordering regimes exhibit a poly-domain structure, in which each domain with an ideally ordered array of nanopores is separated with neighboring domains by a boundary along which defect pores and imperfections in pore arrangement are present.^{18,44} For certain nanotechnology applications, it is highly desirable to utilize long-range ordered AAOs without any defects. Fabrication of ideally ordered AAO with a single-domain configuration over a few mm² area was first demonstrated by Masuda et al. by anodizing a pre-patterned aluminum.⁴⁵ The process involves pre-texturing of the aluminum surface by nanoindentation using an appropriate stamp prior to anodization (see Figure 3). Each indent formed on the aluminum substrate by nanoindentation initiates pore nucleation and leads to a long-range ordered pore arrangement within the stamped area. This method was further extended to fabricate a hole array architecture with square- or triangle-shaped openings in a close-packed square or hexagonal arrangement.⁴⁶ Several groups have achieved pre-patterning of aluminum by employing a focused ion beam (FIB) technique,⁴⁷ holographic lithography,⁴⁸ and microsphere lithography,⁴⁹ and demonstrated fabrication of single-domain AAOs with an arbitrary interpore distance (D_{int}). An economic approach to the fabrication of single-domain AAOs in a wafer-scale is also currently available.⁵⁰

Nanoimprint-assisted anodization

of aluminum provides an effective way to fabricate single-domain AAOs. However, the major limitation of the process is that the attainable maximum aspect ratio or depth of nanochannels maintaining the initial hole configuration depends critically on anodization conditions.¹⁷ High aspect ratio of uniform nanopores can be obtained only under a narrow processing window (i.e., self-ordering regime), which practically limits the range of selection over the interpore distance (i.e., $D_{int} = 63$ nm, 100 nm, 500 nm for 25 V-H₂SO₄, 40 V-H₂CO₄, and 195 V-H₃PO₄ anodization, respectively). When anodization is conducted outside the self-ordering condition, the initial degree of the spatial ordering defined by nanoindentation decreases drastically. These process limitations reduce the potential applications of nanoporous alumina. Substantial efforts have been made to explore a new self-ordering regime in a wider range of D_{int} .^{51–53} The research activity to date includes extending the voltage range by

appropriately tuning of the three well-known acid electrolytes (i.e., H₂SO₄, H₂CO₄, and H₃PO₄) and searching new electrolyte systems. However, applied voltages higher than the optimum value required to maintain stable anodization in a given electrolyte always result in “breakdown” or “burning” of the oxide film caused by catastrophic flow of electric current coupled with a large amount of reaction heat.⁵⁴

HARD ANODIZATION

Recently, Lee et al. showed that the self-ordering regimes can be extended by implementing hard anodization (HA) of aluminum.⁵⁵ The HA process was originally developed in the surface finishing industry in the early 1960s, and has been widely used for various industrial applications by taking advantage of the high-speed oxide growth (50–100 μm h⁻¹).^{56,57} However, the process has not been employed in current nanotechnology research due to the difficulties involved in controlling important structural parameters, such as pore size (D_p), interpore distance (D_{int}), and the aspect ratio of the nanopores of the resulting anodic alumina. By introducing a thin protective oxide layer on aluminum prior to performing HA process and carefully controlling the reaction heat during HA, Lee et al. could suppress the burning event and grow self-ordered AAOs using oxalic acid at anodization potentials $U > 100$ V, establishing a new self-ordering regime with a widely tuneable interpore distance ($D_{int} = 200–300$ nm) (Figure 2f). The rate of oxide growth in HA was found to be 25 to 35 times faster than that in MA. The newly developed method turned out to be applicable to other electrolyte systems.^{8,59}

The HA process is characterized by a high current density (j) that is typically one or two orders of magnitude higher than that of the ordinary MA. The current in anodization of aluminum is related to the passage of ionic species through the barrier layer. Under high field condition, the ionic current density (j) can be related to the electric field strength (E); $j = j_0 \exp(\beta E) = j_0 \exp(\beta \Delta U / t_b)$, where j_0 and β are the material-dependent constants and $\Delta U / t_b$ is the effective electric field strength (E) across the barrier layer of thickness t_b .

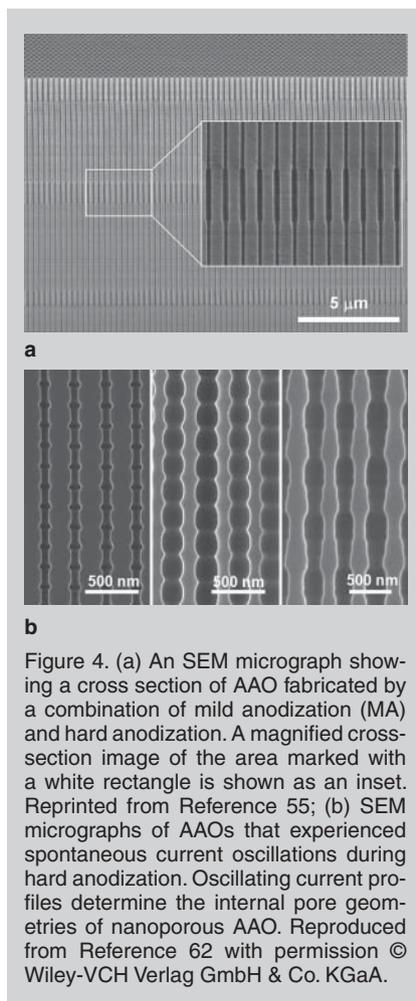


Figure 4. (a) An SEM micrograph showing a cross section of AAO fabricated by a combination of mild anodization (MA) and hard anodization. A magnified cross-section image of the area marked with a white rectangle is shown as an inset. Reprinted from Reference 55; (b) SEM micrographs of AAOs that experienced spontaneous current oscillations during hard anodization. Oscillating current profiles determine the internal pore geometries of nanoporous AAO. Reproduced from Reference 62 with permission © Wiley-VCH Verlag GmbH & Co. KGaA.

Investigation of HA processes revealed that the current density (i.e., the electric field strength E across the barrier layer) is a key parameter governing the self-organization of oxide nanopores in a given anodization potential (U). The barrier layer thickness for HA increases at a rate of $t_b^{MA} = 0.6\text{--}1.0 \text{ nmV}^{-1}$,^{55,60} which is smaller than $t_b^{MA} \sim 1.2 \text{ nmV}^{-1}$ for MA processes.^{6,28} HA-AAOs exhibit a reduced voltage dependence of the interpore distance (D_{int}) with a proportionality constant $\zeta_{HA} = 1.8\text{--}2.0 \text{ nmV}^{-1}$,^{55,58,59} compared to MA-AAOs (i.e., $\zeta_{MA} = 2.5 \text{ nmV}^{-1}$).^{21,24} Similar lines of experimental results have also been reported by other researchers.^{52,61} For oxalic acid-based HA, the porosity (P_{HA}) of HA-AAO turned out to be $P_{HA} = 3.3\text{--}3.4\%$, which is about one-third of the porosity value ($P_{MA} \sim 10\%$) that was proposed as a requirement for self-ordered AAO under MA conditions.²⁴ On the basis of the newly found self-ordering behavior in HA, Lee et al. realized the fabrication of AAO membranes with periodically modulated diameter of nanopores along the pore axes by combining MA and HA process, in which each modulation step required the exchange of the electrolyte solution in order to satisfy both MA and HA processing conditions (Figure 4a).⁵⁵ Quite recently, they further showed that AAOs experienced spontaneous current oscillations (amplitude $\sim 0.8 \text{ Acm}^{-2}$) during a potentiostatic HA can have modulated pore structures, in which the modulation contrast is proportional to the amplitude of current oscillation, and suggested that one may achieve structural engineering of nanoporous AAO by deliberately manipulating the current during anodization of Al (Figure 4b).⁶³

The fabricated AAOs with modulated pore structure could be starting materials for developing three-dimensional (3-D) porous architectures that may offer potential for photonic applications, and also model systems for investigating separations of particles and adsorption characteristics of molecules. In addition, it is expected that these AAOs can be readily utilized as template materials for fabricating novel nanowires or nanotubes, whose diameters are periodically modulated along their axes, and thus, enable one to study the various physical properties

that originated from the surface topography.

PULSE ANODIZATION

As mentioned in the previous section, combination of conventional MA and the newly developed HA could offer a new degree of freedom for tailoring the pore structure of AAOs by combining properties from the two anodization processes. Based on this

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concept, Lee et al. developed a generic approach for continuous structural engineering of nanoporous AAO based on pulse anodization (PA) of aluminum under a potentiostatic condition using H_2SO_4 or $\text{H}_2\text{C}_2\text{O}_4$.⁶³ In a typical PA process, periodic pulses consisting of a low-potential pulse (U_{MA}) followed by a high potential pulse (U_{HA}) are applied to continuously achieve MA and HA conditions, respectively (Figure 5a). During PA in a given electrolyte, anodization current changes periodically to a value corresponding to each pulsed potential (i.e., j_{MA} for U_{MA} and j_{HA} for U_{HA} ; $j_{MA} < j_{HA}$), and thus the pore structure of the resulting AAO is periodically modulated (Figure 5b). Nanoporous AAO formed by a PA process exhibits a layered structure of MA-AAOs with a smaller pore diameter and HA-AAOs with a larger pore diameter, in which the thickness of

each anodized segment is determined by the pulse durations (τ_{MA} and τ_{HA}) at given anodization potentials (U_{MA} and U_{HA}) (Figure 5c).

An interesting finding from the case of sulfuric acid-based PA is that an oxide segment (HA-AAO) formed by a high potential pulse (U_{HA}) contains a higher level of anionic impurity from the electrolyte than an oxide segment (MA-AAO) formed by a low potential pulse (U_{MA}). Therefore, PA in sulfuric acid solution results in a periodic compositional modulation along the pore axes of AAO. HA-AAO segments with a higher impurity content exhibit a poor chemical stability against an etchant (e.g., 5 wt.% H_3PO_4). This enables one to completely delaminate a single as-prepared anodic film into a stack of well-defined AAO membranes sheets by an extended etching of HA-AAO segments (Figure 5d). Accordingly, PA followed by selective etching of HA-AAO segments by an appropriate etchant provides a simple, continuous, and economic way for the mass production of nanoporous AAO membranes.

PA can also be conducted under a galvanostatic condition to tailor the internal pore structure of AAO. In this case periodic current pulses are applied to achieve MA and HA conditions, and anodization potential changes periodically to a value corresponding to each pulsed current. Recently, Lee et al. reported a convenient method for the preparation of structurally well-defined alumina nanotubes with controllable lengths.⁶⁴ The approach is based on the fact that H_2SO_4 -AAO formed under a high electric field strength (E) exhibits a weakened junction strength between cells. They employed galvanic pulses to selectively combine MA and HA conditions, where the pulse duration (τ_{HA}) for HA determines the length of nanotubes. By taking advantage of the weak junction strength between cells and of the modulated pore structures along the pore axis, individual alumina nanotubes could be separated from an as-prepared AAO.

The reaction involved in anodic oxidation of aluminum is exothermic. The dissolution of the resulting oxide by acid electrolyte is endothermic. The main contribution to heat generation in

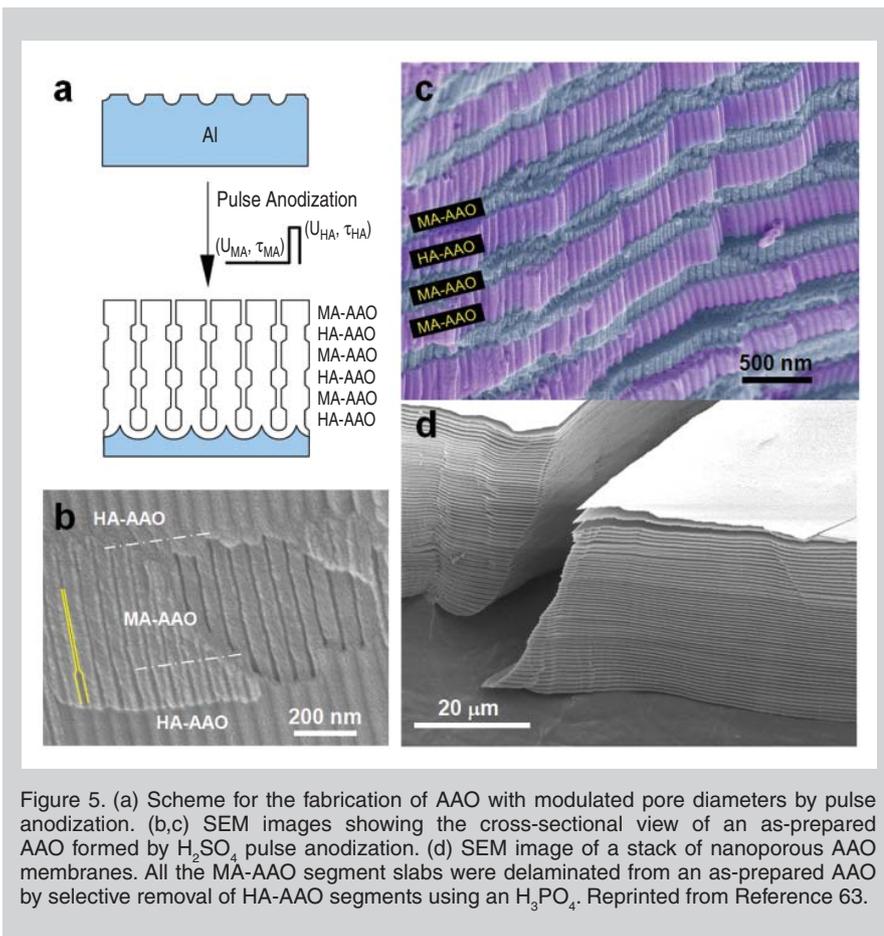


Figure 5. (a) Scheme for the fabrication of AAO with modulated pore diameters by pulse anodization. (b,c) SEM images showing the cross-sectional view of an as-prepared AAO formed by H_2SO_4 pulse anodization. (d) SEM image of a stack of nanoporous AAO membranes. All the MA-AAO segment slabs were delaminated from an as-prepared AAO by selective removal of HA-AAO segments using an H_3PO_4 . Reprinted from Reference 63.

anodization of aluminum is related to current flow through the barrier oxide layer. The production of Joule's heat (Q) is proportional to the square of the current density (j) according to $Q = Ujt = R_b j^2 t$, where R_b and t are the resistance of the barrier layer and the reaction time, respectively. HA is accompanied by a large evolution of heat due to the high anodic current (j) associated with the high electric field (E) at the barrier oxide. Since current density (j_{HA}) in HA is about one or two orders of magnitude higher than that (j_{MA}) in MA, heat production during HA could be roughly two to four orders of magnitude larger. The excessive heat does not only trigger breakdown of an anodic film but promotes undesired acidic dissolution of oxide membrane by the electrolyte. PA promises effective dissipation of reaction heat, which is one of the major causes of burning of an anodic film during anodization of aluminum under high current density (j). The accumulated Joule's heat during an HA-pulse of a high current density can be efficiently dispersed during the subsequent MA-pulse of a low current density, overcoming "burning" of an anodic film.

CONCLUSION

Self-ordered porous alumina formed by anodization of aluminum has increasingly become a popular template system in the development of functional nanostructures. Anodization of aluminum can be categorized into two main groups; mild anodization and hard anodization. The former method produces self-ordered and straight pore structures, but it is slow and only works for a narrow range of processing conditions. The latter method, which is widely used in the industry, is faster, but it produces anodic films with disordered and non-uniform pore structures. In these respects, the newly developed hard anodization process offers substantial advantages over the processes established previously. The process allows 25–35 times faster oxide growth with an improved ordering of the nanopores, compared to the conventional mild anodization. It establishes a new self-ordering regime over a wide range of interpore distance. On the other hand, pulse anodization enables selective combination of the advantages of mild anodization and the new hard an-

odization process. This generic process allows continuous tailoring of the internal pore structure as well as the composition of the anodic oxide by deliberately designing the pulse sequences. Therefore it provides a new degree of freedom in template-based synthesis of functional nanostructures that can be used for developing advanced devices as well as for investigating a diverse range of research problems in chemistry and physics.

In spite of some recent advances in anodization of aluminum, there is still much work to do. Exploration of new electrolytes systems and novel porous architectures will continue to expand the field of applications of anodic alumina. In addition, engineering the properties (e.g., wear or plasma resistance) of anodic films formed by the new processes is an interesting subject of research for the commercial applications. As mentioned in the present overview, there are still many open questions regarding the mechanism responsible for the pore formation and self-organization. Understanding the electrochemical process during the anodization of aluminum could provide a solid foundation for developing ordered porous structures from other valve metals, such as Hf, Ti, W, Zr, Nb, Ta, Sn, etc., which is currently an active area of research.

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References

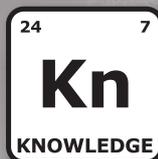
1. M.M. Lohregel, *Mater. Sci. Eng. R*, 11 (1993), pp. 243–294.
2. H. Föll et al., *Mater. Sci. Eng. R*, 39 (2002), pp. 93–141.
3. J.W. Diggle, T.C. Downie, and C.W. Goulding, *Chem. Rev.*, 69 (1969), pp. 365–405.
4. P.G. Sheasby and R. Pinner, *The Surface Treatment and Finishing of Aluminum and Its Alloys* (Materials Park, OH and Stevenage, U.K.: ASM International and Finishing Publications Ltd., 2001).
5. G.D. Bengough and J.M. Stuart, U.K. patent 223,994 (1923).
6. F. Keller, M.S. Hunter, and D.L. Robinson, *J. Electrochem. Soc.*, 100 (1953), pp. 411–419.
7. S.R. Nicewarner-Peña et al., *Science*, 294 (2001), pp. 137–141.

8. W. Lee et al., *Angew. Chem. Int. Ed.*, 44 (2005), pp. 6050–6054.
9. W. Lee et al., *Chem. Mater.*, 17 (2005), pp. 3325–3327.
10. W. Lee et al., *Nature Nanotech.*, 3 (2008), pp. 402–407.
11. Z. Huang et al., *Nano Lett.*, 8 (2008), pp. 3046–3051.
12. L. Liu et al., *Angew. Chem. Int. Ed.*, 47 (2008), pp. 7004–7008.
13. Z. Huang et al., *J. Med. Devices*, 1 (2007), pp. 79–83.
14. D. Ding et al., *Sens. Actuators B*, 124 (2007), pp. 12–17.
15. D. Gong et al., *Biomed. Microdevices*, 5 (2003), pp. 75–80.
16. Z. Fan et al., *Nature Mater.*, 8 (2009), pp. 648–653.
17. H. Asoh et al., *J. Electrochem. Soc.*, 148 (2001), pp. B152–B156.
18. H. Masuda and K. Fukuda, *Science*, 268 (1995), pp. 1466–1468.
19. H. Masuda and M. Satoh, *Jpn. J. Appl. Phys.*, 35 (1996), pp. L126–L129.
20. H. Masuda, E. Hasegawa, and S. Ono, *J. Electrochem. Soc.*, 144 (1997), pp. L127–L130.
21. A.P. Li et al., *J. Appl. Phys.*, 84 (1998), pp. 6023–6026.
22. F. Li, L. Zhang, and R.M. Metzger, *Chem. Mater.*, 10 (1998), pp. 2470–2480.
23. H. Masuda, K. Yada, and A. Osaka, *Jpn. J. Appl. Phys.*, 37 (1998), pp. L1340–L1342.
24. K. Nielsch et al., *Nano Lett.*, 2 (2002), pp. 677–680.
25. I. Vrublevsky et al., *Appl. Surf. Sci.*, 227 (2004), pp. 282–292.
26. J.P. O'Sullivan and G.C. Wood, *Proc. Roy. Soc. Lond. A*, 317 (1970), pp. 511–543.
27. K. Ebihara, H. Takahashi, and M. Nagayama, *J. Met. Finish. Soc.*, 34 (1983), pp. 548–553.
28. M.S. Hunter and P. Fowle, *J. Electrochem. Soc.*, 101 (1954), pp. 481–485.
29. M.S. Hunter and P. Fowle, *J. Electrochem. Soc.*, 101 (1954), pp. 514–519.
30. V.P. Parkhutik and V.I. Shershulsky, *J. Phys. D: Appl. Phys.*, 25 (1992), pp. 1258–1263.
31. G.D. Sulka and K.G. Parkola, *Electrochim. Acta*, 52 (2007), pp. 1880–1888.
32. G. Paolini et al., *J. Electrochem. Soc.*, 112 (1965), pp. 32–38.
33. S. Ono et al., *J. Electrochem. Soc.*, 151 (2004), pp. B473–B478.
34. O. Jessensky, F. Müller, and U. Gösele, *Appl. Phys. Lett.*, 72 (1998), pp. 1173–1175.
35. T.P. Hoar and N.F. Mott, *J. Phys. Chem. Solids*, 9 (1959), pp. 97–99.
36. Z. Su and W. Zhou, *Adv. Mater.*, 20 (2008), pp. 3663–3667.
37. C. Cherki and J. Siejka, *J. Electrochem. Soc.*, 120 (1972), pp. 784–791.
38. J. Siejka and C. Ortega, *J. Electrochem. Soc.*, 124 (1977), pp. 883–891.
39. G.E. Thompson, *Thin Solid Films*, 297 (1997), pp. 192–201.
40. Z. Wu, C. Richter, and L. Menon, *J. Electrochem. Soc.*, 154 (2007), pp. E8–E12.
41. P. Skeldon et al., *Electrochem. Solid-State Lett.*, 9 (2006), pp. B47–B51.
42. S.J. Garcia-Vergara et al., *Electrochim. Acta*, 52 (2006), pp. 681–687.
43. J.E. Houser and K.R. Hebert, *Nature Mater.*, 8 (2009), pp. 415–420.
44. R. Hillebrand et al., *ACS Nano*, 2 (2008), pp. 913–920.
45. H. Masuda et al., *Appl. Phys. Lett.*, 71 (1997), pp. 2770–2772.
46. H. Masuda et al., *Adv. Mater.*, 13 (2001), pp. 189–192.
47. C.Y. Liu, A. Datta, and Y.L. Wang, *Appl. Phys. Lett.*, 78 (2001), pp. 120–122.
48. Z. Sun and H.K. Kim, *Appl. Phys. Lett.*, 81 (2002), pp. 3458–3460.
49. S. Fournier-Bidoz et al., *Adv. Mater.*, 16 (2004), pp. 2193–2196.
50. W. Lee et al., *Small*, 2 (2006), pp. 978–982.
51. S. Shingubara et al., *Electrochem. Solid-State Lett.*, 7 (2004), pp. E15–E17.
52. S.-Z. Chu et al., *Adv. Mater.*, 17 (2005), pp. 2115–2119.
53. S. Ono, M. Saito, and H. Asoh, *Electrochim. Acta*, 51 (2005), pp. 827–833.
54. N. Sato, *Electrochim. Acta*, 16 (1971), pp. 1683–1692.
55. W. Lee et al., *Nature Mater.*, 5 (2006), pp. 741–747.
56. E. Lichtenberger-Bajza, A. Domony, and P. Csokán, *Werkstoffe. Korros.*, 11 (1960), pp. 701–707.
57. P. Csokán, *Metalloberfläche*, 15 (1961), pp. B49–B53.
58. W. Lee, K. Nielsch, and U. Gösele, *Nanotechnology*, 18 (2007), 475713.
59. K. Schwirn et al., *ACS Nano*, 2 (2008), pp. 302–310.
60. K. Schwirn, “Harte Anodisation von Aluminium mit Verdünnter Schwefeläure” (Ph.D. Dissertation, Martin-Luther-Universität Halle-Wittenberg, 2008).
61. Y. Li et al., *Nanotechnology*, 17 (2006), pp. 5101–5105.
62. W. Lee, J.-C. Kim, and U. Gösele, *Adv. Funct. Mater.*, 20 (2010), pp. 21–27.
63. W. Lee et al., *Nature Nanotech.*, 3 (2008), pp. 234–239.
64. W. Lee, R. Scholz, and U. Gösele, *Nano Lett.*, 8 (2008), pp. 2155–2160.

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