Formation of Anodic Aluminum Oxide with Serrated Nanochannels

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ABSTRACT We report a simple and robust method to self-assemble porous anodic aluminum oxide membranes with serrated nanochannels by anodizing in phosphoric acid solution. Due to high field conduction and anionic incorporation, an increase of anodizing voltage leads to an increase of the impurity levels and also the field strength across barrier layer. On the basis of both experiment and simulation results, the initiation and formation of serrated channels are attributed to the evolution of oxygen gas bubbles followed by plastic deformation in the oxide film. Alternating anodization in oxalic and phosphoric acids is applied to construct multilayered membranes with smooth and serrated channels, demonstrating a unique way to design and construct a three-dimensional hierarchical system with controllable morphology and composition.

KEYWORDS Anodic aluminum oxide, serrated channel, plastic deformation

Highly ordered porous anodic aluminum oxide (AAO) has been extensively investigated both for the fundamental understanding of the self-organizing mechanism and for the applications in template synthesis, fluid transport, and bioseparation.1–8 Hexagonal close-packed AAO membranes with straight columnar channels and uniform diameters can be obtained by a two-step self-organized anodization9 or pretexturing method.10 During the steady-state growth of porous film, Al3+ ions are directly injected into the electrolyte while the oxide film is formed at the metal/oxide interface due to the OH−/O2− migration.11 An anion contaminated layer is inevitably formed owing to the incorporation of the electrolyte species.1,12 The field-assisted dissolution model suggests that the development of porous film results from equilibrium established between the formation of oxide at the metal/oxide layer and the field-enhanced dissolution at the oxide/electrolyte interface.11,13,14 Recently, Skeldon and co-workers proposed a flow mechanism by employing a tungsten tracer layer in the aluminum substrate. The evolution and development of porous films arise from the viscous flow of alumina from the bottom toward the cell walls, driven by film growth.15,16 The investigations on the AAO have triggered the study on other valve metal anodization.17,18

In this Letter, we present a simple method to fabricate AAO membranes with periodic serrated channels aligned on one side of stem channels.19 This type of serrated anodic alumina (SAA) membrane can be obtained under a wide operation window with the anodizing voltage ranging from 10 to 80 V. The formation mechanism of SAA is systematically investigated in the morphology, composition, and simulation studies. The resulting well-defined, parallel, serrated nanochannel arrays serve as templates to synthesize sawtoothed metal nanowires via electrodeposition. AAO membranes with periodic straight/serrated channels are subsequently demonstrated by multistep anodization in different electrolytes. This approach provides a unique and robust method to construct three-dimensional hierarchical systems.

Aluminum foil (0.3 mm thickness, 99.999 % purity) is first electropolished in a mixture of perchloric acid (HClO4) and ethyl alcohol (C2H5OH) (volume ratio 1:4) following an annealing process (450 °C for 5 h). Anodization is then performed in 6 wt % aqueous phosphoric acid solutions at ambient temperature. Figure 1 displays the scanning electron microscopy (SEM) images of SAA samples which are fabricated with the anodizing voltage spanning from 10 to 80 V at room temperature. Further increase of the applied voltage (>100 V) results in local breakdown, corresponding to a dramatically increased current density. The periodic serrated channels are aligned along the same direction with an inclination angle of 20–30° to the stem channel. After selective removal of the Al substrate by saturated HgCl2 or SnCl4 solution, the exposed barrier layer is etched by ion milling. From the SEM image of the bottom view (Figure 1f) of the SAA obtained, the channel roots can be observed from the bottom, indicating that the serrated structures initiate to form at the bottom of nanochannels during the growth of the oxide membranes. Serrated Pt nanowire arrays have been investigated by using the SAA as a template in our previous report.19 To illustrate the versatile method, Co
nanowires with serrated morphology are further demonstrated by electrodeposition (see Supporting Information, Figure S1).

It is worth noting that the interpore distance and pore size of AAO can be tuned by the anodization voltage with respective proportionality constants. Reducing the anodic voltage by a factor of \(n^{1/2}\) yields Y-branched \((n = 2)\) and multibranched \((n > 2)\) nanochannel arrays, which can be employed to develop novel nanoelectronics. Due to the nature of the fabrication process, however, the junctions are inclined at the interface between the AAO membranes formed under different voltages. Consequently, the template-synthesized nanowires/nanotubes inherit the branched structures with limited junction areas compared to the serrated nanowires. Therefore, the serrated structures are expected to show better performance than multibranched nanowires in electrocatalysis, chemical sensing, energy storage, etc.

Figure 2a shows the typical current density versus time \((j-t)\) transients under constant voltages from 10 to 80 V. The field-assisted dissolution effect has been widely used to interpret the kinetics of self-organized anodization corresponding to the \(j-t\) transients. It is believed that the steady-state growth starts from stage “I” as marked in Figure 2a; however, there still lacks an explanation on the \(j-t\) curves based on the flow mechanism. Figure 2b depicts the voltage dependence of current density and growth rate under steady state. The inset of Figure 2b shows the growth rate as a function of current density, agreeing well with Faraday’s law \((dn/dt = \eta j/2F)\), where \(n\) is the number of moles, \(\eta\) the anodization efficiency, \(z\) the number of electrons transferred, and \(F\) is Faraday’s constant.

The impurity level for AAO formed in various electrolytes is found to be dependent on pH value and applied voltage. Driven by the electric field, anion species migrate into the oxide film together with \(O^{2-}/OH^-\) ions. Because of the slow migration, the incorporated anion species can be found in the outer oxide layer with a relative depth of \(\sim 70\%\) as reported in ref 1 (for AAO anodized in phosphoric acid). The energy dispersive X-ray spectroscopy (EDX) analysis is performed on the serrated SAA membranes to evaluate the impurity as a function of applied voltage (refer to Figure 2c and Figure S2 and Table S1 in Supporting Information). Each sample is measured at least three times at different positions to average out the experimental fluctuation. Because the Al signals contain those coming from the Al substrates, P:O atomic ratio is used to accurately determine the impurities in the membranes. The impurity level is derived by

\[
\frac{n(PO_4^{3-})}{n(Al_2O_3)} = \frac{3n(P)}{n(O) - 4n(P)}
\]

which is based on the stoichiometric atomic ratio of \(PO_4^{3-}\) and \(Al_2O_3\). The impurity content of SAA anodized under 80 V (\(\sim 25\%\)) is higher than that synthesized under 10 V (\(\sim 12\%\)), which is attributed to the enhanced local anionic \((PO_4^{3-})\) incorporation at the pore bottom accompanied by the increased anodization voltage.

The barrier layer thickness \(T_b\) as a function of bias voltage \(U\) has been discussed in detail when comparing the conventional anodization and hard anodization (i.e., high electric field anodization), in which the inverse field strength across oxide barrier \(t_b (= T_b/U)\) under hard anodization (\(\sim 1.0 \text{ nm/V}\)) is \(\sim 20\%\) smaller than that \(t_b\) under conventional mild anodization (\(\sim 1.3 \text{ nm/V}\)). An increase of current density, corresponding to the increased bias voltage from 10 to 80 V, leads to a \(\sim 53\%\) decrease of \(t_b\) (from 1.97 to 1.12 nm/V) (Figure 2c). According to the high field conduction theory, the current density \(j\)
is exponentially proportional to the potential drop across the barrier layer, i.e.

\[ j = \alpha \exp(\beta U/T_b) = \alpha \exp(\beta U) \]  

where \( \alpha \) and \( \beta \) are material-dependent constants for a given temperature. The field coefficient (\( \beta \approx 4 \text{nm/V} \)) is determined from data fitting from 10 to 80 V, neglecting the potential difference across the acid anion contaminated layer and the pure oxide layer (see Supporting Information, Figure S3).

The formation mechanism of SAA has been qualitatively proposed by combining a field-assisted flow model and oxygen bubble mold effect.\(^\text{19}\) Herein, the 2-D geometry electric field distribution is simulated using COMSOL Multiphysics. The simulation, excluding the electrolyte concentration gradient and electrode double layer in nanochannels, mainly focuses on the electric field distribution in the oxide layer based on steady-state current continuity equation

\[ \nabla \cdot j_b = 0 \]  

where \( j \) is the ionic current density within the oxide. The field dependence of ionic current density can be expressed as

\[ j_b = -2 \frac{\nabla U}{|\nabla U|} \alpha \sinh(\beta |\nabla U|) \]  

where \( U \) is the electric potential. Substituting eq 4 into eq 3 yields the differential equation of electric potential distribution

\[ \nabla \left( \frac{\sinh(\beta |\nabla U|)}{|\nabla U|} \nabla U \right) = 0 \]  

Natural growth process is closely related with the morphology of AAO, especially at the bottom initiation layer. The interpore distance (\( D_m \)), pore diameter (\( D_p \)), and barrier layer thickness (\( T_b \)) are found to linearly increase with the bias voltage at a rate of (\( D_m \)) 2.5 nm/V, (\( D_p \)) 0.9 nm/V, and (\( T_b \)) 1.3 nm/V, respectively.\(^\text{9,14,20,30,31}\) The bottom geometry can be described by the three parameters, as depicted in Figure 2d, i.e., inner radius (\( r \)), outer radius (\( R \)), and the angle (\( \theta \)) from the pore axis to the ridge-top. The geometric features of the oxide film obtained at 60 V are set as \( r = 37 \text{ nm}, R = 115 \text{ nm}, \theta = 46^\circ \) for straight channels taking into account of the experiment results (see Supporting Information, Figure S4) and empirical proportionality constants under conventional anodization,\(^\text{20}\) and \( r = 118 \text{ nm}, R = 191 \text{ nm}, \theta = 55^\circ \) for the serrated channel based on the electron microscopy analysis (see Supporting Information, Table S2). Since the voltage drop across the solution and metal are both negligible, the potentials at the oxide/solution and metal/solution interfaces are equal.
oxide interfaces are set to be zero and $U$, respectively. Free boundary condition is applied at the cell boundaries using symmetry consideration.

Panels a and b of Figure 3 represent the equipotential lines and electric field strength distribution in straight (STAA) and serrated (SAA) AAO channels. Note that the serrated branches are not shown here, as we only focus on the $\theta$ dependence of electric field distribution in the smooth bottom. Figure 3c displays the electric field strength distribution profile along the black dash lines which are tangential to the 30 V equipotential line as shown in parts a and b of Figure 3. The highest values are found at the cell edges due to the existence of aluminum ridges. In the center region as shown in Figure 3c, the electric field strength of point “1” is 2.1% higher than point “2” for SAA, whereas point “3” is 6.0% higher than point “4” for STAA channels. The electric field transients along the $y$ axis indicated by the blue dash lines are plotted in Figure 3d. The rate decrease of electric field strength in SAA is smoother than that in straight channeled membrane. Thus the electric field strength distribution in the SAA bottom barrier layer is relatively uniform compared to that of straight channels according to the profiles along $x$ and $y$ axes. Although we cannot verify the field dependence of oxide morphology, it is believed that the reduced electric field fluctuation influences the viscous flow and the resulting nanostructures.

The anodization process mainly involves the cross transport of $\text{Al}^{3+}$ ions and $\text{O}^{2-}$ ions. The $\text{Al}^{3+}$ ions are directly injected into the electrolyte, yielding the formation of oxide film at the oxide/metal interface (3O$_2^-$ + 2Al$^{3+}$ → Al$_2$O$_3$) with the anodizing efficiency about 60%. The anodic current is dominated by this ionic transport. The oxide is pushed upward during the steady-state growth because of dimensional confinement. The generation of oxygen bubbles contributed by the electric current is usually neglected in the anodizing process. However, on the basis of transmission electron microscopy (TEM) studies, nanosized voids exist in the oxide. Although the formation mechanism of the voids is still unclear, the existence of O$_2$ bubbles generated by the oxidation process 2O$_2^-$ → O$_2$ + 4e$^-$ is believed to trigger the formation of voids. More recently, Zhu et al. proposed that the pore generation is governed by the oxygen evolution within the oxide film. It is known that STAA can also be formed in aqueous phosphoric acid solutions at low temperature (≤3 °C). We believe that the elevated temperature induces pronounced increase of electric current and oxygen generation, which leads to the formation of serrated channels. In addition, the trapped gas bubble inside the barrier layer deforms the electric field, thus the current distribution (Figure 4a). Ionic transport is suppressed through the bubble region, and the current density is concentrated around the bubble. The Al$_2$O$_3$ formation is much enhanced at the local points with significantly increased electric field strength. Consequently, the volume expansion under dimensional confinement promotes the formation of a protuberance at the pore bottom (Figure 4b). As the gas bubble is released from the oxide, a new equilibrium of electric field distribution is established due to the deformations.

FIGURE 3. The potential and field distribution in (a) STAA and (b) SAA simulated by current continuity equation. The background color is the electric field, while the contour lines indicate equipotential surface. The electric field strength distributions in (c) $x$ direction and (d) $y$ direction are along the guidelines shown in (a) and (b).
tion of the barrier layer. In this case, the ionic transport is dominant at the upper side due to the enhanced electric field, as illustrated in Figure 4c and the corresponding SEM image in Figure 4d. During the steady-state growth, the ass-

FIGURE 4. (a) The field and current distribution with the presence of gas bubble in barrier layer. (b) The field and current distribution after the formation of a protuberance at the pore bottom. (c) The field and current distributions after the release of a gas bubble. (d) A SEM image of SAA formed at 60 V in  6 wt % phosphoric acid. One subchannel has been formed at the bottom (as indicated by the white circle) and is on the upward movement in the subsequent anodization process.

FIGURE 5. SEM images of periodic straight/serrated multilayered AAO membranes: (a) two layers, (d) five layers, and (e) nine layers, respectively. (b, c) Close-up views of straight and serrated channels corresponding to (a).
formed protuberance is pushed upward (along the black arrows in Figure 4c) because of the dynamics of oxide, followed by the generation of new channels. The regular interval is believed to be the result of periodic release of oxygen bubbles. Considering the growth rate and interval distance of serrated channels, generating one serrated channel takes ~4 min under 60 V anodization.

To verify the proposed growth mechanism, aluminum is anodized under 45 V alternating in 0.3 M oxalic acid and 6 wt % phosphoric acid to form periodic straight/serrated membranes. Panels a–c in Figure 5 show the AAO film with straight/serrated bilayer formation. Figure 5b displays the upper part of the oxide membrane formed in oxalic acid, indicating the self-organized nanochannels with smooth straight inner surfaces. Serrated channels in the bottom are formed in phosphoric acid. The interfaces between straight and serrated channels are distinctly observed in Figure 5c, which confirms the conclusion that the serrated subchannels are generated at the pore bottom.

From the cross-sectional views of the stacked membranes with various alternating layers (Figure 5, panels d and e), the inner surfaces for both straight and serrated channels are clearly observed, suggesting that different stacks exhibit similar fracture behavior along the channels axis, i.e., the splits propagate along the pore centers. On the other hand, a horizontal crack that propagates along the interface can be observed in Figure 5d as indicated by the white arrow. We believe that the mutation of the composition and microstructure gives rise to a weaker binding force at the interface of the straight/serrated layers. On the basis of the impurity analysis (Figure 2c and Figure S2 and Table S1 in Supporting Information), a 3D system with periodic compositional modulation can be designed and implemented.

In conclusion, nanoporous membranes with serrated subchannels have been achieved in phosphoric acid in a wide range of processing windows at ambient temperature. Comparing simulation and experiment results, the formation of the serrated architectures is determined to be the result of the oxygen bubble evolution and plastic deformation. High field conduction and anionic incorporation at the pore bottom give rise to the variation of the architecture and composition. AAO membranes with serrated channels have been demonstrated as templates to fabricate nanowire arrays, which can be potentially applied in fluid flow controller, biotechnology, energy conversion, and information encoding. Moreover, multilayer stacked architectures, with smooth and serrated channels can be constructed by discretionally alternating anodization steps in oxalic and phosphoric acids.

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Supporting Information Available. Serrated Co nanowires and SAA characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

Supporting Information

Formation of anodic aluminum oxide with serrated nanochannels

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Figure S1 A SEM image of an individual Co nanowire with sawtooth branches. The electrodeposition is performed in a three-electrode cell under constant voltage (-0.9V) at room temperature. The electrolyte used in the Co electrodeposition consists of 1 M CoSO$_4$·6H$_2$O and 45 g L$^{-1}$ H$_3$BO$_3$ in deionized water.$^1$ The as-synthesized nanowires are suspended in isopropyl alcohol, and then pippet-deposited onto the Si/SiO$_2$ substrate.
Figure S2 A set of EDX spectrum of SAA membranes obtained in 6 wt% aqueous phosphoric acid solutions under different voltages. The analytical results are shown in Table S1.
Table S1 Impurity concentration of SAA obtained under different applied voltage.

<table>
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<tr>
<th>Anodizing voltage (V)</th>
<th>Atomic % based on Kα lines</th>
<th>Mean value of $\frac{n(\text{PO}_4^3^-)}{n(\text{Al}_2\text{O}_3)}$</th>
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<tr>
<td></td>
<td>O</td>
<td>Al</td>
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<td>10</td>
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Table S2 The values of $\theta$ for AAO with straight and serrated channels.

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<th>Straight**</th>
<th>Serrated</th>
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<td>$t_b$ (nm/V)</td>
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<td>Porosity ($P$)</td>
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<tr>
<td>$\theta$ ($^\circ$)</td>
<td>46</td>
<td>18.5</td>
</tr>
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</table>

* Taking $D_{outer}=2R\sin\theta$, $D_{inner}=2r\sin\theta$ as shown in Figure 2d, the inter-pore distance ($D_{int}$) and porosity ($P$) are

$$\frac{\sqrt{3}}{2} D_{outer} \quad \text{and} \quad \frac{2\pi}{3\sqrt{3}} \left( \frac{D_{outer}^2}{D_{inner}^2} \right),$$

respectively.

** The values are determined by referring experiment results and empirical proportionality constants$^2$. 
Figure S3 The electric field \( (U/T_b) \) dependence of effective current density

\[
\ln(j_{\text{eff}}) (\text{mA/cm}^2) = \alpha \beta U T_b
\]

where \( \alpha \) and \( \beta \) are constants. The field coefficient \( \beta \) is fitted according to the high field conduction theory \( j_{\text{eff}} = \alpha \exp(\beta U T_b) \) to be 3.9 nm/V, and the value is taken as 4 nm/V in simulation.
Figure S4 A SEM image of AAO with straight channels obtained under 60 V and 5 °C in 0.3 M oxalic acid solution. The geometric parameters employed in the simulation are set as $r=37$ nm, $R=115$ nm, and $\theta=46^\circ$, referring to the experiment results and empirical proportionality constants.

References: