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Chuan Cheng

**Electro-Chemo-
Mechanics of Anodic
Porous Alumina
Nano-Honeycombs:
Self-Ordered Growth
and Actuation**



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Chuan Cheng

Electro-Chemo-Mechanics of Anodic Porous Alumina Nano-Honeycombs: Self-Ordered Growth and Actuation

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Supervisor's Foreword

This book summarizes Dr. Chuan Cheng's work during his Ph.D. study at the University of Hong Kong, from September 1, 2009 to August 31, 2013. By using both theoretical and experimental approaches, Dr. Cheng studied the self-similar growth of anodic aluminium oxide which can be made to form a characteristic nano-honeycomb structure under a small window of processing conditions. Despite the fact that this phenomenon has been known for a few decades, and that such nano-honeycomb structures are nowadays routinely employed as the template materials for making other nanomaterials for a wide range of applications, no one has been able to predict theoretically the conditions under which the self-ordered growth happens, or the detailed mechanisms involved. Dr. Cheng's work is an important step in this direction. In this book, you will see that he developed an electrochemical model, wrote computer codes for its implementation, and was able to predict the self-similar growth of the nano-honeycomb structure within a certain window of processing parameters. Furthermore, he conducted key experiments to verify certain characteristics predicted from his model. In the second part of his work, he also discovered a novel actuation response of such nano-honeycomb structures on electrical charging.

I enjoyed supervising Dr. Cheng toward his doctorate, and I hope that you will enjoy reading his work.

Hong Kong
March 2015

Prof. Alfonso H.W. Ngan

Abstract

Self-ordered anodic porous alumina with a nano-honeycomb structure has recently been extensively used as templates for the synthesis of various nanomaterials for diverse applications. However, due to insufficient knowledge on the combined electro-chemo-mechanical processes, the formation mechanism of self-ordering has been under debate for decades without clear conclusions. Also, fast fabrication of highly self-ordered and mechanically stable anodic porous alumina is still a challenge. Furthermore, the actuation behavior of anodic porous alumina on external mechanical and electrical triggering in an electrochemical cell has not been exploited.

In this work, first, we investigated the self-ordering mechanism by establishing a kinetics model involving the Laplacian electric potential distribution and a continuity equation for current density within the oxide body. Current densities governed by the Cabrera-Mott equation are formed by ion migration within the oxide as well as across the interfaces. The pore channel growth, due to electric-field-assisted reactions, is governed by Faraday's law. Real-time evolution of pre-patterned pore channel growth was simulated in two-dimensional cases by finite element method. The simulations revealed a parameter domain within which pre-patterned pore channels will continue to grow in a stable manner during the subsequent anodization if the pre-patterns are commensurate with the self-ordered configurations, or these are driven into stable if the pre-patterns do not initially match the self-ordered configurations. This was verified in experimentally observed pore channel growth under the guidance of pre-patterns made by focused-ion-beam milling. Furthermore, the simulations revealed that ionization reaction on (001) oriented Al grain is relatively easier than that on (101) grain, which results in stable and unstable pore channel growth on (001) and (101) Al grains, respectively, both of which were observed from the simulations and experiments.

Second, a scheme on quantitative evaluation of self-ordering qualities in anodic porous alumina has been developed, based on which we systematically searched the optimum self-ordering conditions, by varying the key anodization factors, including substrate grain orientation, electrolyte concentration, temperature, voltage, and time. A high acid concentration and high temperature anodization method was

found. Compared with conventional methods, the present method can realize fast formation of highly self-ordered, and mechanically stable anodic porous alumina under a continuous range of anodization voltage with tunable interpore distances.

Third, reversible bending was found in anodic porous alumina-Al composites upon cyclic electric actuation, as directly observed by an optical microscope and detected by in situ nanoindentation. The bending is thought to be the result of charge-induced surface stresses in the nanoporous alumina. The results suggest a new type of composite materials for applications as micro-scale actuators to transform electrical energy into mechanical energy. Furthermore, the composite exhibits a significant softening during in situ nanoindentation when the estimated maximum stress underneath the indenter is exerted on the metal/oxide interface. Softening was further verified by in situ microindentation. Electron microscopy examination indicated that softening is due to a combination of high compression stress and electric field acting near the interface, which enhance ionization reaction and cause the interface to move faster into the substrate.

Acknowledgments

This thesis is based on the work carried out in the Materials and Nanotechnology Laboratory at the Department of Mechanical Engineering at The University of Hong Kong from September 1, 2009 to August 31, 2013.

This thesis could not be completed without the insightful, passionate, effective, and consistent guidance of my Ph.D. supervisor Professor A.H.W. Ngan. I want to thank him for selecting me as one of his students. This changed my whole life and provided me with the precious opportunity to get closer to my childhood dream of being a scientist. During the past 4 years, we maintained an efficient and comprehensive mode of exchanging research ideas, facing and solving research problems together. Many of the research bottlenecks could not be overcome without his keen scientific insight and fruitful guidance. His diligence, passion, ethics, and high efficiency on research have set up a typical example for me of what a real scientist should be. His ideas have reshaped my mind and the way of doing research.

Next I thank both Prof. N.R. Aluru and Prof. A.H.W. Ngan for giving me the opportunity to be a visiting scholar at the University of Illinois at Urbana-Champaign for a half-year exchange during my Ph.D. stage. This provided me a chance to have a glimpse of the innovative research in the US, and also a chance to improve my oral English. Also, I would like to thank Dr. X. Jin for giving me plenty of help during my study while living in the US.

I thank Dr. K.Y. Ng for his design of the electrochemical cell described in Sect. 4.2.2, and his EDX experimental data shown in Fig. 5.5, for verification of the present modeling and simulation results. I also thank Prof. B.J. Duggan, Dr. Y. Lin, Dr. M. Huang, and Dr. B. Tang for the valuable questions and suggestions during my group presentations.

Furthermore, I thank Mr. K.K. Wong and T.K. Liu in our laboratory for providing me all the necessary experimental support. I also thank F. Chan, S.L. Wong, and W.S. Lee at the Electron Microscope Unit of HKU, for their assistance and patience in teaching me to use the facilities. I also thank Mr. W.K. Kwan for his assistance in running my calculation program on the HPCPOWER 64-bit System in the Computer Center of HKU.

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Finally, I thank my parents. During more than 20 years of continuous education in the campus, they have tolerated so much for me on financial and emotional issues which they never mentioned. It is their love that supports me to be here and to go on for the future. I also thank my wife for her complete understanding during the 4 years of separation.

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Chapter 1

Research Background and Motivation

1.1 General Concept of Anodic Porous Alumina

Anodic porous alumina, which exhibits a characteristic nano-honeycomb structure, has received increasing attention both experimentally and theoretically [1–21]. Due to the quasi-periodic arrangement of the nanopore channels, narrow distribution of pore sizes, and interpore distances, relative ease to control the porous scales and self-ordering qualities by anodization conditions, excellent thermal stability, and very low-cost anodic porous alumina has been extensively used as templates for fabrication of various nanostructured materials such as nanodots [22–24], nanowires [25–29], nanotubes [30–32], and many other types [33–35], especially to realize the collective functioning of arrays of nanoelements which may not be realized by individual nanoelements [5, 36], for applications in high-density magnetic media [37–42], photonic crystals [43–50], semiconductor devices [51–59], lithium-ion batteries [60–63], solar cells [64, 65], nanocapacitors [66–70], biosensors [71–77], and so on [78–89].

Anodic porous alumina can be fabricated by anodization of aluminum in an acidic or alkaline electrolyte [1], such as sulfuric acid [90], oxalic acid [91–94], phosphoric acid [95], and chromic acid [95, 96]. For neutral electrolytes with pH in the range of 5–7, such as boric acid solution, ammonium borate, or tartrate aqueous solution, only barrier-type anodic alumina films with a uniform thickness will be formed by anodization [1, 97]. The configuration of anodic porous alumina is composed of closely packed arrays of nanopore channels perpendicular to the aluminum substrate with pore diameters on the order of several to hundreds of nanometers [58, 93–95, 98]. When viewed from the top, the nanopores are usually arranged in a quasi-hexagonal porous pattern. The in-plane arrangement of pore channels generally exhibits local variations with ordered zones separated with disordered zone boundaries, which is much similar to the crystallographic grains and grain boundaries of the Al substrate. However, the perfect ordered zones are at most several micrometers big even for highly self-ordered patterns, while the grain

sizes of the Al substrate are generally hundreds of micrometers or even larger [91]. In structures with self-ordered in-plane patterns, the pore channels are usually straight cylinders with axes perpendicular to the Al substrate, and their aspect ratio, i.e., the pore channel length to pore diameter ratio, can be greater than 1000 under appropriate anodization conditions [93, 99, 100]. However, in structures with disordered in-plane patterns, the straightness of the pore channels is usually not maintained during growth, and on progressing from the top to bottom, the growth of a given pore may fall behind its neighbors or even completely terminated, or the pore can branch to form two or more new ones [95]. As pore merging, termination, or splitting happens, the aspect ratio of the pore channels in disordered structures is usually not larger than 20 [93, 101]. A thin scallop-shaped oxide barrier layer exists at the pore bottom which separates the metal substrate from the electrolyte in the pore channels during the anodization. It has been known for several decades that the barrier layer thickness and interpore distance are primarily linearly dependent on the anodization voltage, while the pore diameter also depends on the electrolyte concentration and temperature, in addition to the voltage [2, 3, 95, 102–104]. For example, under traditional mild anodization (MA) conditions in which the oxide growth rate is several micrometers per hour, the voltage dependency is about 1 nm V^{-1} for both the pore diameter and the barrier layer thickness, and 2.5 nm V^{-1} for the interpore distance [94, 103], but under hard anodization (HA) conditions in which the oxide growth rate is tens of micrometers per hour, the voltage dependency becomes 0.4 nm V^{-1} for the pore diameter, 1 nm V^{-1} for the barrier thickness, and 2 nm V^{-1} for the interpore distance [93].

1.2 Various Applications of Anodic Porous Alumina

1.2.1 Applications in Photonic Crystals

Photonic crystals are composed of periodically arranged dielectric or metal elements in one-dimensional (1-D), 2-D, or 3-D spatial directions, with interelement spacing on the order of wavelength, can exhibit photonic band gaps much similar to the energy band gap in semiconductors [105, 106]. If the frequency of the incident light (electromagnetic wave) falls into the photonic band gap, the light will be forbidden to propagate through the photonic crystals. Based on this property, manipulation of the light transmission in a designed route within a target frequency light range becomes possible, and examples include photonic crystal wave guides and photonic crystal fibers [107]. Recently, photonic crystals, which was fabricated using anodic porous alumina as a template, has been used in enhanced light trapping in thin film solar cells [108]. Stronger light absorption in the red and near-IR spectral ranges was detected with a 21 % increase in the energy conversion efficiency [108]. Actually, self-ordered anodic porous alumina itself is a 2-D photonic crystal in the visible and infrared light regions as reported by Masuda et al.

[109]. Also, by infiltrating metals into the pore channels metallodielectric photonic crystals can be formed with unique optical properties compared with traditional dielectric photonic crystals [105, 106, 110]. Anisotropic light scattering in self-ordered anodic porous alumina in the context of photon density-of-states effects has been experimentally investigated by Lutich et al. [111]. They observed high reflection ($\sim 80\%$) of incident visible light within the porous plane of anodic porous alumina, and also very high ($\sim 98\%$) transmission of the light along the pore channel direction. These indicated strong redistribution of photon density of states in the porous plane with a decrease of density; and an increase of density for the pore channel direction [111]. Mammalian eye cornea has a similar porous structure as anodic porous alumina [112], and due to the same reasons above the porous structure removes reflection at the air/cornea interface and provides superior transmission of light into the eye [111]. In this way, Lutich et al. [111] proposed that porous materials like anodic porous alumina can be used in focusing and spatial concentration of waves based on the anisotropic scattering of incident light.

1.2.2 Applications in Energy Storage and Conversion

Electric energy can be stored as surface charges on conducting electrodes in electrostatic capacitors, or in electrochemical double layers in ultra-capacitors [66]. Due to the large surface area of nanostructured materials, the energy storage density is much larger than those with conventional configurations [113]; thus the total system size and weight can be largely reduced under the same energy capacity [114]. Metal-insulator-metal (MIM) electrostatic capacitors which were fabricated by anodic porous alumina templates have shown profound increase in capacitance of 100 times, or more over planer structured devices [66, 115]. By refining the anodic porous alumina topography, the performance of the fabricated nanocapacitor can be further improved. For example, in the work by Haspert et al. [66], between the first and second steps of anodization, the Al substrate with dimpled texture was anodized within a neutral solution to form a nonporous oxide barrier-type film. As a result, the radius of curvature of the peaks on the second step formed anodic porous alumina template was increased from about 7.8 to 20 nm. Thus, the surface of the anodic porous alumina template was extremely smooth, which was essential to increase the breakdown electric field of the latter formed MIM capacitor from about 4–10 MV cm⁻¹ (already close to the intrinsic dielectric strength of the alumina). As a result, the energy storage density ($=0.5CV^2$, where C is the capacitance of the capacitor, and V is applied voltage) was 2.5 times increased [66]. Also, a thin passivation TiN layer was deposited on the surface of anodic porous alumina by atomic layer deposition (ALD) in order to insulate the contaminated electrolyte ions within the pore walls, which can influence the performance of the capacitor, and as a result the leakage current density was reduced to 10⁻¹⁰ A cm⁻² [66]. Due to the above improvements, energy storage density as high as 1.5 Wh kg⁻¹ was reported [66].