Formation of anodic ZrO$_2$ nanostructures in NH$_4$F/ethylene glycol electrolyte

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Abstract. The aim of this study is to investigate the morphology and surface species of ZrO$_2$ film formed in a fluorinated ethylene glycol electrolyte by anodization process. In this work, no water was added into the NH$_4$F/ethylene glycol electrolyte. Possible formation mechanism of anodic ZrO$_2$ nanostructures in the NH$_4$F/EG electrolyte was also explored. As a result, the porous ZrO$_2$ film with the thickness of 1.5 – 2.5 µm was produced. From the top view, it is observed that the surface consists of rings with diameters of 100 – 160 nm. However, the oxide does not consist of any tubular structure. The FTIR spectrum of the film shows that the top of anodic ZrO$_2$ film is covered by anion contamination, e.g. OH$^-$ and CO$_3^{2-}$.

Keywords: ZrO$_2$, nanostructure, film, anodization, organic electrolyte

1. Introduction

Anodic oxidation or anodization of metals has been used to protect metal components from corrosion for more than 10 decades [1]. However, anodization has become a technique not only for protection or to increase the aesthetic appearance of the metal components but explicitly done to produce a thin oxide film. Anodic thin oxide film on a metal has many unique properties leading to various interesting applications. Anodized titanium (Ti) has been widely investigated as the TiO$_2$ film produced, being a photoactive semiconductor has many applications especially in the field of solar energy utilization [2-4]. TiO$_2$ is also a well-known photocatalyst hence anodizing Ti can be used to produce TiO$_2$ photocatalyst that can degrade organic pollutants in contaminated air and water [5-7].

For anodizing zirconium (Zr) work, Cox anodized Zr to form a compact oxide layer of up to several hundred nanometres thickness. The Zr metal was first etched in mixed nitric/hydrofluoric acid then anodized in aqueous electrolyte [8]. F$^-$ ions in ammonium borate electrolyte was used to anodize Zr as reported by Archibald and Leach [9-10] to produce compact ZrO$_2$. Berger et al. introduced the use of organic electrolyte to form ZrO$_2$ nanostructures [11]. It was revealed that organic electrolyte has the ability to allow significantly thicker tubular layer than in aqueous electrolyte. The use of organic electrolyte e.g. glycerol and ethylene glycol also allows the increase in the nanotubes length.

In this work, anodization of Zr metal was done in ethylene glycol (EG) and NH$_4$F. Not many works on anodization of Zr in EG electrolyte have been done in the current literature [12-18]. In NH$_4$F/EG electrolyte to form ZrO$_2$ nanostructures, water is widely used as oxygen provider. However, in this work...
no water has been added into NH₄F/EG electrolyte. Anodic ZrO₂ in form porous film was then obtained and covered with anion contamination which will be useful for photocatalytic application. Possible formation mechanism of anodic ZrO₂ nanostructures in the NH₄F/EG electrolyte was also explored.

2. Methodology

The ZrO₂ film was synthesized using anodization of zirconium (Zr). The Zr foil (99.20 % purity; 0.10 mm thickness; Nilaco Corp., Japan) with dimension of 40 mm x 10 mm were ultrasonically cleaned in acetone (J.T. Baker, USA) for 15 min and ethanol (Merck, Germany) for 15 min, followed by rinsing in deionized water and dried in air. The Zr foil was used as an anode and platinum rod (diameter of 2 mm, 75 mm in length, Metrohm, Switzerland) was used as cathode. Anodization was carried out in an electrolyte containing 100 mL of ethylene glycol (C₂H₆O₂, Merck, Germany) and 0.3 g of ammonium fluoride (NH₄F, Merck, Germany) for 60 V (Agilent E3647A, USA) for an hour at room temperature. Once completed, the foil was removed from the electrolyte and cleaned with acetone and deionized water before air dried. The as-anodized foil was then annealed in air at 400 °C for 2 h. Morphology of the ZrO₂ nanostructures was observed by Field Emission Scanning Electron Microscopy (FESEM; Variable Pressure Zeiss Supra 35, Germany). Fourier Transform Infrared (FTIR) spectrometer from Perkin Elmer was used to determine the molecular composition of surface species.

3. Result and Discussion

Anodization was conducted in ethylene glycol (EG) electrolyte containing 0.3 g NH₄F. The exposure of electrolyte to the surrounding environment was kept at minimum to reduce water absorption by EG from the environment. The viscosity and conductivity of NH₄F/EG electrolyte were 20 mPa s and 970 µS cm⁻¹, respectively. The electrolyte was colorless and transparent. Figure 1 shows the anodic ZrO₂ formed in this electrolyte at 60 V for 1 h. As seen the anodic ZrO₂ is consisted of pores with coral-like structure. The thickness of the anodic film is in the range of 1.5 to 2.5 µm (Figure 1(a)). From the top view, it is observed that the surface is consisted of rings with diameters of 100 to 160 nm (Figure 1(b) and (d)). Higher magnification image in Figure 1(d) shows the rings resemble tubes surface, even though from the cross section image the oxide does not consist of any tubular structure.

In NH₄F/EG electrolyte, the availability of oxygen for oxidation is limited. This is due to the oxidation of EG, which triggers its transformation into glycolaldehyde (CH₂OH–CHO) and glycolic acid (CH₂OH–COOH), in which oxygen is double-bonded to carbon [19]. Thus the donation of oxygen from NH₄F/EG electrolyte is difficult because it is strongly bonded by double bonding. However as reviewed by Yue, with the oxidation of EG, water and CO₂ will be the by-products [20]. Even though the amount of water may be very small, it is enough to induce the oxide formation. Moreover, donation of oxygen from environment is possible as EG being hygroscopic can absorb water from the environment. During anodization, water may be constantly absorbed by EG as the source of O₂⁻ or OH⁻ ions for oxide formation. The existence of F⁻ ions in electrolyte plays a role as an etchant. F⁻ ions can attack the surface of oxide layer forming random pits. During the course of anodization, pits will grow into stable pores. F⁻ ions then migrate inward to maintain charge neutrality within pores, which increases the local F⁻ concentration. This induces further etching which may result in the formation of porous oxide as seen from the FESEM images of the oxide.
Figure 1: FESEM image of anodic ZrO$_2$ formed at 60 V for 1 h in EG electrolyte containing 0.3 g NH$_4$F: (a) cross sectional view, (b) surface view, (c) high magnification of (a), and (d) high magnification of (b).

Figure 2: Possible formation mechanism of anodic ZrO$_2$ nanostructures in the NH$_4$F/EG electrolyte: (a) bare metal, (b) thin oxide, (c) pits, (d) pores, and (e) porous anodic ZrO$_2$. 
Figure 3 shows the FTIR spectrum for the annealed ZrO$_2$ nanostructures at 400 °C for 2 h in air. A broad band at 3450 cm$^{-1}$ is assigned to the OH$^-$ (hydroxyl group) and peak at 1630 cm$^{-1}$ is attributed to the O$-$H vibration of adsorbed water. Peak of CO$_3^-$ is also observed in FTIR spectra indicating this carbonate ion or any other carboxyl group is also existing at the surface. Typically peak at 490 cm$^{-1}$ corresponds to the Zr$-$O stretching modes. From this result, it is revealed that at the top of anodic ZrO$_2$ nanostructures is covered by anion contamination which will be useful for photocatalytic application.

4. Conclusion
Anodic ZrO$_2$ film was fabricated by anodization method in fluorinated organic electrolyte. The anodic ZrO$_2$ film consists of pores with coral-like structure with the thickness of the film is in the range of 1.5 – 2.5 µm. From the top view, it is observed that the surface consists of rings with diameters of 100 – 160 nm. From FTIR spectrum, it is known that at the top of anodic ZrO$_2$ nanostructures is covered by anion contamination which will be useful for photocatalytic application.

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