

Anodizing of aluminium

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The history of electrochemical oxidation of aluminium dates back to the beginning of the last century. Anodic treatment of aluminum were intensively investigated to obtain protective and decorative films on its surface [1]. More recently, applications of porous alumina with a huge surface area and a relatively narrow pore size distribution have been exploited [2]. For example, several attempts to fabricate inorganic membranes have been reported [3, 4, 5]. Nowadays, porous alumina is one of the most prominent template materials for synthesis of nanowires or nanotubes with monodisperse controllable diameter and high aspect ratios [6, 7, 8, 9, 10, 11, 12, 13, 14]. Moreover, it can be employed as a 2-D photonic crystal.

Numerous patents had been published before the 1950's, concerning the anodization of aluminum for coloring [15]. Since the early years, anodic processes at DC or AC current based on either chromic, sulfuric or oxalic acid as electrolytes have been paid attention to [15]. Consequently, it was observed that additives such as metal salts like copper, nickel, silver, arsenic, antimony, bismuth, tellurium, selenium or tin lead to a change of the physical and mechanical properties as well as of the colors of the oxide. Bengough's and Stuart's patent in 1923 is recognized as the first patent for protecting Al and its alloys from corrosion by means of an anodic treatment [16]. In 1936, Caboni invented the famous coloring method consisting of two sequential processes: anodization in sulfuric acid, followed by the application of an alternating current in a metal salt solution [17].

The development of electron microscopy led to a deeper understanding of the porous alumina structures. In 1953, Keller and his coworkers described a porous alumina model as a hexagonally close-packed duplex structure consisting of porous and barrier layers [18]. Also, they demonstrated the relationship of an applied potential and the geometric features of the hexagonal porous structures such as the interpore distance. This model was the basis for initial studies that aimed at better a understanding of the physical and chemical properties of porous alumina. A review paper dealing with anodic oxide films on [aluminum](#) was already published in 1968 [19]. Structural features concerning anion incorporation and water content in the oxide and theoretical models of formation mechanisms of both the barrier-type oxide and the porous-type oxide were described in detail in this paper.

Between 1970 and 1990, studies by the Manchester group (led by Thompson and Wood) resulted in a deep insight in the growth mechanisms of alumina oxide films. This was possible by the uses of new techniques such as Transmission Electron Microscopy (TEM), marker methods and microtome sectioning. [20, 21, 22, 23]. A corresponding publication by O'Sullivan and Wood is one of the most cited articles on anodization of aluminum to obtain porous alumina structures [24]. Efforts on theoretical modelling of porous oxide growth were carried out by several groups [25, 26, 27, 28, 29, 30, 31, 32, 33]. Fundamentally, an instability

mechanism in terms of a field focusing phenomenon was attributed to create pores in the barrier oxide. In these papers, it is claimed that the theoretic modelling of the pore formation mechanism in alumina is analogous to that for other porous materials which can be obtained via an anodic treatment, for example, microporous silicon.

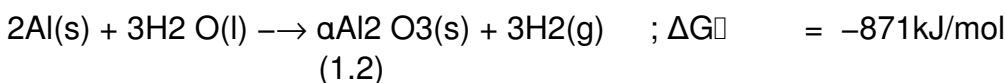
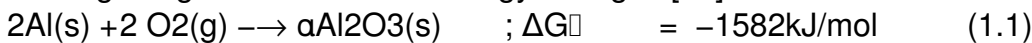
Based on a two-step replicating process, a self-ordered porous alumina membrane with 100 nm interpore distance was synthesized by Masuda and Fukuda in 1995 [34]. This discovery was a breakthrough in the preparation of 2D-polydomain porous alumina structures with a very narrow size distribution and extremely high aspect ratios. Two years later, they combined the aluminum anodization method with nanoimprint technologies, which allowed for the first time the preparation of a monodomain porous alumina structure [35]. Numerous other groups, not mentioned here specifically, have also contributed to an improvement of porous alumina structures.

The purpose of this dissertation is to understand self-assembly of porous alumina under specific conditions (Chapter 1 and Chapter 2). In addition, nanoimprint methods are developed to obtain monodomain porous alumina structures (Chapter 3). These nanoimprint methods are further advanced to fabricate porous alumina arrays with various configurations (Chapter 4). Furthermore, the combination of nanoimprint and anodization will be applied to obtain porous oxides grown on titanium, which is also a valve metal (Chapter 5). Finally, in the last two chapters, applications of the alumina templates will be discussed, for example, templates for monodisperse silver nanowires (Chapter 6) and 2D-phonic crystals (Chapter 7).

1.2 Electrochemistry of anodic alumina

1.2.1 Thermodynamics

The spontaneous reaction leading to the formation of aluminum oxide in air can be ascribed to the large negative Gibbs free energy changes [36].



If aluminum is electrochemically anodized, an oxide grows at the anode electrode [37],

$$2\text{Al}(s) + 3\text{H}_2\text{O}(l) = \text{Al}_2\text{O}_3(s) + 6\text{H}^+ + 6\text{e}^- \quad (1.3)$$

and hydrogen evolves at the cathode



Assuming there are no complex anions, the Nernst equation reads

$$E = E^0 - \frac{RT}{zF} \ln([\text{ox}]) \quad (1.5)$$

where R is the universal gas constant, T is the absolute temperature in Kelvin, z is the charge number of the electrode reaction, and

F is the Faraday constant (96,500 C mol⁻¹). The electrode potential

E at the anode can be written as

$$E = -1.550 - 0.0591\text{pH} \quad (1.6)$$

Table 1.1: Alumina oxide forms [39]

Name	Crystalline form	Density (g/cm ³) / Crystal System
Corundum		
α -Al ₂ O ₃		
		3.97 / hexagonal
		found in nature

Boehmite	$\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	3.44 / ortho-rhombic	
Gibbsite	$\alpha\text{-Al}_2\text{O}_3 \cdot (\text{H}_2\text{O})_3$	2.42 / monoclinic	
Diaspore	$\beta\text{-Al}_2\text{O}_3 \cdot (\text{H}_2\text{O})$	3.4 / ortho-rhombic	no occurrence in nature
Bayerite	$\beta\text{-Al}_2\text{O}_3 \cdot (\text{H}_2\text{O})_3$	2.53 / monoclinic	
Gamma alumina	$\gamma\text{-Al}_2\text{O}_3$		
anhydrous alumina	with ill-defined structure		

This explains that the reaction at the anode electrode (Al) thermodynamically depends on the pH value, which is determined by electrolyte and temperature.

1.2.2 Kinetics

The current density passing across the oxide film can be written as [19, 37]

$$j = j_a + j_c + j_e \quad (1.7)$$

where j_a , j_c and j_e are the anion-contributing, cation-contributing and electron-contributing current density, respectively. Since the electronic conductivity in the aluminum oxide is very low, the ionic current density ($j_i = j_a + j_c$) is the predominant mode to transport the charges. The relationship between the ionic current,

j_i , and the electric field, E

, can be expressed in terms of the Guntherschultze-Betz equation

$$j_i = j_0 \exp(\beta E) \quad (1.8)$$

where both j_0 and β are temperature- and metal-dependent parameters. For the aluminum oxide, the electric field E , j_0 and β are in the range of 10^6 to 10^7 V/cm, 1×10^{-16} to 3×10^{-2} mA/cm² and 1×10^{-7} to 5.1×10^{-6} cm/V, respectively [38]. Based on the Guntherschultze-Betz equation, the rate-limiting steps of the film formation are determined by the ionic transport either at the metal/oxide interface, within the bulk oxide or at the oxide/electrolyte interface [19]. Nowadays, it is generally accepted that the oxides simultaneously grow at both interfaces, e.g., at the metal/oxide interface by Al^{3+} transport and at the oxide/electrolyte interface by oxygen ion transport [21, 24]. For example, the transport number $t_{\text{Al}^{3+}}$ of Al^{3+} anions, and the cation transport number, $t_{\text{O}^{2-}}$, were reported as 0.45 and 0.55, respectively, for 5mA/cm² [22].

1.3 Composition of the oxide

Due to a number of polymorphs, hydrates, and incorporated ions, anodic Al_2O_3 can exist in various forms, e.g., $\text{Al}_2\text{O}_3 \cdot (\text{H}_2\text{O})_n$ where $n = 0$ to 3 [37, 40]. Six forms are mostly discussed

(see Table 1.1). Gibbsite and Boehmite are converted to several transition alumina minerals such as γ series (e.g., γ , ρ , ξ) and δ series, (e.g., δ , κ , θ) by heating. Corundum, which thermodynamically is the most stable form among alumina oxides, is generated above 1100 °C, regardless of the transition course. Boehmite heated at between 400 ~ 500 °C yields γ -Al₂O₃ consisting of irregular structures [40]. Generally speaking, anodic Al₂O₃ was mostly reported as a form of X-ray amorphous solid [19, 24, 37]. For the barrier layer, the presence of nanocrystallites of γ -Al₂O₃ with sizes of 2-10 nm was demonstrated by several authors. γ -Al₂O₃ is considered as an intermediate form between amorphous and γ -crystalline Al₂O₃. Thompson and Wood suggested that aluminum oxides may consist of nanocrystallites, hydrated alumina, anions, and water molecules [20, 24].

1.4 Barrier-type and porous-type alumina

Depending on several factors, in particular the electrolyte, two types of anodic films can be produced. Barrier type films can be formed in completely insoluble electrolytes (5 + 3/4 C₂H₅OH (Fig. 1.6 (b))). Electropolishing is a prerequisite for the formation of self-ordered porous alumina with large domain size. Note that caution is needed when perchloric acid/ethanol is used due to its explosiveness at moderate temperatures.

After the pretreatment, anodization is performed either at 19 V in 2 M H₂SO₄, at 25 V in 0.3 M H₂SO₄, at 40 V in 0.3 M (COOH)₂, at 160 V in 1 M H₃PO₄, or at 195 V in 0.1 M H₃PO₄ for more than 1 day (Fig. 1.6 (c)). Since pores are randomly created on the surface, the initial pore arrangement is very irregular (Fig. 1.7 (a)). However, due to the repulsive forces between neighboring pores during the long-anodization, self-organization occurs. As a result, hexagonally close-packed arrays are obtained at the interface between the porous alumina layer and the

aluminum substrate (Fig. 1.7 (b)). Then, the porous alumina film is selectively dissolved in a solution containing chromic acid (Fig. 1.6 (d)) [53]. Patterns that are replicas of the hexagonal pore array are preserved on the fresh aluminium surface. This allows the preparation of pores with a high regularity by a subsequent second anodization under the same conditions as the first anodization (Fig. 1.6 (e)). If needed, the resulting pores can be isotropically widened by chemical etching with 0.5 ~ 1 M phosphoric acid (Fig. 1.6 (f)).

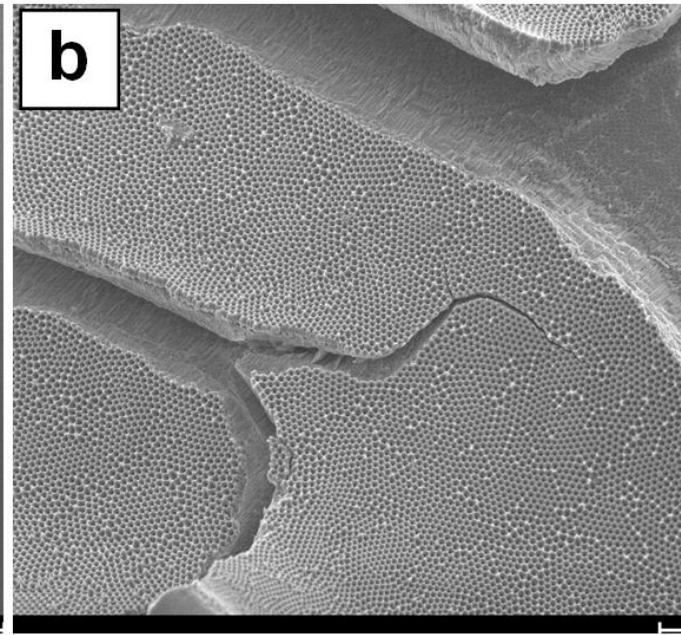
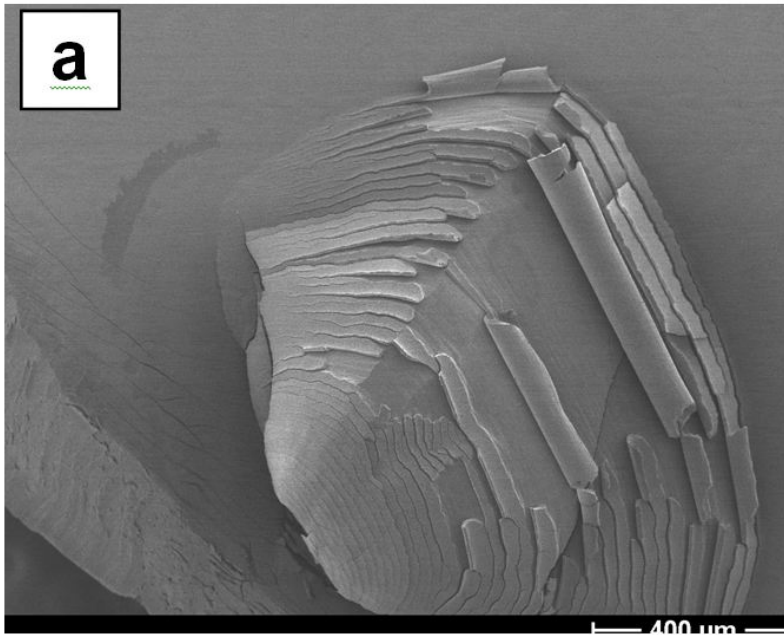
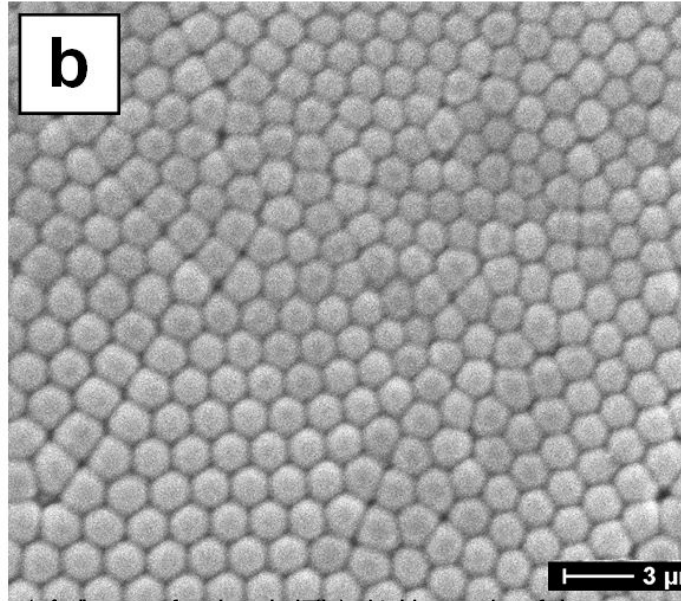
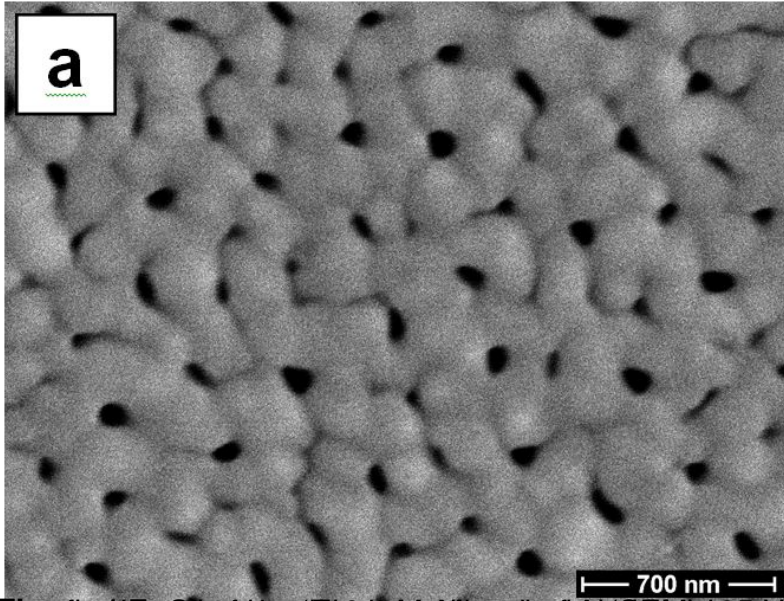


Figure 1: (a) SEM image of the porous anodized aluminum surface. (b) SEM image of the porous anodized aluminum surface. P&A International, Anodizing, Anodizing of aluminium