Controllable Fabrication of Networked Three-Dimensional Nanoporous Anodic Alumina Films on Low-Purity Al Materials

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Networked three-dimensional (3D) nanoporous alumina nanostructures—consisting of vertical cylindrical stem pore arrays (170–310 nm in diameter) and periodical transverse branched pores (20–80 nm in diameter) interspersed regularly by 190–220 nm across the vertical pore walls—were controllably fabricated from low purity Al materials (99.0%, 99.3%, and 99.56%) and anodization in a phosphoric acid solution at 110–190 V. The formation of transverse pores depended predominantly on the purity of the Al base materials and the corrosion resistance of the anodic porous alumina films, which can be mainly attributed to anodic and/or chemical dissolution of impurities such as Fe, Cu, Zn, Mg, and Mn incorporated in the Al base materials. Moreover, the effects of the purity of Al materials on the growth and morphology of porous alumina films in oxalic and sulfuric acid solutions were also investigated by a two-step anodization of Al sheets with different purities, namely 99.0%, 99.3%, 99.56%, and 99.99% Al. The alumina films grew more slowly in all electrolytes with decreasing Al purity, which can be attributed to the lower corrosion resistance of the PAA films containing small quantities of Fe oxides and/or hydroxides produced during anodization.

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Experimental

Specimens.— As starting materials, four kinds of commercial aluminum sheets (20 × 50 mm; anodized area: 20 × 40 × 2 mm) with purities of 99.0% (A1100, Kanto Chemicals Co. Ltd.), 99.3% (1N30, Japan Foil Co. Ltd.), 99.56% (A1050, Nippon Light Metal Co. Ltd.), and 99.999% (SN, Nilaco Co. Ltd.) were used as received, the elemental compositions of which are given in Table I.

Anodization.— Anodization was performed by using a high-voltage direct current power supply (KIKUSUI Co. Ltd., 600 V/2 A) connected to a computer-controlled system, in a two-electrode mode with a graphite plate as a counter electrode. A powerful cooling system (YAMATO–Coolnics Circulator–CTE42A) and a large electrolytic cell (1 L) with vigorous magnetic stirring were used to maintain the low temperatures required for the high-voltage anodization without burning. Before anodizing, the specimens were first cleaned in acetone ultrasonically and then electrochemically polished in a solution of 70% HClO3 mixed at a 1:4 ratio with 99.5% ethanol at 25 V and 280 K for 2 min. Anodization was performed in solutions of 0.9 M phosphoric (denoted as P), 0.3 M oxalic (denoted as O), and 0.7 M sulfuric (denoted as S) acids at 20–190 V and 273–278 K for between 30 min and 5 h. Anodization was carried out in two steps, i.e., prior to the procedure mentioned above, pre-anodization was carried out in the same solution and under the same conditions for 30–60 min, and the PAA films formed in this first step were removed by chemical dissolution in a mixed acid solution containing 0.9 M H3PO4 and 5 wt% CrO3 at 343 K. Moreover, the anodizing voltage was initially increased at a rate of 1–2 V/s up to the required values and then maintained for the durations specified. In order to avoid ‘break-down’ or burning phenomenon at high voltages, limited currents were set at 0.1 A and 0.2 A for anodization in phosphoric, and in oxalic and sulfuric acid solutions, respectively, which were determined by preliminary experiments.

Characterization.— The surface and cross-sectional morphologies of the anodized specimens were observed by field emission scanning electron microscopy (FE-SEM: JOEL-JSM-7001F) with energy-dispersive X-ray spectroscopy (EDS) at voltages of 10–15 kV. To minimize electron charging during FE-SEM observation, the specimens were covered with a 2 nm thin osmium film by vacuum evaporation. The composition and chemical states of the porous alumina films were analyzed by X-ray photoelectron spectroscopy (XPS: ULVAC-PHI-5600CIM, Mg Kα), using a five channel analyzer (VG Scientific

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Manuscript submitted July 29, 2014; revised manuscript received November 3, 2014. Published November 11, 2014. This was Paper 1716 presented at the San Francisco, California, Meeting of the Society, October 27-November 1, 2013.

Porous anodic alumina (PAA) films with ordered parallel nanopore arrays obtained from Al anodization have been widely used as nanotemplates in the past decade, to fabricate various one-dimensional (1D) nanostructures such as nanowires and nanotubes for many applications, including in photocatalysts, perpendicular magnetic recording media, and electrode catalysts, and for solar energy conversion. However, most studies so far have used Al with a purity greater than 99.99% as starting material to produce highly ordered porous structures. From the viewpoint of practical applications, using low-purity Al or Al alloy materials to fabricate nanoporous alumina nanostructures is highly desirable in terms of lowering costs and gaining satisfied mechanical strength.

Recently, much effort has been dedicated to fabricating tailored nanoporous alumina films with varying pore diameters gradually or step-wise from high-purity Al foils (e.g., 99.997% Al), by means of changing the anodizing voltages or current densities, the electrolytes, temperature 15–20 or by using oscillatory currents, followed by chemical etching. However, to the best of our knowledge, there has been no report so far on the fabrication of 3D networked nanoporous alumina films with both vertical and transverse pores, whether from high- or low-purity Al materials. Moreover, Skeldon et al. recently reported the generation of defects or branched pores on the pore walls of PAA films by anodizing a commercial Al sheet (A1050–99.5% Al) and a Al-0.05%Cu sputtered film in phosphoric electrolytes, and proposed a mechanism that the formation of branched pores was related to the Cu component in Al base materials. Zaraska et al. reported the effects of anode surface area on the oxide formation during anodizing of A1050 alloy in oxalic and sulfuric baths. Chung et al., on the other hand, proposed a hybrid pulsed anodizing method to improve the pore distribution uniformity of nanoporous anodic aluminum oxide on low-purity aluminum foils. Nevertheless, the effects of the purity of low-purity Al materials on the formation and nanoporous morphology of PAA films in different electrolytes has not been investigated systematically.

This paper reports a simple anodizing method to fabricate novel three-dimensional networked porous anodic alumina nanostructures from various industrial-grade Al materials. Moreover, the effects of the purity and impurities of the Al materials on the formation and morphology of anodic alumina films were investigated, and a possible explanation for the mechanism is discussed.
Table I. Compositions of the different Al base materials used in this study.

| No. | Materials | Si  | Fe   | Cu  | Zn  | Mg  | Mn  | Others | Thickness (mm) |
|-----|-----------|-----|------|-----|-----|-----|-----|--------|----------------|
| 1   | Al-1100   | 0.1 | 0.6  | 0.1 | <0.10| –   | –   | <0.15  | 0.5            |
| 2   | Al-1N30   | <0.7| <0.1 | <0.05| <0.05| <0.1| <0.03| 0.1    |                |
| 3   | Al-1050   | 0.07| 0.31 | 0.01| 0.01| 0   | 0   | 0.04   | 0.5            |
| 4   | Al-5N     | –   | –    | –   | –   | –   | –   | 0.001  | 0.5            |

ESCALAB 200-X) in an operating vacuum better than $1 \times 10^{-7}$ Torr (1 Torr $\equiv$ 133 Pa). The binding energies of the spectra were corrected using the C 1s signal at 284.5 eV, with an accuracy of less than 0.1 eV. Moreover, the depth distributions of elements in the as-anodized specimens were investigated by glow discharge optical emission spectrometry (GDOES: HORIBA-JY-5000RF, 4 mm diameter, 13.56 MHz, 35 W, Ar-600 Pa).

Results and Discussion

Anodizing behavior of Al sheets with different purities.— Figure 1 shows the time variation of current density for the Al materials with different purities during anodization in different electrolytes. In the case of anodization in phosphoric acid solution (Figures 1a and 1b), a surge of 20–30 A $\cdot$ m$^{-2}$ is initially observed in the current-time response of all specimens (Figure 1a), which can be ascribed to the anodic dissolution of Al and impurities on the surface of the base materials. Subsequently, the current density increased gradually with the anodizing voltage. Although the voltage raised at a rate of 2 V/s in all cases, the rate of increase of the current as a function of the anodizing time (i.e. the slope of the current-time curves) was inversely related to the Al purity, with, in terms of slopes, 99.999% $< 99.56% < 99.3\% < 99.0\%$. Here, because a limited overall current was set at 0.1 A during anodizing to prevent ‘burning’, the current-time response plateaued for the low-purity Al materials. As the voltage reached 130 V, the anodic current density decreased rapidly to the steady-state current values of 5–10 A $\cdot$ m$^{-2}$ (Figure 1b). Similar to the rate of increase during the initial stage, the steady-state current densities were inversely related to Al material purity. During anodization, the formation of anodic alumina and the anodic dissolution of impurities (i.e. Fe, Cu, Zn, Mg, Mn, etc.) may occur concurrently on the Al anode according to the following reactions:

$$2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}$$ \[1\]

$$\text{M} \rightarrow \text{M}^{2+} + 2\text{e} \quad (\text{M} = \text{Fe}, \text{Cu}, \text{Zn}, \text{Mg}, \text{Mn}, \text{etc.})$$ \[2\]

The increase of the anodic current density with the lowering of the purity of the Al materials can be mainly attributed to the anodic dissolution of impurity components driven by the high electric field at 130 V, which also leads to lower growth rates for PAA films on the low-purity Al materials, as discussed later.

![Figure 1](image-url)
In contrast, for anodization in oxalic (Figure 1c) and sulfuric (Figure 1d) acid solutions, both the surge and steady-state currents increase with the purity of the Al materials, with in terms of currents 99.999% > 99.56% > 99.3% > 99.0%, which is different from the anodizing behavior in the phosphorous electrolyte. This indicates that the anodizing behavior of the low-purity Al materials is complicated, involving not only the chemical dissolution ability of the acidic electrolytes but also the anodic dissolution as a function of the applied voltages.

Effects of purities on the morphology of porous alumina films.— Figure 2 shows the surface morphologies of PAA films formed in a phosphoric acid solution at 160 V on Al sheets with varying purity. A typical PAA film with an ordered pore arrangement was obtained with the 99.999% pure Al as usual, whereas unique PAA films with irregular porous structures formed on the low-purity Al sheets, indicating that material purity is an important factor in achieving ordered porous alumina nanostructures. Even though the same anodizing conditions were used, the pore sizes of the PAA films increased with decreasing material purity. The average pore diameters were 155, 250, 260, and 310 nm for the 99.999%, 99.56%, 99.3%, and 99.0% pure Al sheets, respectively. This indicates that the corrosion resistance of the PAA films formed on the low-purity Al materials decreased with the purity of the base materials. Accordingly, the porosity of the PAA films increased the lower the purity of the Al material.

Furthermore, some minute dents can be seen at the junctions of pore cell walls (indicated by white arrows in Figure 2), whose number increased with the lowering of the Al material purity. Particularly, for the 99.0% Al specimen, some transverse pores or voids containing small particles also formed at the cell boundaries in the alumina pore walls with a regular interspacing of around 200 nm, thereby interconnecting all of the pores in the film and forming a nanoporous network, i.e., a three-dimensional porous nanostructure.

Figure 3 presents cross-sectional images of the central part of the PAA films formed from different Al materials. For the PAA films formed from low-purity Al sheets, apart from the parallel stem pores (~250 nm in diameter) perpendicular to the alumina film/metal interface, numerous smaller transverse branched pores 20–80 nm in diameter are also formed on the pore walls with a regular interspacing of around 200 nm (Figures 3b–3d). In contrast, a conventional two-dimensional (2D) porous alumina film was obtained from the high purity (99.999%) Al sheet, in which highly ordered but independent pores around 180 nm in diameter formed along the electrical field. Moreover, the periodicity of the transverse branched pores in the PAA films formed from low-purity Al materials is irrespective of the material purity, whereas the number of transverse branched pores increased with the lowering of the Al purity. This indicates that the formation of branched pores occurred preferentially in low-purity Al and the periodicity of branched pores was not affected by the content of impurities of Al materials. Noticeably, the transverse branched pores that formed in the PAA films on the 99.0% Al sheet penetrated the alumina pore walls with a regular interspacing of around 200 nm, thereby interconnecting all of the pores in the film and forming a nanoporous network, i.e., a three-dimensional porous nanostructure.

Figure 4 exhibits the cross-sectional morphologies in the vicinity to the barrier layers of the same PAA films. The barrier layers of all the specimens were devoid of transverse pores and defects compared to the middle parts of the films (Figure 3), suggesting that the generation and growth of transverse pores across the pore walls is mainly caused by chemical dissolution occurring during prolonged anodization in the phosphoric acidic solution. Some transverse branched pores can be observed on the pore walls for the low-purity Al materials (see white arrows in Figures 4b–4d). In particular, for the 99.0% Al specimen, some transverse pores or voids containing small particles also formed at the cell boundaries in the alumina pore walls with a
Figure 3. Cross-sectional FE-SEM images of porous alumina films on Al sheets of (a) 99.999%, (b) 99.56%, (c) 99.3%, and (d) 99.0% purity. (Anodization: 0.9 M H₃PO₄, 160 V, 273 K, 5 h.)

Figure 4. Cross-sectional FE-SEM images near the barrier layers of porous alumina films on Al sheets of (a) 99.999%, (b) 99.56%, (c) 99.3%, and (d) 99.0% purity. (Anodization: 0.9 M H₃PO₄, 160 V, 273 K, 5 h.)
Figure 5. Cross-sectional FE-SEM images of porous alumina films formed on 99.0% pure Al sheets in a 0.9 M H₃PO₄ solution at (a) 110 V, (b) 130 V, (c) 160 V, and (d) 190 V at 273–278 K over 5 h, respectively.

Effects of the anodizing voltage on the microstructure of PAA films.—Figure 5 shows the PAA films formed in the phosphoric acid solution at different anodizing voltages from the 99.0% Al sheet. Networked nanoporous structures with cylindrical stem pores and periodical transverse branched pores across the pore walls were obtained for all experimental conditions. This indicates that varying the anodizing voltage has little effect on the formation of transverse pores in the PAA films formed from Al sheets with different purities. Nevertheless, the average interspacing of the transverse branched pores was measured to be around 160 nm, although these decrease in number and become less discernable with decreasing voltages. Similar to high-purity Al materials, the thickness of the barrier layer of the PAA films was proportional to the anodizing voltage, increasing by 1.1 nm/V. Here, the variation of periodicity of transverse pores with anodizing voltage can be explained by formation mechanism proposed by Molchan et al. Because the defects or the initial branched pores are attributed to the enrichment of Cu impurity at the metal/film interface and the transportation to ridges of cell boundaries, the thickening of barrier layer and the increase of cell size of PAA films at high voltage delayed the rate of supply of Cu to triple points, thus leading to the increment of interspacing of transverse branched pores.

Effects of the electrolyte on the porous structures of anodic alumina films formed on Al materials with different purities.—Figure 6 shows the microstructures of PAA films formed on the 99.56% pure Al sheet in sulfuric, oxalic, and phosphoric acid solutions over a short period of 30 min. Uniform PAA films with ordered hexagonal-packed vertical pore arrays were obtained for all electrolytes, highlighting the applicability of using low-purity Al as low-cost nano-template materials for the fabrication of various nanostructures. Noticeably, the transverse branched pores are observed only in the PAA film formed in the phosphoric acid solution. This can be attributed to the applicable anodizing voltages for uniform PAA films in different acidic solutions, which is associated with potential-driven oxygen generation and Cu accumulation, and/or to the higher dissolving ability of the phosphoric acid solution compared with the oxalic and sulfuric ones. In particular, the transverse branched pores inside the cylindrical stem pores and the cell boundaries (see the white and black arrows in Figures 6e–6f) formed close to the film surface. This indicates that the
formation of transverse branched pores and Al anodization occurred simultaneously.

In order to further investigate the influence of the electrolyte on the formation of transverse branched pores, we performed anodization in oxalic and sulfuric acidic solutions using Al sheets with different purities. Figure 7 shows cross-sectional FE-SEM images of PAA films formed in an oxalic acid solution at 60 V for 2 h. Periodical transverse branched pores can be seen with almost the same pore diameter as that of the vertical stem pores in the PAA film formed on the lowest purity (99.0%) Al (see the framed region and arrows in Figure 7d). Subsequent chemical etching in a mixed acidic solution of phosphoric and chromic acids for 15 min clearly revealed that the transverse pores perforated the stem pore walls (Figure 7f), thus leading to a highly porous alumina film. In contrast, the transverse branched pores did not form for the specimens with more than 99.3% purity even after chemical etching (Figure 7e). This indicates that even a subtle change in the purity of the Al base materials can lead to a noticeable difference in the morphology of PAA films, and that Al material purity is an important factor in the formation of transverse branched pores. Moreover, it is noticeable that the interspacing of the transverse pores here is around 105 nm (see the arrow in Figure 7d), which is much less than in the films formed in phosphoric acid solution (Figure 5). This evidences that the generation cycle (i.e., the interval between transverse branched pores) is mainly dependent on the applied anodizing voltage, i.e., the barrier thickness and cell size of anodic films corresponding to the electric field, which affects the accumulation of Cu impurity at cell boundaries. Furthermore, transverse branched pores were not observed in PAA films formed in sulfuric acid solutions either with the low- or high-purity Al materials (data not shown). This may be ascribed to the FE-SEM resolution limit (around 2 nm) and/or to the mitigation of Cu accumulation and oxygen evolution at the low anodizing voltage of 20 V.

Effects of Al material purity on corrosion resistance and growth rate of PAA films in different electrolytes.— In order to elaborate the influence of the Al base materials on the growth of PAA films and to eliminate the corrosive factor of chemical dissolution in acidic solutions, we adopted a novel two-step anodization in an oxalic acidic solution, i.e., first anodized at 60 V for 1 h to get a top-layer PAA film, followed by a soft chemical etching in a mixed acidic solution.
Figure 7. Cross-sectional FE-SEM images of PAA films formed in a H$_2$C$_2$O$_4$ solution at 60 V and 278 K over 2 h on Al sheets of (a) 99.999%, (b) 99.56%, (c) 99.3%, and (d) 99.0% purity Al, with specimens shown (a–d) as-anodized or (e–f) after etching in a mixed phosphoric and chromic acid solution at 353 K for 3 min.

of phosphoric and chromic acids at 353 K for a short time of 3 min to widen the alumina pores, and then re-anodized at the same voltage for 2 h. As shown in Figure 8, a through-mask anodization occurred in the 2nd step anodization via the upper-tier films that formed in the 1st anodization, thus producing a two-tiered PAA film with different pore diameters between the tiers (see insets in Figure 8). Here, the upper-tier PAA film not only induced the initial sites of the pores in the 2nd anodization but also protected effectively the underlying as-anodized PAA films from the corrosive attack of the oxalic acid solution, thus endowing the film thickness that solely relates to the anodizing process. It is clearly seen that the thickness of lower-tiered as-anodized PAA films decreased with the lowering of Al purity, giving growth rates of around 16.1, 9.4, 7.0, and 4.5 μm h$^{-1}$ for Al materials of 99.999%, 99.56%, 99.3%, and 99.0%, respectively. This revealed that the material purity played a pivotal role in the formation of porous alumina in anodization, which can be attributed to the lowering of anodizing efficiency for low-purity Al materials due to the inclusion of impurities of Fe, Cu, Si, Zn, Mn, etc. In addition, the thickness of the upper-tiered PAA films is irrespective of the Al purity, which is probably ascribed to the inhomogeneity of the locations and stirring in the electrolytic cell during etching.

Figure 9 shows the cross-sections of the PAA films formed in sulfuric acid solution by a two-step anodization at 20 V for 1 h and 2 h, also with a chemical etching in the mixed phosphoric and chromic acid solution for 3 min between the anodizing steps. Unlike anodization in oxalic solutions, the upper-tiered PAA films on low-purity Al materials that formed in the 1st anodization were removed due to the thin alumina walls, only the upper-tier film on high purity Al of 99.999% survived in the chemical etching, thus indicating its higher corrosion resistance than those formed on low-purity Al materials. Similar to oxalic acid solution, the film thickness decreased slightly with the lowering of Al purity, leading to growth rates of around 10.0,
Figure 8. Cross-sectional FE-SEM images of two-layered PAA films obtained by a two-step anodization in a H$_2$C$_2$O$_4$ solution on Al sheets of (a) 99.999%, (b) 99.56%, (c) 99.3%, and (d) 99.0% Al: 1st anodization – 60 V, 278 K, 1 h; chemical etching – 5% H$_3$PO$_4$ + 3%CrO$_3$, 353 K, 3 min; 2nd anodization – 60 V, 278 K, 2 h. Insets in the images show the interface regions of the layers.

Figure 9. FE-SEM images of PAA films formed by a two-step anodization in a H$_2$SO$_4$ solution on Al sheets of (a) 99.999%, (b) 99.56%, (c) 99.3%, and 99.0% Al: 1st anodization – 20 V, 278 K, 1 h; chemical etching – 5% H$_3$PO$_4$ + 3%CrO$_3$, 353 K, 3 min; 2nd anodization – 20 V, 278 K, 2 h. Inset in (a) – enlarged image at the layer interface; insets in (b – d) – surface images.
The purity of Al base materials on the thickness of PAA films formed over 2–5 h in sulfuric (S), oxalic (O), and phosphoric (P) acid solutions at 20, 60, and 160 V, respectively.

8.5, 7.5, and 7 μm h⁻¹ for Al materials with purities of 99.999, 99.56, 99.3, and 99.0%, respectively. Moreover, comparing the pore diameters from the surface images (insets in Figure 9) revealed that the corrosion resistance of the PAA films formed in sulfuric acid solution decreased with the lowering of Al materials purity.

Figure 10 summaries the influence of Al material purity on the thickness of the as-anodized PAA films formed at P-160 V, O-60 V, and S-20 V. For all the acidic solutions, the thickness of PAA films decreased greatly with the purity of the sheets in the following order: 99.0%, 99.56%, 99.3%, and 99.0%. This means that the anodizing efficiency also decreased with the purity of the Al materials, due to the anodic dissolution of impurity components as described in Reaction 2. Moreover, it can be deduced from the slopes of plots of film thickness versus purity that the impact on film growth of lowering the material purity is the greatest for oxalic, and the smallest for sulfuric acid solution. Generally, the growth rate (i.e. the thickness of the PAA films) corresponds to the steady-state current density during anodization. For the oxalic and sulfuric acid solutions, the variation in film thickness caused by decreasing Al material purity corresponds well with the ordering of steady-state current values during constant-voltage anodization (see Figures 1c and 1d). In contrast, for the phosphoric acid solution, the relationship between film thickness and material purity is opposite to the one for steady-state current density, which can be attributed to the greater dissolving ability of the phosphoric acid solution and to the deterioration of the corrosion resistance of PAA films with more impurities, as discussed in the following section.

Elements contained in the anodic alumina films.— In order to investigate the link between the presence of impurities in Al materials and the formation of transverse pores, the surface compositions of different Al materials were analyzed before and after anodization in a phosphoric solution at 160 V by XPS, the results of which are listed in Table II. Compared with the chemical compositions of the raw materials shown in Table I, the Fe, Zn, Mg, and Mn impurities in the low-purity Al materials were completely removed by electro-polishing, while the Cu impurities remained or increased in proportion on the surface of the Al sheets for all specimens, which is consistent to the results of Caicedo-Martinez et al. Here, the surface of the 99.0% specimen becomes enriched in Si impurities, possibly in the form of segregates. Following anodization, the Cu on the Al surface disappeared completely, which can be attributed to anodic and/or chemical dissolution accompanying the preferential oxidation of Al, thus leading to the formation of tiny pores on the surface of the alumina walls of the low-purity Al materials (see white arrows in Figure 2). Moreover, Fe enrichment was also detected on the surface of the PAA films formed on the 99.0% and 99.3% pure Al specimens. This suggests that Fe impurities formed in the anodic alumina films during anodization.

Figure 11 shows high-resolution Al 2p, O 1s, P 2p, and Fe 2p XPS spectra for a PAA film formed in the phosphoric acid solution on a 99.0% pure Al sheet. Beside Al and O that can be ascribed to anodic alumina, P and Fe were also detected. According to the peak binding energy, P is present as phosphoric ions, which are attributed to the inclusion of electrolyte anions driven by the high electric fields during anodization, which is consistent with previous studies. The Fe component can be attributed to a mixture of oxide and hydroxide in the form of FeOOH and Fe₂O₃, formed by anodization of Fe in the Al material. It can be has been suggested that the inclusion of Fe oxide and hydroxide in the anodic films, in addition to the accumulation of Cu impurity in Al materials, also facilitates the formation of transverse pores across the alumina wall of vertical stem pores due to its lower corrosion resistance in comparison with anodic alumina. This therefore explains the increase in the number of transverse pores with the lowering of the purity or the increasing of Cu and Fe impurities in the Al materials (Figure 3 and Table I).

Moreover, in order to investigate the inclusion of impurity elements in PAA films, the elemental depth profiles of the films on 99.0% and 99.56% pure Al sheets were established by GDOES analysis, as shown in Figure 12. This clearly reveals a small amount of Fe in the anodic film region of the low-purity Al material (99.0%), thus confirming the inclusion of Fe in the matrix of this alumina film. The Fe signal decreases toward the film surface, which can be attributed to chemical dissolution in the corrosive phosphoric acid solution during prolonged anodization. This indicates that the inclusion of Fe oxides and hydroxides in PAA films plays an important role in the formation of networked 3D nanoporous alumina films with both vertical and transverse pores for 99.0% pure Al specimens.

### Table II. Surface compositions of Al materials before and after anodization in 0.9 M H₃PO₄ solution at 160 V and 273 K for 5 h.

| No. | Materials | Specimens | Compositions (at%) |
|-----|-----------|-----------|--------------------|
|     |           |           | O 1s   | Al 2p | Fe 2p | Si 2p | Cu 2p | P 2p |
| 1   | Al-1100   | As-anodized | 69.5   | 21.1  | 1.5   | 1.5   | 1.1   | 5.4  |
| 2   | Al-1N30   | As-anodized | 71.7   | 23.5  | 1.5   | 1.5   | 1.1   | 5.4  |
| 3   | Al-1050   | As-anodized | 73.5   | 21.7  | 1.2   | 1.2   | 1.1   | 5.4  |
| 4   | Al-5N     | As-anodized | 75.1   | 19.6  | 1.5   | 1.5   | 1.1   | 5.4  |
Figure 11. High-resolution XPS spectra of the (a) Al 2p, (b) O 1s, (c) P 2p, and (d) Fe 2p binding energy regions for porous alumina films formed from 99.0% pure Al sheets in 0.9 M H₃PO₄ solution at 160 V over 5 h.

Figure 12. GDOES depth profiles of PAA films formed on (a) 99.56% and (b) 99.0% pure Al sheets by anodization in 0.9 M H₃PO₄ solution at 160 V for 2h.
phosphoric (Figures 3d and 5) and oxalic acid solutions (Figures 7d and 7e). Moreover, Figure 12 also gives the depth profiles of P in the films. A small amount of P included in the anodic alumina films throughout the whole thickness, which can be attributed to the porous structures.

Conclusions

We investigated the effects of the purity of Al materials on the morphology and the formation rate of PAA films in phosphoric, oxalic, and sulfuric acid solutions by constant-voltage anodization of Al sheets with different purities, namely 99.0% (A1100), 99.3% (A1103), 99.56% (A1050), and 99.999% (A15N).

Numerous transverse branched pores were generated in the PAA films formed on the low-purity Al materials during anodization in the phosphoric acid solution and the number of transverse pores increased with decreasing Al purity. In particular, these results show that three-dimensional networked nanoporous alumina nanostructures—consisting of vertical cylindrical stem pore arrays 170–310 nm in diameter with periodical transverse branched pores 20–80 nm in diameter interspaced regularly by 190–220 nm across the stem pore walls—can be controllably fabricated from the lowest purity Al material (i.e., 99.0%) by directly anodizing in phosphoric acid solutions at 110–190 V, without any chemical etching.

The generation of transverse branched pores was predominantly affected by the purity of the Al base materials, with more pores forming on the lower purity Al. The generation cycle or the interspacing of the transverse branched pores, on the other hand, narrowed with decreasing anodizing voltages. The generation of transverse branched pores can be attributed to anodic and/or chemical dissolution of Cu, Fe, Mn, Si, and Zn impurities in the Al base materials, the accumulation of Cu at triple points of cell boundaries during anodizing, as well as the chemical dissolution of Fe oxides and hydroxides that included in PAA films during prolonged anodization. Moreover, transverse branched pores formed more readily in PAA films in phosphoric acid solutions than in oxalic ones, which can be attributed to enhanced electrochemical dissolution in the corrosive phosphoric electrolyte driven by the high electrical field during anodization.

Furthermore, the growth rate (i.e., the thickness) of the PAA films decreased in all the acidic solutions with the lowering of the purity of Al base materials. This can be attributed to the low anodizing efficiency for low purity Al sheets containing various impurities and the low corrosion resistance of the PAA films containing Fe oxides and/or hydroxides that were produced by the partial oxidation of Fe in the Al base materials during anodization.

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