



Interfacial Barrier Layer Properties of Three Generations of TiO₂ Nanotube Arrays



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ABSTRACT

Three generations of TiO₂ nanotubular arrays (TiNT) were obtained by anodization of titanium foil in three different solutions: Aqueous acid containing fluoride media, organic based containing fluoride media and chloride containing electrolyte.

This paper investigates the effect of the electrolyte composition on barrier layer characteristics of TiNT. Correlation between the dimensional aspect of TiNT and the electrochemical properties was investigated. Electrochemical characteristic from Electrochemical Impedance Spectroscopy (EIS) were discussed. EIS is considered to be a highly sensitive technique that allows determining barrier oxide layer characteristics. Semiconducting properties as well as thicknesses are discussed in correlation with anodizing electrolyte. Scanning electrochemical microscopy (SECM) was employed for in situ characterization of surface chemical activity of titanium in chloride containing electrolyte. The SECM has detected corrosion pits as well as the surrounding cathodic reaction. Nucleated pits on titanium takes place on the top of grain most probably with surface orientation (0001).

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1. Introduction

Nanostructures gained a lot of attention of the scientific community in the last few decades due to their unique properties and potential applications in various fields. TiO₂ is technologically very functional material that provides a wide range of specific applications that are based on its semiconductive nature. TiNT have been successfully produced and several important applications have already been found for these structures, such as water-splitting [1–4], dye-sensitized solar cells [5,6], gas sensors for production of hydrogen [7], high photoelectrochemical performance under UV [8], self-cleaning [9], photocatalysis and biological applications [10–13].

TiNT have been fabricated in different electrolytes via anodization of pure Ti. During the last decade, four generations of anodic titanium oxide nanotubes were prepared in different electrolytes with various conditions. The first generation was reported by Zwilling in 1999 [14], where nanoporous TiO₂ arrays were obtained using electrolyte containing chromic acid (CA) and hydrofluoric acid (HF). In 2001 Gong et al. [15] discovered that nanotubular structure could be grown by using aqueous electrolytes consisting

primarily of hydrofluoric acid media. These aqueous electrolytes lead to limiting length of 500–600 nm because of the high chemical dissolution rate of TiO₂ in HF. They found that a sample anodized in 0.5% HF solution under 20 V for 6 h has the same thickness as a sample anodized for only 20 min under otherwise identical conditions.

The second generation of nanotubes was obtained using either KF, or NaF electrolytes of variable pH. The desired pH was obtained by adding NaOH, sulfuric acid or citric acid to the electrolyte contained KF or NaF [16]. The TiNT lengths were increased to a few micrometers. The third generation was obtained using organic viscous electrolytes (ethylene glycol, glycerol, formamide. . .). A great breakthrough in the fabrication of TiO₂ nanotubular structure was achieved by Macak et al. [17,18], and Grimes and co-workers [19], where they reported very smooth, regular, and very long nanotubes. The fourth generation, also known as the Rapid Breakdown Anodization (RBA) was obtained using non-fluoride electrolytes (HCl, NaCl, H₂O₂ . . .) [20,21]. Hahn et al. [22] demonstrated that the anodization in perchlorate or chloride containing electrolyte produced nanotubes with several dozens of micrometers in length and several dozens of nanometers in diameter in a very short time (some minutes).

The physical and chemical properties of these structures are strongly dependent on their geometrical features such as tube length, diameter and wall thickness. These geometrical features are

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controlled by a variety of parameters mainly, electrolyte composition [23–25] and anodization potential [26].

TiO₂ film consists of a thick porous part and a thin compact barrier layer. Interfacial barrier layer plays a major role in the growth of TiNT. It is considered as a key factor in the morphology of the porous outer layer and performance of TiNT [27,28]. Growth of metal/oxide nanowires inside of TiNT has several applications such as electrodes for energy storage and energy conversion devices. Electrodeposition of nanowires within the nanotubes require the knowledge of the electronic properties of the barrier layer. In the case of dye sensitized solar cells, barrier layer characteristics have a noticeable effect on the electron transport. According to Rho et al. [29], the improvement of the conversion efficiency is mainly due to the improvement of the electron transfer efficiency by modifying the barrier layer properties.

In spite of the relatively large amount of research on the morphological properties and applications of TiO₂ nanotubes; however, to date, there has been very limited work to investigate the electronic properties of barrier layer oxides by EIS. The extensive use of TiNT as electrodes for energy conversion warrants a better understanding of the elements that can affect the electron transport and electrodeposition. Accordingly it is of particular importance to evaluate the barrier layer characteristics. The principal aim of the present paper is to evaluate the effect of anodizing electrolyte on the properties of TiO₂ barrier layers like thickness and semiconducting properties. For this purpose, three generations of nanotubes were synthesized using three kinds of electrolytes: (A) aqueous acid media, (B) organic based electrolyte and (C) chloride containing electrolyte.

While a lot of reviews describe the formation mechanism of TiO₂ nanotubes formed in (A) and (B), very limited works have dealt with the formation mechanism of TiNT formed in (C). The present study is a contribution to the knowledge of the growth mechanism of TiNT formed in chloride containing electrolyte. While a number of publications has been achieved on the identification of precursor sites for pitting corrosion on titanium in aggressive bromide solution by applying polarization [30–32], to the best of our knowledge, the use of SECM in the examination of pits initiation on titanium in chloride solution at the open circuit potential has never been reported. So, we report here the observation of pits nucleation on titanium far below the pitting potential.

2. Experimental

Prior to experiments, high purity titanium foils (2 mm thickness, 1 cm × 1 cm) were mechanically polished, degreased in an ultrasonic bath with acetone for 15 minutes, hereafter, rinsed with de-ionized (DI) water and dried in warm air. The anodization process to obtain TiNTs was performed in two electrode configuration connected to the power supply, with the Ti as the anode and the platinum foil as a counter electrode. Three generations of TiO₂ nanotubes were grown by imposing an anodizing voltage of 20 V, using three kinds of electrolytes: (A) 1 wt% HF (for 20 minutes), (B) ethylene glycol + 0.3 M NH₄F + 0.2 M H₃PO₄ + 0.15 wt% H₂O (for 120 minutes), and (C) 0.3 M NaCl (for 1 minute). The chosen Anodization times plays an important role in achieving of the nanotubular morphology. In the case of NaCl solution, the tubular morphology is lost at anodizing durations greater than three minutes.

The as-fabricated nanotube arrays have an amorphous crystallographic structure. In order to induce the crystallization, annealing was carried out at 450 °C for 3 hours [33]. Crystallinity improved connectivity between grains and eliminated any amorphous regions that provide defects.

For morphological characterization of the anodized samples, top-view and cross-sectional observations were carried out with scanning electron microscope, XL30 ESEM.

For EIS measurements, a Saturated Calomel reference Electrode (SCE) and platinum counter electrode were used in pH 9.2 borate buffer solution (0.075 M Na₂B₄O₇, 10 H₂O + 0.05 M H₃BO₃). An Autolab PGSTAT-30 driven by FRA 4.9 Software (Eco Chemie, the Netherlands) was used, controlled by a PC. The measurements were carried out from 50 kHz to 50 mHz. An ac amplitude voltage of 10 mV and an applied potential ranging from –0.6 to 1 V have been used. The polarization is applied by successive steps of 0.1 V. For EIS data modeling and curve fitting, the Equivalent Circuit Software (Equivcrt) was used.

All potential values mentioned in EIS measurements were measured with respect to SCE.

SECM measurements were carried out with scanning electrochemical workstation from Sensolytics with a stepper motor driven x, y and z stage. A platinum microelectrode of 25 μm radius was used as the working electrode. An Ag/AgCl/KCl (saturated) was used as the reference electrode and a platinum wire as the counter electrode. The SECM was used without a mediator. One of the possible operating modes to use the SECM is in the sample generation-tip collection mode. In this case, the microelectrode is used to monitor the flux of electroactive species generated at the surface and variations in current were plotted versus the tip position. The tip potential was set at 0.6 V_{Ag/AgCl}. The specimen was mounted horizontally facing upwards and set at its open circuit corrosion potential.

Before SECM measurements, the approach curves were measured over the chosen scan area, and the tip was approached to the sample surface. When all the peripherals of the cell were mounted in position, the appropriate electrolyte was inserted to the cell and the probe tip scanned over the surface. The SECM-tip has been scanned parallel to the surface to detect local variations in chemical reactivity of polycrystalline titanium, which may be the onset sites for pitting corrosion. Local features at the surface of the substrate cause changes in the current response at the SECM-tip when scanned at a distance, 25–30 μm, above the sample. The tip electrode was scanned stepwise within a distance of 1000 μm in x direction with dx = 4 μm and 600 μm in y direction with dy = 8 μm. The scan rate of the microscope tip over the specimen surface was 20 μm/s.

3. Results and Discussion

3.1. Morphological characteristics of the porous layer of the three generations of TiNT

3.1.1. SEM images

Fig. 1 shows a sequence of SEM images taken from Ti samples anodized at 20 V in different anodizing electrolytes. As can be seen, well-defined TiO₂ with nanotubular structure appeared with the different solutions. The average length and diameter of the nanotubes are clearly affected by the anodization conditions. In acidic aqueous electrolyte, top view morphology (Fig. 1(a)) reveals an uniform pore distribution over the whole surface. Cross sectional view (Fig. 1(b)) clearly shows that the nanotubes are vertically oriented hollow cylinders with wavy-shaped walls. In organic based electrolyte (Fig. 1(c)), the high viscosity of the electrolyte strongly influences the resulting morphology. As can be seen, the tubes are smooth and present the highest degree of ordering (Fig. 1(d)). In chloride containing electrolyte, different and exciting microstructure feature has been observed. The surface structure is macroscopically of a somewhat powdery nature. White powders were clearly observed on some sites of the electrode surface. SEM images

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