



Fabrication of Anodic Porous Alumina by Squaric Acid Anodizing



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ABSTRACT

The growth behavior of anodic porous alumina formed via anodizing in a new electrolyte, squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione), is reported for the first time. A high-purity aluminum foil was anodized in a 0.1 M squaric acid solution at 293 K and a constant applied potential of 100–150 V. Anodic oxides grew on the aluminum foil at applied potentials of 100–120 V, but a burned oxide film was formed at higher voltage. Anodic porous alumina with a cell size of approximately 200–400 nm and sub-100-nm-scale pore diameter was successfully fabricated by anodizing in squaric acid. The cell size of the anodic oxide increased with anodizing time because of the uneven growth of the porous layer. The anodic porous alumina obtained by squaric acid anodizing consists of amorphous Al_2O_3 containing 5–6 at% carbon from the electrolyte.

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1. Introduction

Porous anodic oxide films of aluminum (anodic porous alumina) have been widely investigated as nanotemplates and resist films with good insulating properties for various micro- and nano-technology applications, such as magnetic recording media [1,2], electronic devices [3], biosensors [4], photonic crystals [5–7], microlens arrays [8,9], plasmonic devices [10–12], three-dimensional microstructures [13–15] and other basic nanodevices [16]. When aluminum is anodized in appropriate acidic electrolytes, porous alumina develops, which exhibits a uniform array of hexagonal cells, each containing a uniform cylindrical nanopore at the center [17–22] (lower right in Fig. 1). The morphology of anodic porous alumina, especially its cell size (identical meaning to interpore distance) and pore diameter in the porous layer, is limited by the electrolyte and voltage (electrochemical potential) applied during anodizing [23,24]. Fig. 1 summarizes the anodizing electrolytes that have been reported to date for porous alumina fabrication. Sulfuric (H_2SO_4), oxalic ($(\text{COOH})_2$), and phosphoric (H_3PO_4) acids are well-known, self-ordering anodizing solutions for porous alumina fabrication, and highly ordered porous alumina can be obtained by anodizing in these solutions at constant voltages of 18–25 V, 40 V, and 160–195 V, respectively [24–29]. Malonic acid ($\text{HOOC}-\text{CH}_2-\text{COOH}$) and tartaric acid ($\text{HOOC}-(\text{CHOH})_2-\text{COOH}$), typical dicarboxylic acids, have also been reported to support the fabrication of highly ordered

porous alumina fabrication at 120 V and 195 V, respectively [30,31]. In addition, several other electrolytes, such as chromic (H_2CrO_4) [32,33], malic ($\text{HOOC}-\text{CH}(\text{OH})-\text{CH}_2-\text{COOH}$) [23,34], citric ($\text{HOOC}-\text{CH}_2-\text{C}(\text{OH})(\text{COOH})-\text{COOH}$) [23], and glycolic ($\text{CH}_2\text{OH}-\text{COOH}$) [23] acids, have been reported as anodizing electrolytes to date. However, the formation of thick porous alumina with straight nanopores by anodizing in chromic acid is difficult because of branching and colony-forming nanopores [35]. Although citric acid anodizing has already been used for nanostructure fabrication [36], other organic electrolytes, including malic and glycolic acid solutions, cause the formation of non-uniform anodic porous alumina [23,34]. Therefore, five self-ordering electrolytes, namely, sulfuric, oxalic, and phosphoric acids, are generally selected for anodic porous alumina fabrication by many researchers.

In recent years, new anodizing procedures using an effective experimental approach and optimal anodizing conditions have been reported by several researchers to control the nano-scale features of anodic porous alumina. Lee et al. studied the rapid formation of ordered porous alumina by a hard anodizing procedure involving a powerful cooling stage and obtained an ultra-high aspect ratio (>1,000) of anodic porous alumina by anodizing in oxalic acid at 120–150 V [24]. They also reported the structural control of porous alumina by the pulse anodizing of aluminum and obtained well-defined three-dimensional nanoporous alumina membranes [26]. The fabrication of self-ordered anodic porous alumina at a previously unutilized ordering voltage was achieved by Almasi-Kashi et al. in a mixture of sulfuric and oxalic acid electrolytes [37]. The fabrication of high-aspect-ratio anodic porous alumina templates with 15-nm nanopores was realized by Martin et al. by anodizing aluminum in an ethylene glycol containing

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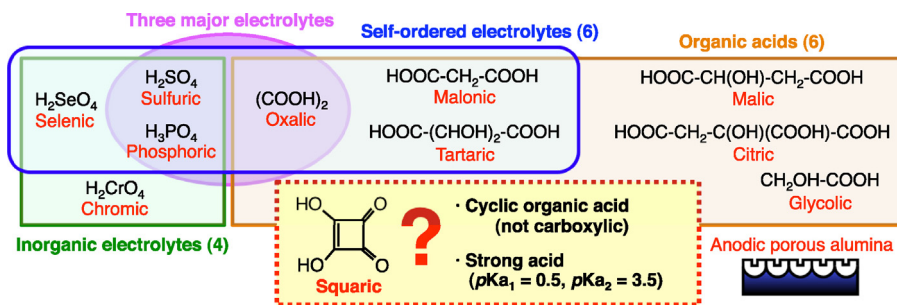
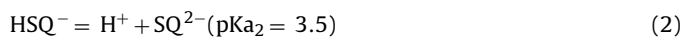
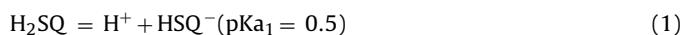


Fig. 1. Summary of the anodizing electrolytes used for anodic porous alumina fabrication. The inorganic acids sulfuric, phosphoric, selenic, and chromic acids and the organic acids oxalic, malonic, tartaric, malic, citric, and glycolic acids have been reported to date. In this study, squaric acid's potential as an anodizing electrolyte was investigated.

sulfuric acid electrolyte [38]. However, the potential applications of anodic porous alumina are still limited by the narrow range of available electrolytes, as mentioned above. Thus, the discovery of additional electrolytes would greatly expand the applicability of anodic porous alumina. Very recently, we reported a self-ordered porous alumina formed via anodizing in a new self-ordered electrolyte, selenic acid (H₂SeO₄, Fig. 1) [39]. Selenic acid anodizing works effectively at a previously unutilized self-ordering voltage (48 V) with 110 nm cell size.

In this research work, the authors report, for the first time, an anodic porous alumina formed via anodizing in a new electrolyte, squaric acid (C₄H₂O₄ or H₂SQ, 3,4-dihydroxy-3-cyclobutene-1,2-dione, Fig. 1). Squaric acid was first synthesized by Cohen, et al. in 1959 [40] and is currently the most popular cyclic oxocarbon acid. It is typically used as a bioorganic and medicinal compound formed by organic synthetic chemistry [40–44]. Squaric acid is a strong diacid that exhibits two acidic hydroxyl groups with pKa values of 0.5 and 3.5 [42].



It is believed that squaric acid has the potential to behave as a suitable electrolyte for anodic porous alumina fabrication because of its diacid dissociation constants, which are similar to those of well-known anodizing electrolytes such as sulfuric, oxalic, and phosphoric acids. This paper describes how anodic porous alumina can be formed on the aluminum substrate via squaric acid anodizing under typical anodizing conditions. The growth behavior and nanostructure of the formed porous alumina are examined in terms of electrochemical measurements and SEM observations.

2. Experimental

2.1. Squaric acid anodizing of aluminum

Highly pure aluminum foils (99.99 wt%, 110 μm thick, Showa Aluminum Co., Japan, impurities: Fe 10 ppm, Si 9 ppm, and Cu 57 ppm) were used as the specimens. The specimens were cut into 20 mm x 20 mm pieces with a handle and then ultrasonically degreased in an ethanol solution for 10 min as a pretreatment. In this investigation, no electropolishing was carried out to avoid the delay of porous alumina formation, as reported previously [30]. Squaric acid anodizing was carried out under typical anodizing conditions using high concentrated solution at room temperature. The degreased specimens were immersed in a 0.1 M squaric acid solution (11.41 gL⁻¹, pH of the solution is 1.16 at 293 K) and then anodized for up to 360 min at a constant current density of 10–200 Am⁻² or applied potential of 100–150 V (Direct current power supply PWR400H, Kikusui, Japan). A platinum plate (99.98 wt%, 110 μm thick, Nilaco, Japan) was used as the counter

electrode. During the anodizing, the temperature of the squaric acid solution was held at 293 K by a water bath (UCT-1000, AS ONE, Japan), and the solution was stirred with a magnetic stirrer. The current density during the constant-voltage anodizing was measured using a digital multi-meter (DMM4040, Tektronix). After anodizing, the specimens were washed with distilled water and then dried in a desiccator.

2.2. Characterization of the anodized specimens

Several anodized specimens were immersed in a 0.20 M CrO₃/0.54 M H₃PO₄ solution (T = 353 K) for up to 10 min to selectively dissolve the anodic oxide film. The surface morphology of the anodized and post-treatment specimens was examined by field-emission scanning electron microscopy (FE-SEM, JSM-6500F and JIB-4600F/HKD, JEOL). Distributions of aluminum, oxygen, and carbon on the anodized specimens were also examined by energy dispersive X-ray spectroscopy (EDS, JIB-4600F/HKD, JEOL). The phase compositions of the anodized specimen were determined using X-ray diffraction (XRD, XpertPro, Phillips) analysis. For vertical cross-sectional observations, two treated specimens were prepared: a) one group of specimens was embedded in an epoxy resin, polished mechanically, and then immersed in a 0.25 M K₃[Fe(CN)₆]/4.17 M NaOH solution at room temperature for 25–90 s to clearly observe the anodic oxide. b) the other group of specimens was mechanically cut in liquid nitrogen. For each SEM observation, the anodized specimens were sputter-coated with platinum using a sputter coater (MSP-1S, Vacuum Device, Japan).

3. Results and discussion

3.1. Constant-Current and -Voltage Anodizing in Squaric Acid Solution

Fig. 2 shows the changes in applied potential, ΔV, with anodizing time, t_a, in a 0.1 M squaric acid solution at 293 K and constant current density of j = 10, 25, 50, 100, and 200 Am⁻² for 30 min. For j = 10 Am⁻², the applied potential initially increased linearly with anodizing time and then reached a maximum value of ΔV = 125 V at t_a = 12 min. After this linear increase, the applied potential slightly decreased for a few minutes and then remained at a steady value of approximately 120 V. This current density-anodizing time transient, namely, a) increasing, b) slightly decreasing, and c) steady, is similar to that observed for anodic porous alumina growth in typical acidic solutions [45], and the changes correspond to a) barrier oxide growth on the aluminum substrate, b) porous layer formation by selective dissolution of the oxide, and c) steady-state growth of the anodic porous alumina, respectively. At 25 and 50 Am⁻², the applied potentials show nearly the same steady value of 120 V after the initial period, although the slope of the ΔV-t_a lines for barrier layer formation is much steeper than that for 10 Am⁻² due to the

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