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Fabrication of Self-ordered Porous Alumina via Anodizing in Sulfate Solutions

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Abstract

Self-ordered porous alumina was fabricated via anodizing in an acid salt electrolyte solution, sodium hydrogen sulfate (NaHSO_4). High-purity aluminum specimens were anodized in a NaHSO_4 solution under various operating conditions with adjusted concentrations, temperatures, applied voltages, and times. Self-ordering was achieved via NaHSO_4 anodizing at appropriate applied voltages ranging from 20 to 28 V, and ordered cell arrangements with the cell size of 55-77 nm were successfully fabricated. Sulfur atoms originating from the electrolyte anions were incorporated into the ordered porous alumina. A honeycomb distribution consisting of a thick outer layer with a high concentration of sulfur and a very thin inner skeleton with a relatively low concentration sulfur was formed via NaHSO_4 anodizing. Our results suggested that there are now many electrolyte options for the fabrication of self-ordered porous alumina with a wide range of nanosizes.

Keywords: Aluminum; Anodizing; Sodium hydrogen sulfate; Porous materials; Self-ordering; Structural

1. Introduction

Ordered porous alumina fabricated via electrochemical anodizing has a characteristic honeycomb structure with periodic nanoscale pores, and their fundamental behaviors and engineering were actively investigated for their use in challenging and novel nanomaterials, such as metamaterials [1], plasmonics [2], and surface-enhanced Raman scattering [3], and multifunctional materials [4]. The self-ordering of porous alumina can be achieved via anodizing in appropriate acidic electrolyte solutions under the corresponding appropriate applied voltage [5]. The size of each unit cell in the ordered porous alumina was determined by the applied voltage during self-ordering anodizing [6, 7]. Although to date several acidic electrolytes, including sulfuric [8], selenic [9], phosphonic [10], phosphoric [11], etidronic [12], dicarboxylic, [13] and these mixture acids [14, 15], have been reported for self-ordering electrolytes, new, additional electrolytes must be continuously discovered and examined to increase the self-ordering voltage and corresponding cell size.

Sulfuric acid anodizing is the most widely used approach for the formation of transparent porous alumina on aluminum substrates in many industrial applications. Ordered porous alumina with a cell size of 50 to 60 nm can be easily obtained via sulfuric acid anodizing at 19-25 V [6-8]. On the other hand, it is well known that sulfuric acid is a highly toxic and corrosive acid, and its usage, transportation, and storage are restricted by law for safety reasons in most countries. Therefore, the discovery of more safety self-ordering electrolytes based on sulfuric acid is required for future anodizing applications. Sodium hydrogen sulfate (NaHSO_4) is a solid acid salt that is produced by sodium hydroxide and sulfuric acid, which is widely used as safe chemicals for food additives, surface finishing, and pH adjusting. It is interesting to study aluminum anodizing in such an acid salt electrolyte solution regarding the increasing the cell size and the safety of the anodizing science and technology.

In the present work, we described the self-ordering of porous alumina with increasing cell sizes fabricated via NaHSO_4 anodizing. Nanocharacterization of the ordered porous alumina was investigated via high-resolution electron microscopy and elemental analysis.

2. Experimental

High-purity aluminum plates (99.999 wt%, 0.25-1.0 mm thick, GoodFellow) were degreased in ethanol for 10 min and then electropolished in a 13.6 M

CH₃COOH/2.56 M HClO₄ (78 vol% CH₃COOH/22 vol% 70% HClO₄) solution at 280 K and 28 V for 1 min. The electropolished specimens were anodized in a 0.25-2.0 M NaHSO₄ solution (273-313 K, pH = 0.45-1.1 at 293 K in 2.0-0.25 M NaHSO₄) at a constant voltage of 17 to 29 V for up to 24 h. A platinum plate was used as the cathode, and the electrolyte solutions were vigorously stirred with a cross-head stir bar during anodizing. The current density was measured by a digital multimeter (DMM4040, Tektronix) during constant voltage anodizing. After anodizing, the specimens were immersed in a 0.2 M CrO₃/0.51 M H₃PO₄ solution at 353 K to selectively dissolve the anodic oxide on the aluminum substrate. Finally, the exposed aluminum surface was anodized again in a 0.25 M NaHSO₄ solution to form ordered porous alumina (two-step anodizing) [16, 17].

The anodized specimens were examined by field emission scanning electron microscopy (FE-SEM, JSM-6500F and JIB-4600F/HKD, JEOL) and image-aberration-corrected scanning transmission electron microscopy (STEM, Titan G2 60-300, 300 kV, FEI). For the SEM observations, a thin platinum electroconductive layer was coated onto the specimens. For the STEM observations, ordered porous alumina fabricated via two-step anodizing was lifted off of the aluminum substrate in a 0.5 M SnCl₄ solution, was pasted on a molybdenum single-hole TEM grid, and was thinned by an argon ion beam using a precision ion polishing system (PIPS, Gatan). The elemental distribution in the porous alumina was examined by STEM-energy dispersive X-ray spectrometry (EDS). The extent of the self-ordering behavior was evaluated by fast Fourier transform (FFT) using the Image-J software package (Wayne Rasband, National Institutes of Health, USA) [18, 19].

3. Results and Discussion

Figure 1a shows the changes in the current density, j , with anodizing time, t , during anodizing in a 0.25 M NaHSO₄ solution (293 K) at various constant voltages of $U = 20-27$ V for 60 min. Plateau current densities corresponding to a steady growth of anodic oxide were measured after the initial 5-min-anodizing at $U = 20-26$ V, and the plateau current increased with anodizing voltage due to the rapid growth rate under the applied high voltage. However, the current density increased rapidly in the initial stage of anodizing at an excess applied voltage of 27 V due to the oxide burning phenomenon with non-uniform anodic alumina growth and oxygen gas evolution. These electrochemical behaviors were typically obtained via constant voltage anodizing under

the formation of porous alumina on the aluminum substrate. The SEM images of the nanostructured aluminum surface exposed by selective oxide dissolution after anodizing are shown in Fig. 1b. A disordered aluminum dimple array was formed on the surface at a low applied voltage of 20 V (i.e., low current density), and the resulting FFT image exhibited a halo pattern based on the irregularity of the dimples. The regularity of the arrangement was improved with increased applied voltage (i.e., current density increased), and ideal dimple arrangements with several tens of cells and the resulting FFT image with weak spots were observed at the maximum applied voltage of 26 V without any oxide burning. The self-ordering of porous alumina is typically achieved by the combination of ionic migration in the oxide and strong stress-driven interface diffusion of metal atoms due to the application of high voltage without oxide burning (flow model) [20, 21]. Therefore, the maximum voltage anodizing in a NaHSO₄ solution under various concentrations, temperatures, and times was carried out for the following studies.

Figure 2a shows SEM images of time changes of a nanostructured aluminum dimple arrangement fabricated via 0.25 M NaHSO₄ anodizing (273 K) at a maximum voltage of 28 V for 1, 6, and 24 h. These images clearly show that the regularity of the dimple array was greatly improved with long-term anodizing, and an ideal dimple arrangement with several hundreds of dimples was constructed on the aluminum surface via 24-h-anodizing. In addition, the resulting FFT image for the 24-h anodizing specimen exhibited a clear spot pattern based on the ideal dimple arrangement. The periodicity of each dimple corresponding to the “cell size” or “interpore distance” was measured to be approximately 77 nm at 28 V. These experimental results show that ordered porous alumina can be fabricated via long-term maximum voltage anodizing in a NaHSO₄ solution. Further fabrication of ordered porous alumina with different nanosizes could be realized by investigating the optimum anodizing conditions by varying the concentration, temperature, and voltage.

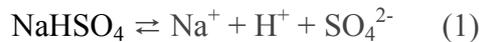
Figure 2b shows SEM images of various ordered dimple arrays fabricated via NaHSO₄ anodizing at voltages in the 20-27 V range. Periodic nanostructures with dimple diameters of 74 nm, 71 nm and 55 nm at 27 V, 26 V and 20 V, respectively, were successfully formed via NaHSO₄ anodizing under optimum conditions. Two-step NaHSO₄ anodizing using these nanostructured aluminum specimens as a template allowed for the fabrication of ordered porous alumina across the entire vertical regions. Previous studies have reported that sulfuric acid anodizing caused a self-ordering

voltage of 19 to 25 V for a cell size of 50 to 60 nm [6-8]. Comparing our study with sulfuric acid anodizing, the self-ordering voltage (20-28 V) and corresponding cell size (55-77 nm) obtained via NaHSO₄ anodizing were slightly larger than those of sulfuric acid anodizing and were expanded over much broader ranges compared to conventional sulfuric acid anodizing. This cell size expansion is due to the low solubility of anodic aluminum oxide into a NaHSO₄ solution with relatively high pH values. The relationship between of the cell size (D) and applied voltage (U) can be expressed by the following equation [17]:

$$D = k U \quad (1)$$

where k is a proportional constant (2.5 nm V⁻¹). Although our cell sizes were only slightly larger than that obtained by the equation (1), these values are in good agreement with the linear relationship. We note that anodizing in a high pH solution is also advantageous for the fabrication of high-aspect-ratio ordered porous alumina because the formation of thick porous alumina can be achieved via anodizing in NaHSO₄ due to its low chemical dissolution. Moreover, it is important to note that as-received NaHSO₄ chemicals can be safely transported, stored, and used in industrial applications.

Ordered porous alumina fabricated via two-step NaHSO₄ anodizing was examined in detail by high-angle annular dark-field (HAADF) STEM observations and STEM-EDS measurements. Figure 3a shows an EDS spectrum measured for the ordered porous alumina formed via 0.25 M NaHSO₄ anodizing at 273 K and 28 V for 24 h for the first anodizing and for 3 h for the subsequent 3 h anodizing. While no sodium was detected in the porous alumina by EDS measurement, there were three clear peaks for oxygen, aluminum, and sulfur. NaHSO₄ electrolytic dissociation occurs in an aqueous solution according to:



If a weak ion-pair, such as NaSO₄⁻, was formed in the solution [22], the anion should also be incorporated into the porous alumina by a high electric field during anodizing. However, anions that had a sodium atom were not contained in the porous alumina because they were present in only a small amount in solution.

Figure 3b shows a HAADF-STEM image and the corresponding aluminum, oxygen, and sulfur distribution in the ordered porous alumina. Light gray hexagonal cell “skeleton”-like boundaries measuring approximately 4 nm in width were clearly observed in the HAADF-STEM image around each nanopore in the ordered porous alumina. These cell boundaries correspond to the distribution of sulfur originating from

anions incorporated during NaHSO₄ anodizing. The sulfur concentration profile of the hexagonal nanostructure is indicated by the yellow dotted line in Fig. 3c. The amount of sulfur in the skeleton was slightly smaller than that in the outer anodic oxide (green arrows). By using these sulfur concentration differences, a truly honeycomb nanostructure consisting of an ultrathin alumina skeleton may be formed via low speed chemical etching (pore-widening).

In summary, we demonstrated aluminum anodizing in an acid salt sulfate NaHSO₄ solution for the fabrication of ordered porous alumina. A further increase of the self-ordering voltage and the resulting cell size was achieved via NaHSO₄ anodizing. Due to our investigations, in addition to the previously known simple acid electrolytes, such as sulfuric and phosphoric acid, there are now many options for the fabrication of self-ordered porous alumina with a wide range of nanosizes.

4. Conclusions

A new approach to anodizing with an acid salt electrolyte solution, NaHSO₄, for self-ordered porous alumina was investigated to increase the self-ordered voltage and corresponding cell size. Ordered porous alumina with an ideal hexagonal nanostructure at the measured periodicity of 55 to 77 nm was successfully fabricated via NaHSO₄ anodizing at a maximum constant voltage of 20 to 28 V. A hexagonal distribution with different sulfur concentrations originating from the electrolyte species was formed in the ordered porous alumina during NaHSO₄ anodizing.

Acknowledgments

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Figures

Fig. 1 a) Changes in the current density, j , with anodizing time, t , during anodizing in a 0.25 M NaHSO₄ solution (293 K) at different applied voltages ranging from 20 to 27 V. b) SEM images of the nanostructured aluminum surface after anodizing and selective oxide dissolution. The insert figure shows the resulting FFT image obtained from the aluminum dimple array.

Fig. 2 a) SEM images of the nanostructured aluminum surface formed via 0.25 M NaHSO₄ anodizing at 273 K and 28 V for 1, 6, and 24 h. b) SEM images of ordered porous alumina fabricated via NaHSO₄ anodizing under various operating conditions at 20, 26, and 27 V.

Fig. 3 a) STEM-EDS spectra of the ordered porous alumina fabricated via NaHSO₄ two-step anodizing at 28 V. b) A HAADF-STEM image and corresponding STEM-EDS elemental maps of aluminum, oxygen, and sulfur. c) An EDS line profile of the sulfur in the porous alumina.

Figure 1

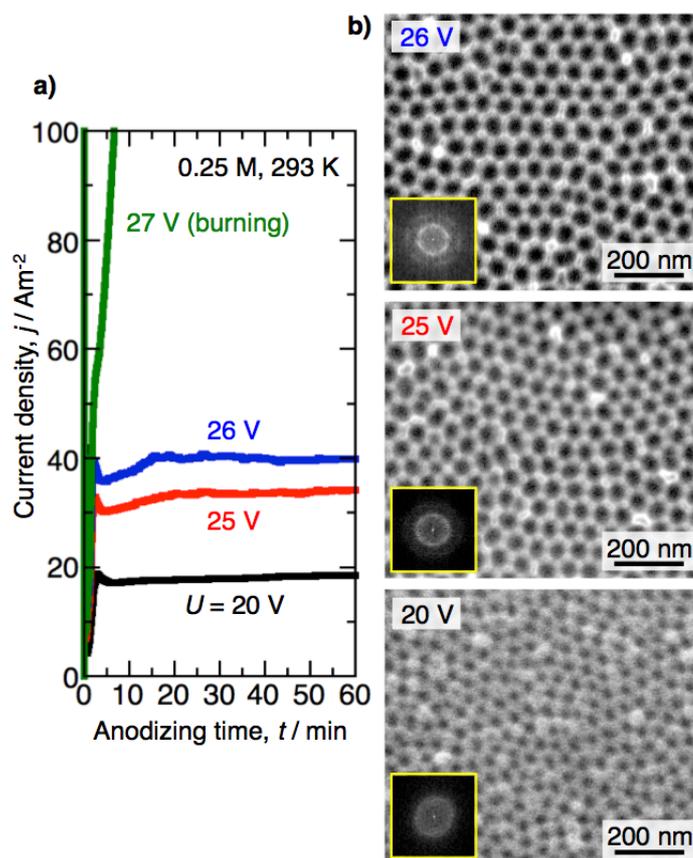


Figure 2

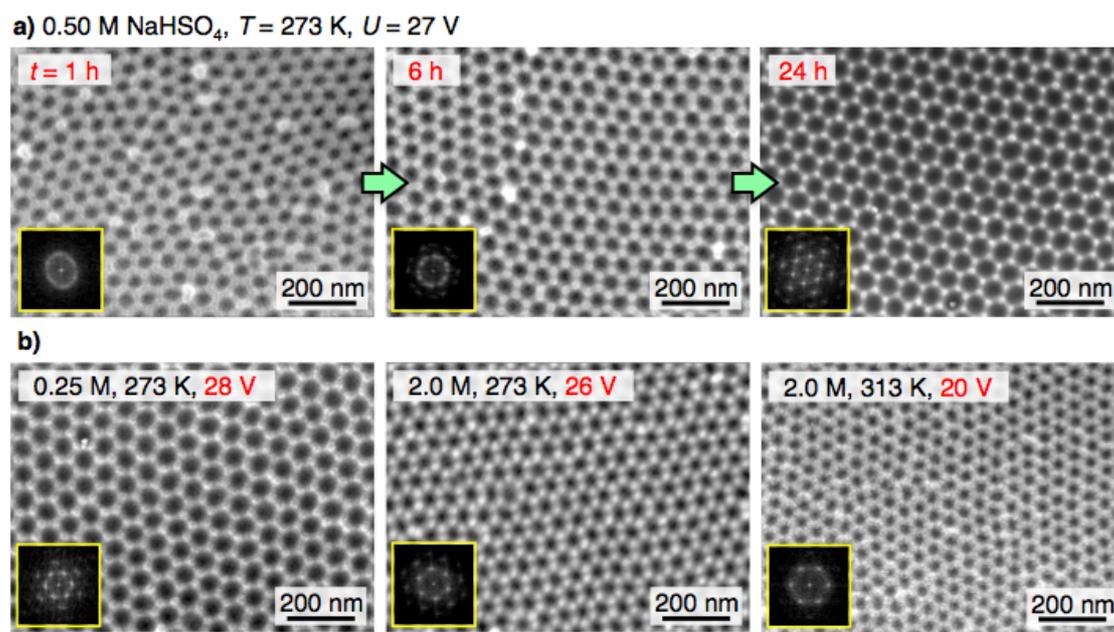


Figure 3

