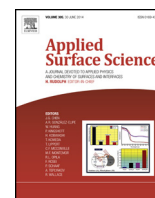




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Fabrication of anodic porous alumina via anodizing in cyclic oxocarboxylic acids

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ABSTRACT

The growth behavior of anodic porous alumina formed by anodizing in novel electrolyte solutions, the cyclic oxocarboxylic acids croconic and rhodizonic acid, was investigated for the first time. High-purity aluminum specimens were anodized in 0.1 M croconic and rhodizonic acid solutions at various constant current densities. An anodic porous alumina film with a cell size of 200–450 nm grew uniformly on an aluminum substrate by rhodizonic acid anodizing at 5–40 A m⁻², and a black, burned oxide was formed at higher current density. The cell size of the porous alumina increased with current density and corresponding anodizing voltage. Anodizing in croconic acid at 293 K caused the formation of thin anodic porous alumina films as well as black, thick burned oxides. The uniformity of the porous alumina improved by increasing the temperature of the croconic acid solution, and anodic porous alumina films with a uniform film thickness were successfully obtained. Our experimental results showed that the cyclic oxocarboxylic acids croconic and rhodizonic acid could be employed as a suitable electrolyte for the formation of anodic porous alumina films.

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1. Introduction

The anodizing of aluminum in several different acidic solutions causes the formation of anodic porous alumina (i.e., porous anodic oxide film) with characteristic nanostructures on aluminum substrates. Porous alumina consists of nano-scale hexagonal cells perpendicular to the substrate, and each cell possesses a nanopore at its center [1,2]. These cells are self-ordered by anodizing under appropriate electrochemical conditions, especially under a high electric field [3,4]. When anodic porous alumina is immersed in boiling distilled water after anodizing, the nanopores are filled by hydroxide (pore-sealing) [5,6]. The sealing process causes the formation of a highly crystalline hydroxide layer on the surface of the anodic oxide, and the hydroxide layer is highly dissolution-resistant in acidic and alkaline solutions. Using these characteristic structural and chemical properties, anodic porous alumina has been widely investigated for many applications: antireflection structures [7,8], reflectors [9], memory devices [10], diodes [11], sensors [12], optical devices [13,14], nanocontainers [15], plasmonic devices [16], nano-templates [17,18], evaporation masks

[19], catalyst supports [20], resist masks [21,22], and corrosion protection [23,24].

The electrolytes used to fabricate anodic porous alumina can be clearly classified by the use of the following two chemical species: inorganic and organic acids. Four types of electrolytes based on the following inorganic acids have been reported to date for the fabrication of anodic porous alumina: sulfuric (H₂SO₄) [25–27], phosphoric (H₃PO₄) [28–30], chromic (H₂CrO₄) [31–33], and selenic (H₂SeO₄) [34] acid. Among these inorganic electrolytes, the use of sulfuric, phosphoric, and selenic acid for anodizing under suitable anodizing conditions results in the formation of highly ordered anodic porous alumina via self-ordering. On the other hand, poorly arranged nanoporous structures are formed by chromic acid anodizing due to pore branching. Several carboxylic acids, including oxalic ((COOH)₂) [35–38], malonic (HOOC-CH₂-COOH) [39–41], tartaric (HOOC-(CHOH)₂-COOH) [42–44], citric (HOOC-CH₂-C(OH)(COOH)-CH₂-COOH) [45–47], malic (HOOC-CH(OH)-CH₂-COOH) [45,48], glycolic (HOOC-CH₂OH) [45], formic (HCOOH) [49], tartronic (HOOC-CH(OH)-COOH) [50], and acetylenedicarboxylic (HOOC-C≡C-COOH) [51] acid have been reported to date for the fabrication of anodic porous alumina. Oxalic and malonic acid anodizing have been reported to give rise to self-ordering behavior under suitable anodizing conditions. The organic and inorganic electrolytes used to fabricate anodic porous alumina possess low dissociation constant (pK_a) in aqueous solution,

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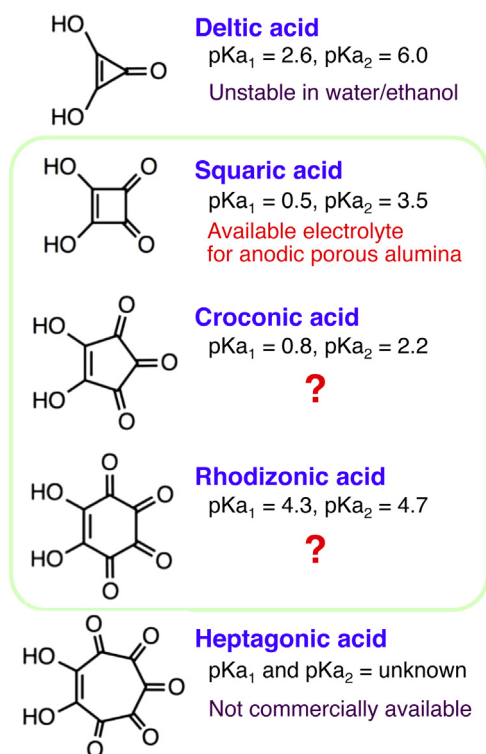


Fig. 1. Summary of the characteristics of cyclic oxocarboxylic acids and their dissociation constants (pK_{a_1} and pK_{a_2}). Five oxocarboxylic acids have been reported to date: deltic, squaric, croconic, rhodizonic, and heptagonic acid.

except for glycolic and formic acid, are diacids or triacids. However, glycolic and formic acid form dimers via hydrogen bonding in aqueous solution and may behave like diacids [52,53]. The nanofeatures of anodic porous alumina, including cell size (i.e., interpore distance) and pore diameter, are limited by these electrolytes during anodizing. Therefore, the discovery of additional electrolytes is very important in expanding the applicability of porous alumina. However, it is a well-known experimental fact that anodic porous alumina cannot be formed by anodizing in many organic and inorganic acid solutions [48]. Indeed, to date, there have been no reports of available organic electrolytes, except for carboxylic acid, that can be used to this end. This limitation may thus present an obstacle to further expanding to the nanomorphologies of anodic porous alumina.

Very recently, we discovered a new organic electrolyte for anodic porous alumina fabrication, squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) [54], which is different from the carboxylic acids described above. Squaric acid is currently the most popular cyclic oxocarboxylic acid used in organic chemistry and is a strong diacid composed of two acidic hydroxyl groups with low dissociation constants of $\text{pK}_{a_1} = 0.5$ and $\text{pK}_{a_2} = 3.5$ [55]. Squaric acid anodizing is performed at voltages of 100–150 V under typical anodizing conditions [54]. An anodic porous alumina film with micrometer-scale thickness, submicron-scale-cell size, and sub-100-nm-scale pore diameter can be successfully obtained by squaric acid anodizing. These findings demonstrate that anodic porous alumina can also be fabricated by anodizing in organic acids other than carboxylic acids.

Oxocarboxylic acids such as squaric acid are widely investigated in the field of organic synthetic chemistry. Fig. 1 summarizes characteristics of the members of the series of cyclic oxocarboxylic acids that have been reported to date. Deltic acid, with a three-membered ring, was first synthesized by Eggerding and West in 1975 [56]. Although deltic acid possesses low diacid dissociation constants

($\text{pK}_{a_1} = 2.6$ and $\text{pK}_{a_2} = 6.0$) [57], similarly to squaric acid, the acid is difficult to use as an anodizing electrolyte because it easily decomposes in aqueous and ethanol solutions [56]. Croconic acid, with a five-membered ring, and rhodizonic acid, with a six-membered ring, are long-known chemical species whose detailed chemical structures were only recently determined. Croconic acid possesses low pK_a values of 0.8 and 2.2 [57,58], and similarly, rhodizonic acid possesses low pK_a values of 4.3 and 4.7 [57,59,60]. Heptagonic acid, with a seven-membered ring, is not commercially available at the present time, although the possibility of synthesizing heptagonic acid was reported by Seitz and Imming [61]. Based on the considerations outlined above, it is strongly believed that croconic and rhodizonic acid have the potential to behave as suitable electrolytes for the fabrication of anodic porous alumina.

In the present report, we describe the fabrication of an anodic porous alumina films with uniform thickness via croconic and rhodizonic acid anodizing. Anodic porous alumina was successfully fabricated by constant current anodizing in croconic and rhodizonic acid solutions under suitable electrochemical conditions. The growth behavior of the porous alumina films and their nanomorphologies were examined in detail by electrochemical measurements and electron microscope observations.

2. Experimental

High-purity aluminum foils (99.99 wt%, 110 μm thick, 20 mm \times 20 mm with a handle, Showa Aluminum Co., Japan) were used as the starting materials. In the present investigation, no electropolishing was carried out to avoid the delay of anodic porous alumina formation, as reported previously [43,48]. The aluminum specimens were ultrasonically degreased in $\text{C}_2\text{H}_5\text{OH}$ for 10 min, and a silicone resin was then coated on the bottom of the handle. After drying the coated silicone resin, the specimens were immersed in 0.1 M croconic acid ($T = 293\text{--}323\text{ K}$, $\text{pH} = 1.17$ at room temperature, 4,5-dihydroxy-4-cyclopentene-1,2,3-trione, Tokyo Chemical Industry, Japan) and 0.1 M rhodizonic acid ($T = 293\text{ K}$, $\text{pH} = 1.72$ at room temperature, 5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetrone, Santa Cruz Biotechnology, USA) solutions and then anodized for up to 60 min at constant current densities of $i = 5\text{--}80\text{ A m}^{-2}$. The electrochemical anodizing setup consisted of a simple two-electrode system, in which a platinum plate was used as the counter electrode. The croconic and rhodizonic acid solutions were stirred with a magnetic stirrer during anodizing, and the temperature was maintained at a constant value using a water bath. The corresponding anodizing voltage during constant current anodizing was recorded by a PC-controlled direct current power supply (PWR-400H, Kikusui, Japan). After anodizing, the specimens were immediately removed from solution and then washed with distilled water and dried in a desiccator.

The anodized specimens were immersed in a 0.20 M $\text{CrO}_3/0.51\text{ M H}_3\text{PO}_4$ solution ($T = 353\text{ K}$) for up to 30 min to selectively dissolve the anodic oxide. Through this treatment, the interface between the anodic oxide and the aluminum substrate, which corresponds to the growth plane of the anodic oxide, was exposed to the surface. The nanomorphologies of the surface and the interface of the anodized specimens were examined by field-emission scanning electron microscopy (FE-SEM, JIB-4600F/HKD, JEOL). The crystallinity of the anodic oxide was determined by X-ray diffraction (XRD, XpertPro, Phillips). A vertical cross-section of the anodic oxide was observed after preparing two treated specimens: (a) the anodized specimens were embedded in an epoxy resin (EpoFix, Struers) and polished mechanically and (b) the specimens were mechanically cut. For the observation of the anodic oxide, a thin platinum conductive layer was coated on the oxide by a sputter coater (MSP-1S, Vacuum Device, Japan).

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