Pore Nucleation Mechanism of Self-Ordered Alumina with Large Period in Stable Anodization in Citric Acid

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We have demonstrated that self-ordered porous alumina with large period can be obtained by stable anodization in citric acid at high voltage (400 V). Pore nucleation, which determines the final morphology of the alumina, is a very slow process. By comparing the alumina films obtained in different citric acid concentrations and temperatures, we found the amount of free citric acid anions is critical to pore nucleation. Surface chemistry and the detail structural composition of the porous alumina were investigated by XPS and TEM, respectively. The results show that uniform black alumina surface (formed ordered nanopores) cannot be obtained in low or high citric acid concentrations; the carbon element content of the black is obviously higher than that of gray surface (pores cannot well develop); citric acid is incorporated into the porous alumina cell, where the thickness ratio of compact skeleton and acid incorporated part is 1:3. Accordingly, the pore nucleation has two stages: I, fast forming flat barrier-type alumina film, alumina form and deposit at metal-oxide and oxide-electrolyte interface, respectively. II, Al-citric complex in electrolyte slowly transform to citric acid incorporated alumina and unevenly deposit on barrier-type alumina, which results in electric field concentration between protuberances and pore development.

Efforts to custom-tailor the structural parameters (dimension, regularity and shape) of arrayed porous materials has produced a profound influence on nanoscience and nanotechnology.1–10 As a sort of very popular porous materials, self-organized porous anodic alumina (PAA) formed by electrochemical anodization has been widely utilized in the fields of optics,3 drug delivery,4 energy storage,5 and so on, due to their predominance in tunable pore dimensions and thickness, excellent chemical and thermal stability, and low-cost and large-area fabrication. However, in typical mild anodization (MA) processes, hexagonally packed nanopores with fixed interpore distance (Dint) of 63 nm, 100 nm and 500 nm can only be obtained in the three corresponding processing windows: sulfuric acid (H2SO4) at 25 V, oxalic acid (H2C2O4) at 40 V, and phosphoric acid (H3PO4) at 195 V.11–13 In order to explore the potential novel properties that arise from the size effects, hard anodization (HA) characterized by the high current density has been developed to efficient and inexpensive to get long-range ordered PAA films with continuously tunable Dint in the range of 70–490 nm in the compatible electrolyte systems and anodization voltage.14–17 Recently, the self-organization behaviors of PAA in novel electrolyte (e.g. selenium acid and etidronic acid) have been studied. Self-ordered PAA with Dint between 530–670 nm have been successfully fabricated by anodizing in etidronic acid.18 However, it is still a great challenge to further fabricate the self-ordered PAA with larger Dint.

Citic acid is thought to be a good alternative electrolyte to fabricate PAA with large Dint.18–24 It is believed that its lower dissociation constants would make the alumina tolerant high anodization voltage.24 To date, by the efforts of searching compatible electrochemical anodization conditions, large Dint greater than 500 nm can be formed by anodizing in pure citric acid solution or the mixture solution of citric acid and other electrolytes.18–24 However, the catastrophic flow of electric current density (j) at higher potentials, called “burning” or “breakdown events”, easily causes the undesired non-uniform black burned oxide and makes the anodization cannot carry on.18–21 Thus, the intrinsic self-ordered regime for citric acid is still unestablished by the reported research works.21–23 The fabrication of perfectly ordered porous oxide remains the aid of expensive imprinting stamp.24

Recently, we have reported that self-ordered PAA with ultra large Dint in the range of 675–884 nm can be realized by stable anodization in citric acid at high voltage.25 Interestingly, different from the typical MA and HA process, this anodization shows its unique characteristics. j quickly decreases from the high initial value to the lowest value at the beginning and then slowly increases to the peak value (>25 mA/cm2), which is very similar to the pore nucleation process of MA. However, it takes about 30 min to accomplish this variation which is much longer than that (<30 s) of MA, and j is also much higher than that of MA (<10 mA/cm2). After that, j shows nearly exponential decrease which like the unequilibrium self-organization process of HA, but the decrease speed is much slower than that of HA.26 This anodization process may become an alternative technology to facile and controllable fabrication of microstructured or hybrid micro and nanostructured materials as combined with nanoimprinting and electrochemical deposition. However, to have a better control of this anodization and to further broaden the Dint range in the comparable electrochemical parameters, a deep insight into the formation mechanism (e.g. pore nucleation) of this type anodization is needed.

An interesting thing about this type anodization is that it has a very low pore nucleation speed compared with MA.26 For example, as this anodization performed in 1.5 M citric acid at 400 V under 0 °C, it was found that pores began to randomly appear on the surface of the alumina at 90 s, and pores haven’t covered the whole alumina surface until anodization reached to 34 min (Figure 1). While, for MA in common electrolyte system (i.e. sulfuric acid, oxalic acid and phosphoric acid), pores can well develop on the whole surface within 30 s.11–13 Besides, during the pore nucleation, the macroscopic color of the sample surface gradually changed from gray to black (Figure 1), which cannot be observed in MA or HA. And regular arranged nanodents can only be formed under the black region. Highly ordered nanodents with interpore distance of 884 ± 28 nm can be obtained as anodizing for 5 h (Figure 1). The reasons that result in these interesting phenomena are not clear, which are needed to be further investigated.

In this paper, the morphology of the alumina film and current density evolution of the anodization processes, in different citric acid concentrations (0.15 M, 1.5 M and 3 M) and temperatures (from 0 °C to 25 °C), were compared. It was found that uniform black alumina surface, which presents for forming ordered nanopores, cannot be obtained in low (0.15 M) or high (3 M) citric acid concentration due to the low amount of free citric acid anions. And Pore still cannot well develop on the whole alumina surface in 0.15 M citric acid even by raising the temperature to 25 °C. The X-ray photoelectron spectroscopy (XPS) and Transmission electron microscopy (TEM) investigations showed that the carbon element content of the black surface is obviously higher than that of gray surface (the place that...
After the anodization, the as-prepared nanosamples were immersed into a mixed solution of 1.8 wt% CrO₃ and 6 wt% H₃PO₄ for 12 h. The electropolished disk was then placed in a mixture of perchloric acid and ethanol (V/V = 1:4) for 11 min (20 V, 0 °C). The electropolished disk was then placed in a custom-tailored electrochemical cell equipped with a circle cooling system (DC-3006, Ningbo Scientz Biotechnology Co., Ltd), where the cooling liquid (ethanol) can remove the reaction heat from both the back of Al foils and electrolyte. The circle reaction zone exposed to the electrolyte was 25.4 mm in diameter. A platinum electrode was employed as a counter electrode. Citric acid solution with concentrations of 0.15, 1.5 and 3 M were used as electrolyte, which were under violent agitation. The anodization was last for 8 h at 400 V with temperature range from 0 to 25 °C. Current densities (j) were calculated by dividing the current values measured from the power supply system (IT 6726A, ITECH) by the anodized sample area. After the anodization, the as-prepared nanosamples were immersed into a mixed solution of 1.8 wt% CrO₃ and 6 wt% H₃PO₄ for 12 h at 70 °C to dissolve the alumina films to obtain the corresponding nanodents.

Characterization.—The morphologies of the nanodents and the alumina were observed under a field-emission scanning electron microscopy (SEM, Nova NanoSEM 450, FEI) after sputtering a 15 nm thickness of Au layer. The conductivities of citric acid solution with different concentrations and temperatures were measured by Lei Ci DDS-307A conductivity meter with temperature compensation mechanism. The surface chemical compositions of the black and gray surfaces of the alumina were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA, Kratos Analytical Ltd) with a monochromated Al Kα X-ray source (1486.71 eV of photos). Samples were fastened to stainless-steel holder after respectively ultrasonic cleaning in acetone, ethyl alcohol and deionized water for 5 min and dried by nitrogen flow. The pressure in the analysis chamber was better than 5 × 10⁻⁹ Torr. Survey scan (binding energy range from 0 to 1200 eV) was acquired from a rectangle of 300 × 700 μm of the sample in constant analyzer energy mode at pass energy of 160 eV and step size 1 eV for all regions; high-resolution scans of the core levels of the Al 2p, O1s, C1s photopeaks were recorded at pass energy of 40 eV and step size 0.05 eV. XPS data was analyzed with CASA software package. Before curve fitting, the energy scale of the XPS spectra was calibrated relative to the binding energy of advantageous hydrocarbon in the C1s peak at 284.8 eV. Curve fitting was done after a Shirley-type background removal, using mixed Gaussian (85–100%)-Lorentzian shapes. The detailed structural compositions of porous alumina cells were characterized by using transmission electron microscopy (TEM, Tecnai G2 F20) operated at 200 kV. The samples for TEM investigations were prepared by standard method. The as-prepared sample was tailored to a disk with diameter of 3 mm and mechanically grounded to 70 μm thickness from one side by Leica EM TXP, dimpled to get a thickness of 20 μm at the central of samples by Gatan dimple grinder II, glued and ion-thinned using Gatan PIPS II with an incident angle of 10° at 5 kV.

Results and Discussion

Distinct characteristic of the anodization in citric acid solution with different concentration.—A rational speculation about the reason that causes the special pore nucleation process of this type anodization is that it should be highly related to citric acid, which is used as electrolyte. Accordingly, we first compared the alumina films and anodization process in the citric acid solution with concentrations of 0.15 M, 1.5 M and 3 M (400 V, 0°C), respectively (Figure 2). It can be seen that the sample obtained in 0.15 M has two apparent different regions with gray (I) and black color (II), respectively; flaten surface with sparsely distributed nanodent patterns is left after dissolving the formed barrier-type aluminum film in region I, whose average thickness is only 500 nm; whereas nearly hexagonally arranged nanodents can be founded after dissolving the porous alumina film in region II, whose average thickness is 5 μm (Figure 2a). For
Figure 2. (a-c) SEM images of the nanodents left on the aluminum surface (top part) and side-views of the corresponding alumina films (bottom part), which were obtained by stable anodization in citric acid with different concentrations of 0.15 M (a), 1.5 M (b) and 3 M (c) for 8 h at 0°C. The as-prepared alumina films show apparently different color (the inset optical images), although they undergo the same anodization condition except for citric acid concentration. Note that, for the 0.15 M sample, pore is like a protrusion sitting on flat barrier-type alumina film. (d) current-time transients during stable anodization of aluminum foils in the electrolyte with concentration of 0.15, 1.5 and 3 M, respectively. (e) Conductivities of the electrolyte with different citric acid concentrations under 0°C.

the sample obtained under 1.5 M, porous alumina film with homogeneous black color and uniform thickness of 175 μm can be obtained; highly ordered hexagonally arranged nanodents can be observed after dissolving the alumina film (Figure 2b). However, when the citric acid concentration further increases to 3 M, the alumina surface shows uneven distributed gray (I) and black (II) colors without clearly demarcation line; irregularly distributed nanodents and relatively ordered nanodents are left on the aluminum surface after dissolving the alumina in I with thickness of 6 μm and II with thickness of 60 μm, respectively (Figure 2c). It should be noted that, for the sample formed in 0.15 M, pores were sparsely distributed on region I, which looks like protrusions sitting on the flat barrier-type alumina film (Figure 1a). The height of the protrusion is about 150 nm. Pore start from the top central of the protrusion, and the size of pore open-mouth is larger than that of pore channel. Interestingly, the porous oxide surfaces of samples that obtained in 0.15, 1.5 and 3 M are all rugged due to the protrusion around the pore, which suggests that the accumulation of film-forming materials on barrier oxide layer at the early stage of anodization may play a significant role in the formation of pore.

To have a deep insight into the distinctive surface morphology under each citric acid concentration, we investigated into the current density (j) evolution in the electrolyte with citric acid concentrations of 0.15, 1.5 and 3 M under 400 V at 0°C (Figure 2d). It can be clearly seen that the current-time transient of 1.5 M shows typical characteristic variation due to the change of electric field strength. j quickly decreases from the high initial value to the lowest value of 25 mA/cm² at the beginning, corresponding to the rapid formation of the barrier layer. And then j slowly increases to the peak value of 44 mA/cm² at 34 min, which means the full pore development process. After that, the current density shows nearly exponential decrease, indicating the unequilibrium self-organization process. However, for 0.15 M and 3 M, j increases with an extremely low speed after it quickly drops down to the minimum value of 3.62 mA/cm² and 0.06 mA/cm², respectively. The maximum value of current density (j_p) is 6.97 mA/cm² at 23830 s for 0.15 M and 2.78 mA/cm² at 22366 s for 3 M. To find the reason that leads to the differentiations above, we compared with the conductivity of citric acid solution with different concentrations at 0°C. Here, to clarify the variation trend of the conductivities, we chose five concentrations (0.15 M, 0.375 M, 0.75 M, 1.5 M and 3 M) to test. As shown in Figure 2e, the conductivities first increase and then decrease with concentration. It is because the conductivity of electrolyte directly relates to the amount of free ions (i.e. H⁺, H₂Cit⁻, HCit²⁻ and Cit³⁻), which will increase as increasing the concentration of citric acid but decrease at high concentrations because there is insufficient water present to ionize the electrolyte. The values for 0.15, 1.5 and 3 M are 41.98, 71.25 and 39.40 mS/cm, respectively, which corresponding to the current density variation very well. It is well known that j is mainly related to the mobile ions through the barrier layer. As the black color is caused by the incorporated carboxylate ions, it can be inferred that the amount of free citric acid anions of the electrolyte may influence the morphology of barrier layer at the early
stage of anodization, which results in the current density variation and pore nucleation.

**Anodization in 0.15 M citric acid at different temperatures.—** It is well known that raising the electrolyte temperature (T) can accelerate the field assistant dissolution of alumina as well as promote the velocity of mobile ion in anodization, which can facilitate the pore development.\(^3\)\(^,\)\(^3\)\(^4\) Thus, we wonder whether nanopores can well develop on the whole surface of the alumina that anodized in 0.15 M citric acid by only change T. Accordingly, we investigated into the morphology and current density variation of the alumina films anodized at different T in 0.15 M citric acid at 400 V for 8 h. As shown in Figure 3, the black region, where ordered nanodents can be obtained after dissolving the alumina, become larger as T increases from 0°C to 10°C. However, with T further increasing, the area of black surface cannot become larger, which turn to bundled fibers instead of porous surface due to the enhanced corrosive effects of citric acid (Figure 3c).

It can be seen that, with T increasing, the current density-time transient of 0.15 M citric acid becomes more and more similar to that of 1.5 M citric acid in Figure 2d. \(j_p\) of the anodization in 0.15 M citric acid gradually increases from 6.97 mA/cm\(^2\) at 23830 s of 0°C to 48.54 mA/cm\(^2\) at 3230 s of 25°C (Figure 3e). However, pore still cannot well develop on the whole surface of the alumina anodized in 0.15 M. To make clear about the reason that results in this different morphology appearance, the conductivities of 0.15 M citric acid as temperature increase from 0°C to 25°C. (f) Conductivity varied with temperature at fixed citric acid concentration of 0.15 M.

**Surface chemical analyses of gray and black regions.—** To further comprehend the differences between the gray and black regions of the alumina surface which was prepared in 0.15 M citric acid electrolyte at 400 V for 8 h, we investigated into the surface chemistry of these two regions by XPS, respectively. To minimize the influence of the carbon contaminations that adsorbed from the atmosphere,\(^3\)\(^,\)\(^3\)\(^6\)\(^,\)\(^3\)\(^7\) intimately after anodization, the samples were respectively ultrasonically cleaned in acetone, ethyl alcohol and deionized water for 5 min and dried by nitrogen flow, and then analyzed by XPS as soon as possible. As shown in Figure 4, the survey XPS spectra from the gray and black oxides show the same composition elements, which are aluminum, oxygen and carbon. Typical high-solution spectra of Al2p, O1s and Cls are also shown, which can be curve fitted into subcomponents of O\(^2-\), O = C-O and OH\(^-\) for O1s and C-C/H, C-O and O = C-O for Cls, respectively. The insert tables in survey scan of XPS spectra give the binding energy and the full width half-maximum (fwhm) of the peak intensities for Al2p, O1s and Cls, and the calculated atomic compositions of the gray and black oxide surface, respectively. To correct the charging effect, all the components of the spectra have been shifted by the amount necessary to get the C-C bond at 284.8 eV. It should be noted that the gray and black oxides in this study have very similar Al2p, O1s binding energies, but the content of carbon elements increases from 18.8% in gray region to 27.0% in black region. This result suggested that more citric acid anion may incorporate into the black surface compared with the gray surface, though the carbon adsorbed from the atmosphere onto these surfaces prevents accurate qualification of the carbon composition of the oxide film.\(^3\)\(^,\)\(^3\)\(^7\)

**Detail structural composition of porous alumina cell.—** It has been reported that the porous alumina cell that formed in common electrolyte (i.e. \(\text{H}_2\text{SO}_4\), \(\text{H}_3\text{C}_2\text{O}_4\) and \(\text{H}_3\text{PO}_4\)) is made up of different textured alumina, where the thin skeleton is composed of relatively pure alumina and the thick amorphous internal part is incorporated with acid anions from the electrolyte.\(^3\)\(^,\)\(^3\)\(^9\) In TEM images, the virtually pure alumina skeleton shows dark color, whereas the amorphous internal part is bright. As a new type of electrolyte, we wonder if citric acid anions are also incorporated into the porous alumina film.
Figure 4. (a, b) From left to right, survey-scan spectra and high-resolution XPS spectra for Al 2p, C 1s, and O 1s of the gray (a) and black (b) regions of alumina surface which was prepared in 0.15 M citric acid electrolyte at 400 V for 8 h (10 °C), respectively. The C 1s and O 1s photopeaks are curve fitted into their subcomponents, which are denoted by the dot line. The insert tables show the relative atomic concentrations of Al, O and C.

Figure 5. (a) Low magnification and (b) High magnification TEM images (TEM) of an ion beam thinned anodic film formed in 1.5 M citric acid under 400 V at 0 °C for 8 h. (c) High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) show the details of different parts of the porous alumina cell, which consists of pore, compact skeleton and acid incorporated internal part.

Figure 5 shows the TEM images of the porous anodic film formed in 1.5 M citric acid under 400 V at 0 °C for 8 h, which is ion beam thinned from bottom to suitable thickness. It is evident that pore is in hexagonally arrangement (Figure 5a), which is in good agreement with the SEM images (Figure 2b). The high magnification image clearly shows the pore cell is composed of two clearly differentiated regions: a thick amorphous internal part and a thin compact skeleton (Figure 5b). The thickness ratio of compact skeleton and amorphous internal part is 1:3, which can be calculated from the detailed structure of the cell obtained by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) (Figure 5c). Clearly, citric acid anions indeed incorporate into the porous alumina during anodization and play an important role in the pore growth.

**Pore nucleation process in stable anodization in citric acid.**—Accordingly, the pore nucleation stage in stable anodization in citric acid can be divided into two stages: I fast flat barrier-type alumina film formed by simultaneous alumina formation at metal-oxide (m/o) interface and deposition at oxide-electrolyte (o/e) interface; II citric acid incorporated alumina slowly and unevenly deposited on barrier-type alumina, which results in electric field concentration between protuberances and pore development (Figure 6). Firstly, a flat barrier-type anodic oxide layer is quickly formed on the top of Al surface, which is corresponding to $j$ quickly decreases from the high initial value to the lowest value of 25 mA/cm$^2$ at the beginning (Figure 2d). In this time, under electric field, Al$^{3+}$ egress from the metal-oxide (m/o) to oxide-electrolyte (o/e) interfaces and O$_2^-$/$OH^-$ ingress from o/e to m/o interfaces. It is believed that typical barrier-type alumina was formed by two simultaneous process: (1) Al$^{3+}$, OH$^-$ and O$_2^-$ form anodic alumina near the m/o interface. (2) Al$^{3+}$ ions not consumed in growth by ionic migration are ejected to the electrolyte at o/e interface, which can form colloidal Al-hydroxide particles and immediately deposited to form new outer o/e interface by aggregation and deprotonation. However, step 2 can be dramatically influenced by the particular interfacial conditions near o/e interface. It should be noted that citric acid anions is a kind of coordination agent which can chelate to metallic ions (Al$^{3+}$) and prepare stable metal chelate complexes (Al-citrate complexes). At the initial anodization, large amount of Al$^{3+}$ eject to the electrolyte from o/e interface. When the concentration of free acid anions is very low, almost all the Al$^{3+}$ can transform to colloidal Al-hydroxide particles and uniformly deposited on the alumina surface, which leads $j$ reducing to nearly zero; When the free acid anions at high concentration, a certain amount Al$^{3+}$ were stabilized in the electrolyte in the form of Al-citrate complexes, which leads $j$ reducing to a relative high level where the ionic still can move under the electric field.

Subsequently, under the electric field effect, Al-citrate complexes may slowly agglomerate to form citric acid incorporated alumina.
The pore nucleation process of the stable anodization in citric acid can be divided into two processes: I, fast flat barrier-type alumina film formation by simultaneous alumina formation at metal-oxide (m/o) interface and deposition at oxide-electrolyte (o/e) interface (a). This process is corresponding to quickly decreasing from the high initial value to the lowest value of 25 mA/cm² at the beginning. In this time, under electric field, Al³⁺ egress from the m/o to o/e interfaces and O²⁻ /OH⁻ ingress from o/e to m/o interfaces. A certain amount Al³⁺ are stabilized in the electrolyte in the form of Al-citrate complexes. II, Al-citric complex in electrolyte are slowly transformed to citric acid incorporated alumina and unevenly deposited on barrier-type alumina, which results in electric field concentration between protuberances and pore development (b and c). It should be noted that citric acid incorporated alumina randomly and slowly precipitate on the formed alumina surface to form protuberances, which make the electric field concentrate between the protuberances (b). The concentrated electric field facilitate field-assisted dissolution at the o/e surface, which thin the formed flat barrier layer, and results in the quickly formation of the alumina at o/m interface. Consequently, oxide growing at m/o with a scallop shape is determined by the morphology at o/e interface to maintain the equifield field strength, which results in the pore forming (c).

Conclusions

We have demonstrated that the amount of free citric acid anions play a key role in pore nucleation in stable anodization in citric acid, which can be divided into two stages: I, fast flat barrier-type alumina film formation by simultaneous alumina formation at metal-oxide (m/o) interface and deposition at oxide-electrolyte (o/e) interface. At this stage, certain amount of Al³⁺ are stabilized by the citric acid anions in the electrolyte to form Al-citric complex, which cannot be immediately deposited on o/e interface. II, Al-citric complex in electrolyte are slowly transformed to citric acid incorporated alumina and unevenly deposited on barrier-type alumina, which results in electric field concentration between protuberances and pore development. This finding takes a deep insight into the pore nucleation mechanism of this anodization, which is very helpful to find compatible electrolyte to further broaden the Dint range. It can be predicted that the anodization process of Al foils in gluconic acid, saccharic acid, bicine and tartaric acid may be similar with that in citric acid, because these acids also can chelate to Al³⁺ and prepare stable metal chelate complexes.

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