RuO₂-Doped TiO₂ Nanotube Membranes Prepared via a Single-Step/Potential Shock Sequence

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ABSTRACT

Anodic TiO₂ nanotubes were simultaneously grown and doped with RuO₂ by single-step anodization in a negatively-charged RuO₄⁻ precursor. Subsequently, a high positive voltage was imposed on the nanotubes in an F⁻-based electrolyte (a process referred to as potential shock), which led to the formation of a through-hole RuO₂-doped TiO₂ nanotube membrane without significant loss of the RuO₂ catalyst. XPS results confirmed that the doped Ru metal was converted into RuO₂ as the potential shock voltage increased. Further increases in the potential shock voltage led to the formation of RuO_x/Ru in the TiO₂ nanotubes. All of our results clearly showed that a through-hole catalyst-doped TiO₂ nanotube membrane can be produced by a sequence consisting of single-step anodization and the potential shock process.

Keywords : TiO₂ Nanotubes, Membrane, Doping, Potential Shock, Single-Step Anodization

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1. Introduction

Highly-ordered anodic TiO₂ nanotubes, which can be produced by simple electrochemical oxidation of Ti in F⁻-based electrolytes, have been widely used in various applications such as photocatalytic pollutant degradation [1-3], water splitting [4,5], dye-sensitized solar cells [6,7] biomaterials for implants [8] high cycling retention Li ion batteries [9,10], and so on.

Since through-hole anodic TiO₂ membranes can effectively enhance the physical properties of devices in energy and environmental fields, [11] several methods have been developed based on ultrasonic-assisted separation, [12] solvent evaporation, [13] selective dissolution of metallic Ti in CH₃OH/Br₂, [1] voltage decreasing, [14] and voltage increasing (potential shock) [15]. In addition, doping of foreign elements into TiO₂ nanotubes has been reported as an alternative method to tailor the physical properties of

TiO₂ [16-18]. For example, water splitting for hydrogen generation was enhanced in anodic TiO₂ nanotubes containing RuO₂ catalysts, [16-18] and electrochromic performance was dramatically improved by the doping of WO₃ into TiO₂ nanotubes [19]. Using the potential shock process, where a high anodic voltage is applied suddenly for a short period of time (e.g., 140 V for 10 s) immediately after the fabrication of nanotubes, can produce either through-hole membranes in an F⁻-containing electrolyte (**MPS**, membrane potential shock) [15] or metal oxide doping (**DPS**, doping potential shock) in negatively-charged dopant precursors [16-18]. Thus, electrolytes are very important factors to make either the membranes or doping of TiO₂ nanotubes. In addition, a newly-grown thick barrier oxide is unavoidably formed if the potential of **DPS** is above 100 V, which prevents easy formation of completely through-hole TiO₂ in **MPS** [16]. Thus, the optimized combination of potential shock is necessary to produce through-hole TiO₂ containing functional catalysts.

In this report, we suggest an effective way to produce through-hole RuO₂-doped TiO₂ membranes by a simple electrochemical method, which can be easily applied to through-hole TiO₂ nanotube membranes with a doping of other catalysts.

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Fig. 1. Scheme of strategies used to dope RuO₂ into high aspect ratio TiO₂ nanotubes. (a) Twice-potential shock (**DPS** and **MPS**) and (b) single-step anodization for doping and subsequent **MPS**.

2. Experimental

Ti foil (0.127-mm-thick, 99.7% purity, Sigma-Aldrich) was cleaned with acetone, ethanol, and distilled water (DI) via ultra-sonication for 15 min, 10 min, and 5 min, respectively. The foil was subsequently dried in an oven at 60°C overnight. Anodization was conducted at 40 V for 2 h at room temperature using a power supply (source meter 2400, Keithley) in a two-electrode-type electrochemical cell. The electrolyte consisted of ethylene glycol (**EG**, Sigma-Aldrich), 0.25 wt. % ammonium fluoride (NH₄F, Sigma-Aldrich), and 1 vol. % DI. The TiO₂ nanotubes that were prepared initially were mechanically eliminated with epoxy [20], and a second anodization was carried out on the same Ti foil. In the case of **DPS** (Fig. 1 (a)), a second anodization was carried out in the electrolyte that was used during the first anodization at 40 V for 3 h. Subsequently, an anodic voltage (140 V for 10 s) was imposed on the nanotubes for doping in 0.002 M KRuO₄ [17]. During single-step anodization doping (**SSA**) (Fig. 1 (b)), the second anodization was carried out in ethylene glycol, 0.25 wt. % ammonium fluoride, 1

vol. % DI, and 0.002 M KRuO₄ (purity 97%, Sigma-Aldrich) for simultaneous fabrication and RuO₂-doping of TiO₂ nanotubes. Anodization was carried out at 40 V for 3 h at room temperature. For the fabrication of through-hole membranes, a constant high voltage (ranging from 100 to 180 V for 10 s) was imposed on the RuO₂-doped nanotubular TiO₂ in the F⁻-based solution (**MPS**). The electrolyte for **MPS** was the same as the one used in the first anodizing solution, in which fluoride ions drilled the bottom of the RuO₂-doped TiO₂ nanotubes. The morphologies of the fabricated TiO₂ membrane were examined by a field-emission scanning electron microscope (FE-SEM, 4300SE, Hitachi, Japan). The presence of ruthenium ions in the membrane was confirmed by energy dispersive X-ray spectroscopy (EDX, 4300SE, Hitachi, Japan) and X-ray photoelectron spectroscopy (XPS, VGESCALAB 220i-XL spectrometer, Fisons, Al-K α X-ray source). For the XPS measurements, nanotubes were detected from a Ti substrate, and the bottom sides of the nanotubes were measured to confirm that RuO₂ doped both the surface of the nanotubes and also inside of the TiO₂.

3. Results and Discussion

Fig. 1 shows the two processes used to produce through-hole RuO_2 -doped TiO_2 membranes. In the first method (Fig. 1 (a)), potential shock was applied twice for the doping (**DPS**) and through-hole membrane (**MPS**) processes. In the case of **DPS**, a negatively-charged dopant (RuO_4^-) was used, whereas aggressive F^- ions were employed for **MPS**. Since a thick barrier oxide is formed during **DPS** [18], through-hole membranes are not easily obtained, even at a high voltage in the subsequent **MPS** process (see Fig. 2 (a)). It has been well established that barrier oxide is newly grown on the bottom of TiO_2 , which is linearly increased by the potential of **DPS**, leading to less effective catalytic properties. In addition, further higher potential shock (for example, 200 V) leads to formation of voids in the oxide film, which further increases overpotential for electrochemical catalytic reactions [17].

Thus, **SSA** was employed as an alternative second method to avoid the formation of additional barrier oxide layer. Note that **SSA** is known as the method to dope the foreign catalysts into the TiO_2 films without the formation of barrier oxides. Instead, the thickness of nanotube wall is increased up to more than twice, compared to that obtained under conventional anodization [18,21].

Since anodic nanotubes were simultaneously grown and doped with RuO_2 and thick barrier oxide growth could be avoided during **SSA**, [16] the formation of through-hole membranes is possible in the subsequent **MPS** process. For example, through-hole membranes are clearly obtained on the RuO_2 -doped TiO_2 nanotubes in Figs. 2 (b-f). The through-hole membrane prepared at 140 V shows the clearest hole on the barrier oxide (Fig. 2 d), whereas unclear openings on the barrier oxide are exhibited at potential shock voltages lower or higher than the optimized value [15,17]. Please notice that the potential shock time for making the through-hole TiO_2 membranes from the pristine non-doped TiO_2 nanotubes was optimized for 10 s [15]. Herein, since the thickness of barrier oxide is little increased when the TiO_2 is doped by **SSA**, the potential shock time was optimized for 10 s. In fact, 5 s did not entirely open the bottom of pores.

Fig. 3 shows the cross-sectional view of through-hole membranes, demonstrating that any structural

Fig. 2. Bottom-side view of SEM images of anodic TiO_2 nanotubes after MPS at different voltages: (b) 100 V, (c) 120 V, (d) 140 V, (e) 160 V, and (f) 180 V. The results of pore-opening on the bottom of TiO_2 by **DPS** (at 140 V)-**MPS** (at 180 V) are shown in Fig. 2 (a).

Fig. 3. Cross-sectional SEM images of membranes: (a) as-prepared TiO_2 nanotubes, through-hole membrane prepared by MPS (b) at 100 V for 10 s and (c) at 180 V for 10 s

Fig. 4. XPS analysis of the bottom of the through-hole TiO₂ membrane. (a) Not-opened RuO₂-doped TiO₂ (before MPS), (b) MPS at 100 V, (c) 120 V, (d) 140 V, (e) 160 V, and (f) 180 V. (b) Table of Ru/RuO₂/RuO_x in XPS peaks

deformation on 9- μ m-thick TiO₂ membrane does not happen during MPS even at high voltage. The straight nanochannels were clearly observed on all the samples.

Fig. 4 confirms that the through-hole TiO₂ membrane contains ruthenium oxides. Compared to non-doped TiO₂ nanotubes showing C-C binding energy at 285 eV (Fig. 4 (a) A), peaks at 280 and 286 eV, which are attributed to Ru metal and RuO₂, respectively, were detected on the as-prepared RuO₂-doped TiO₂ nanotubes made by SSA (Fig. 4 (a) B). The peak at 280 eV disappeared after MPS, indicating that the Ru metal was oxidized or dissolved in the electrolyte. Interestingly, as the MPS voltage increased, the peak intensity at 286 eV, which corresponds to RuO₂, increased (Fig. 3 (a)). This indicates that the RuO₂ inside of the TiO₂ film moves deeply into the interface between the oxide and the Ti substrate during MPS. The peak at 288.6 eV, corresponding to RuO_x/Ru, appeared above 140 V; this demonstrates that further increases in the MPS voltage led to the formation of multiple amorphous ruthenium oxides. All of the XPS results indicated that there was not a significant loss of ruthenium oxide in the TiO₂ nanotubes during MPS. Thus, the suggested method is a reasonable way to produce through-hole-type catalyst-doped TiO₂ nanotube membranes. In addition, we found that the morphol-

Fig. 5. EDX analysis of bottom of through-hole TiO₂ nanotube membrane, showing that 0.04 at.% Ru is successfully doped into TiO₂.

ogy of the nanotubes is not destroyed, even after experiencing very high voltages during MPS.

Fig. 5 confirms again that Ru is incorporated into TiO₂ with a concentration of 0.04 at%, which is sufficient to improve TiO₂ chemical properties, which were demonstrated in the previous works [17,18].

4. Conclusions

We demonstrated an effective method to produce through-hole TiO₂ membranes containing a RuO₂ catalyst. Since **DPS** produced a thick barrier oxide on the bottom of TiO₂ nanotubes, subsequent **MPS** could not easily produce through-hole membranes, even at a high **MPS** voltage. Thus, doping RuO₂ into the TiO₂ nanotubes was carried out by **SSA** in an electrolyte containing a negatively-charged RuO₄⁻ precursor, which avoided forming a thick barrier oxide. Subsequent **MPS** at the optimized voltage (140 V in this study) led to the formation of through-hole RuO₂-doped TiO₂ membranes. In the XPS analysis of the bottom sides of TiO₂ nanotubes, peaks at 286 and 286.6 eV were observed. These were attributed to RuO₂ and RuO_x/Ru, respectively, and clearly confirmed that RuO₂-doped TiO₂ nanotubes were successfully formed by the suggested method. EDX analysis showed that 0.04 at% Ru is successfully doped into TiO₂ nanotubes.

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