Electrochemical Activity of a Blue Anatase TiO₂ Nanotube Array for the Oxygen Evolution Reaction in Alkaline Water Electrolysis

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ABSTRACT

An anatase TiO₂ nanotube array (NTA) was fabricated by anodization and successive heat treatments. When the anatase TiO₂ NTA was cathodically polarized, its color changed to blue, and it could be used as an electrochemically active anode for an oxygen evolution reaction (OER) in alkaline water electrolysis. The structure of the blue anatase TiO₂ NTA was controlled by the anodization conditions and its catalytic activity increased with an increase of the surface area. The activity of the blue anatase TiO₂ NTA gradually reduced with the continued OER because of the partial oxidation of Ti³⁺ to Ti⁴⁺. However, an intermittent cathodic regeneration process could significantly slow its reduction rate. The blue anatase TiO₂ NTA could be an alternative anode for alkaline water electrolysis.

Keywords : Blue TiO₂ nanotube array, Titania electrode, Electrocatalyst, Electrochromism, Cathodic polarization, DSA electrode, Water electrolysis, Oxygen evolution reaction

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1. Introduction

Alkaline water electrolysis is an effective method for the production of high purity hydrogen without the emission of environmental contaminants [1,2]. A dimensionally stable anode (DSA) is widely used for alkaline water electrolysis [3,4]. However, the fabrication of a DSA is complicated and expensive because of the use of noble metal oxides, such as IrO₂ and RuO₂. Many approaches have reduced the required amount of noble metals and simplified the manufacturing process of DSA [5-9]. Ti metal substrate can be covered with a thin oxide film consisting of amorphous or low crystalline TiO₂. TiO₂ is a

non-toxic, chemically inert, and corrosion-resistant material [6]. TiO₂ has been extensively studied under ultraviolet light for photocatalysis because it has semiconductor properties (anatase: 3.2 eV bandgap). Reduced titania (TiO_{2-x}), which contains oxygen vacancies (V_O-Ti³⁺), has recently been reported to exhibit improved photocatalytic activity under visible light. Black titania nanotubes with a substantial amount of Ti³⁺ were prepared by melted aluminum reduction and applied as the anode for photoelectrochemical water splitting [10]. Schumuki et al. reported that anatase black TiO₂ nanotubes with a stable Ti³⁺ defect-structure (formed by high-pressure H₂ treatment) exhibited a high photocatalytic behav-

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ior for cathodic hydrogen evolution [11].

The low electrical conductivity (10^4 - 10^7 $\Omega\cdot\text{cm}$) and electrocatalytic activity of TiO_2 prohibit its use as an electrocatalyst without a co-catalyst. Ti^{3+} may control the conductivity of TiO_2 , and the thermally reduced anatase TiO_2 has a conductivity of 10^{-1} $\Omega\cdot\text{cm}$. Ti^{4+} inside the TiO_2 lattice can be reduced to Ti^{3+} when a cathodic potential is applied, and the cathodic coloration of TiO_2 is the result of the double injection of a monovalent ion and an electron into the oxide matrix,

where M is the monovalent ion [12]. Yoon et al. reported the preparation of a blue TiO_2 nanotube array (NTA) by cathodic polarization and applied it to the anodic generation of chlorine and the hydroxyl radical [8]. In line with the effect of the Ti^{3+} defect-structure on the electrocatalytic behavior of TiO_2 , the increase of the TiO_2 surface area is a critical issue because it determines the extent of the reaction. Therefore, either TiO_2 nanoparticles or nanotubes could be applied as the anode for alkaline water electrolysis.

In this work, a one-dimensional TiO_2 nanotube was electrochemically fabricated and applied to the oxygen evolution reaction (OER) in alkaline water electrolysis. The durability of the TiO_2 nanotube structure and its effect on the OER were investigated with electrochemical methods. Surface analysis was performed using scanning electron microscopy and X-ray photoelectron spectroscopy.

2. Experiment

Ti foil (99.7 %, 0.127 mm thickness, Sigma Aldrich) was degreased by ultra-sonication in a solution of acetone, ethanol, and deionized (DI) water for 30 min. The degreased Ti foil was anodized in an electrolyte (0.2 wt% NH_4F , 2.5 wt% DI water in ethylene glycol). An amorphous TiO_2 NTA was fabricated by the application of a constant voltage at room temperature using a DC power supply (HP/Agilent 6035A). The electrochromism of the TiO_2 NTA was tested in a 0.1 M KH_2PO_4 buffer solution at pH 7.2 with cyclic voltammetry (CV). The blue TiO_2 NTA was obtained by cathodic polarization at -3 mA/cm^2 for 90 s. Pt wire was used as a counter electrode and $\text{Ag}/\text{AgCl}/\text{sat. KCl}$ was used as a reference electrode.

The crystallinity of the TiO_2 NTA changed from amorphous to anatase by annealing at 450°C for 1 h. The surface characterization of the TiO_2 NTA was investigated with a scanning electron microscope (SEM, S-4300, HITACHI), X-ray diffractometer (XRD, DMAX 2200, RIGAKU), and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific).

The electrochemical activity of the TiO_2 NTA as an anode in 1 M KOH was analyzed with a potentiostat/galvanostat (Autolab, PGSTAT301N, METROHM) in a three-electrode system. Pt wire and $\text{Hg}/\text{HgO}/1$ M NaOH were used as a counter electrode and reference electrode in 1 M KOH solution, respectively.

3. Results and Discussion

Fig. 1 shows the effect of the heat treatment on the crystallinity of the electrochemically fabricated anodized TiO_2 NTA. After the heat treatment at 450°C for 1 h, the amorphous TiO_2 changed to the gray crystalline anatase phase. Fig. 2 shows the CVs of the amorphous and anatase TiO_2 NTA in a 0.1 M KH_2PO_4 buffer solution at pH 7.2. The potential was anodically scanned from 0.0 V to 3.0 V, reversed to -2.0 V, and repeated. Both specimens changed to the blue TiO_2 at around -1.5 V by the double injection reaction (1). During the repetitive CV, the amorphous TiO_2 underwent reversible electrochromism reactions (i.e., a cathodic coloration and anodic bleaching, as shown in Fig. 2a) but did not show any anodic reactivity above 1.5 V. After the first cycling for the anatase TiO_2 , the anodic current started to flow above

Fig. 1. XRD spectra of the anodized TiO_2 nanotube array; (a) amorphous (b) anatase (after 1 h of annealing at 450°C).

Fig. 2. Cyclic voltammograms of the (a) amorphous and (b) anatase TiO_2 nanotube arrays in a buffer solution (0.1 M KH_2PO_4 , pH 7.2 with NaOH). Potential sweep rate: 40 mV/s.

1.5 V (due to the reaction: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) and continued until the end of the CV (Fig. 2b), which is in contrast to the amorphous TiO_2 NTA. During the first CV between -1.5 V and 0.0 V, the anatase TiO_2 NTA experienced a cathodic color change to dark blue caused by reaction (1), but bleaching did not occur despite the anodic current flow, which suggests an irreversible electrochromism. The blue anatase TiO_2 NTA persisted during the entire cycling in Fig. 2b and its catalytic activity for the anodic reaction was investigated. The blue anatase TiO_2 NTA was cathodically fabricated at -3 mA/cm^2 for 90 s in a pH 7.2 buffer solution and applied as the anode for the OER in 1 M KOH. Fig. 3 indicates that the blue anatase TiO_2 NTA has an excellent catalytic activity for the OER ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$), but the anatase TiO_2 NTA did not participate in the reaction. The XPS spectra in Fig. 4 show that the Ti^{3+} peaks (457.7 eV, 462.9 eV)

Fig. 3. Comparison of the oxygen evolution reaction activity of the blue and anatase TiO_2 nanotube arrays in 1 M KOH solution. The potential was linearly swept from 1.5 V to 2.5 V at 20 mV/s. Anodization conditions: 45 V for 20 h.

Fig. 4. XPS spectra of the blue anatase TiO_2 nanotube array before and after 100 repetitive linear sweep voltammtries for the oxygen evolution reaction. Potential sweep rate: 20 mV/s.

decreased and the Ti^{4+} peaks (459.5 eV, 464.7 eV) increased after the repeated 100 cycles of linear sweep voltammetry (LSV) for the OER. The Ti^{3+} in the blue anatase TiO_2 NTA, which can be $\text{K}_x\text{Ti}^{3+}\text{O}_2$, generated by cathodic polarization is responsible for the OER. However, the oxidation of $\text{K}_x\text{Ti}^{3+}\text{O}_2$ to TiO_2 ($\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$) during the OER, may cause the loss of its catalytic activity as the anodic OER continues.

Fig. 5 presents the surface morphology of the anatase TiO_2 NTA prepared at 45 V of anodization voltage with reaction times of 4 h, 8 h, and 16 h. Fig. 6 indicates that the length (l) and diameter (D) of the TiO_2 nanotubes increased with the anodization time.

Fig. 5. Morphology of the TiO_2 nanotube array (NTA) with respect to anodization time. Top view of the TiO_2 NTA prepared at 45 V for (a) 4 h, (b) 8 h, and (c) 16 h. Insets are cross-sectional views. Anodization solution: 0.2 wt% NH_4F , 2.5 wt% DI water with ethylene glycol.

Fig. 6. Average diameter and length of the TiO_2 nanotube array with different anodization times. Anodization voltage: 45 V, anodization solution: 0.2 wt% NH_4F , 2.5 wt% DI water with ethylene glycol.

Since the inner surface area of the 1-D nanotube is expressed as $N \cdot \pi \cdot D \cdot l$ (where N is the number density of the nanotubes), the surface area for the OER increases with the anodization time. The LSV in Fig. 7a coincides with the expected surface area increase, i.e., the specimen prepared at 45 V over 16 h shows the highest catalytic activity for the OER. However, the OER activity decreased with each LSV iteration, and the color of the blue anatase TiO_2 NTA gradually tarnished because of the oxidation of Ti^{3+} to Ti^{4+} , as suggested by the XPS spectra in Fig. 4.

Fig. 7b shows that the extent of the catalytic activity degradation, i_n/i_1 , increases with the increase in the number of LSV cycles, where i_n/i_1 is defined as the ratio of the anodic current density of the n^{th} cycle and 1st cycle at 2.5 V. Irrespective of the anodization time, 35-40 % of the initial activity of the blue ana-

Fig. 7. Effect of anodization time on the oxygen evolution reaction activity and durability of the blue anatase TiO_2 nanotube array in 1 M KOH solution. The anodization voltage, 45 V, i_n/i_1 is defined as the ratio of the anodic current density of the n^{th} cycle and 1st cycle from the linear sweep voltammetry at 2.5 V.

Fig. 8. Average diameter and length of the TiO₂ nanotube array with different anodization voltages. Anodization time: 16 h, anodization solution: 0.2 wt% NH₄F, 2.5 wt% DI water with ethylene glycol.

Fig. 9. Effect of the anodization voltage on the oxygen evolution reaction activity and durability of the blue anatase TiO₂ nanotube array in 1 M KOH solution. Anodization time: 16 h. i_n/i_1 is defined as the ratio of the anodic current density of n^{th} cycle and 1st cycle from the linear sweep voltammetry at 2.5 V.

tase TiO₂ NTA was lost after 10 LSV cycles. To investigate the effect of the different TiO₂ NTA fabri-

Fig. 10. Effects of regeneration on the durability of the blue anatase TiO₂. Blue anatase TiO₂ was regenerated in a pH 7.2 KH₂PO₄ buffer solution with -3 mA/cm² for 90 s after every 10 cycles of linear sweep voltammetry. i_1^* is the current density at 2.5 V after the initial 10 cycles of linear sweep voltammetry. i_n is defined as the anodic current density of n^{th} cycle at 2.5 V.

cation methods on the catalytic activity for the OER, the anodization voltage was varied from 35 V to 45 V and 55 V with the same anodization time of 16 h. Fig. 8 indicates that, as the anodization voltage increased from 35 V to 55 V, the tube diameter increased by ~25 %, but the tube length increased to nearly 4 times its initial length (from 6 μm to 22 μm). Fig. 9 (in agreement with the data in Figs. 6 and 7) suggests that the blue anatase TiO₂ NTA with a large surface area has high OER activities and their activity losses reach 35-42 % of the initial activities.

To overcome the catalytic activity degradation, the tarnished blue TiO₂ NTA was regenerated by cathodic polarization after repeated LSVs (-3 mA/cm² for 90 s in a pH 7.2 buffer solution). Regeneration occurred after every 10 LSV cycles. Fig. 10 shows the effect of regeneration on the OER, where i_1^* is the current density at 2.5 V after 10 cycles. Although the catalytic activity of the blue anatase TiO₂ NTA for the OER was not completely recovered during the regeneration, its degradation rate was significantly reduced. This suggests that the blue anatase TiO₂ NTA has good catalytic activity for the OER and its degradation can be recovered by an intermittent cathodic polarization.

4. Conclusions

This work showed the development of an alterna-

tive material for the OER in alkaline water electrolysis. The anatase TiO_2 NTA was fabricated by anodization and successive heat treatments. In contrast to the amorphous TiO_2 NTA, the anatase TiO_2 NTA showed an irreversible electrochromism (its color changed to blue by the cathodic polarization) and can be used as an electrochemically active anode for the OER. XPS spectra suggested that this catalytic activity was closely related to the presence of Ti^{3+} . The surface area of the anatase TiO_2 NTA was controlled by the anodization voltage and time, and the analysis of the nanotube length and diameter indicated that the largest surface area was obtained at 55 V during 16 h of anodization. The catalytic activity increased with an increase of the surface area. The activity of the blue anatase TiO_2 NTA gradually degraded with the continuation of the OER and its blue color tarnished because the electrochemically active Ti^{3+} was partially oxidized to Ti^{4+} during the anodic reaction. To overcome the degradation of the blue anatase TiO_2 NTA activity, it was continually regenerated by cathodic polarization, which resulted in the reduction of Ti^{4+} to Ti^{3+} . A cathodic regeneration process significantly regenerated the catalytic activity of the blue anatase TiO_2 NTA. The blue anatase TiO_2 NTA could be an alternative anode for use in alkaline water electrolysis.

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References

- [1] K. Zeng and D. Zhang, *Prog. Energ. Combust.*, **96**, 224 (2010)
- [2] J. Otero, J. Sese, I. Michaus, M. S. Maria, E. Guelbenzu, S. Irusta, I. Carrilero and M. Arruebo, *J. Power Sources*, **247**, 967 (2014)
- [3] S. Trasatti, *Electrochim. Acta*, **45**, 2377 (2000)
- [4] R. D. Coteiro, F. S. Teruel, J. Ribeiro and A. R. de Andrade, *J. Braz. Chem. Soc.*, **17**, 771 (2006)
- [5] M. Yousefpour and A. Shokuhy, *Superlattice. Microstruct.*, **51**, 842 (2012)
- [6] P. Roy, S. Berger and P. Schmuki, *Angew. Chem. Int. Ed. Engl.*, **50**, 2904 (2011)
- [7] S.-Y. Huang, P. Ganesan and B. N. Popov, *Appl. Catal. B*, **96**, 224 (2010)
- [8] C. Kim, S. Kim, J. Choi, J. Lee, J. S. Kang, Y.-E. Sung, J. Lee, W. Choi and J. Yoon, *Electrochim. Acta*, **141**, 113 (2014)
- [9] M. S. Hamdy, R. Amrollahi and G. Mul, *ACS Catal.*, **2**, 2641 (2012)
- [10] H. Cui, W. Zhao, C. Yang, H. Yin, T. Lin, Y. Shan, Y. Xie, H. Gu and F. Huang, *J. Mater. Chem. A*, **2**, 8612 (2014)
- [11] N. Liu, C. Schneider, D. Freitag, M. Hartmann, U. Venkatesan, J. Muller, E. Spiecker and P. Schmuki, *Nano Lett.*, **14**, 3309 (2014)
- [12] M. P. Cantao, J. I. Cisneros and R. M. Torresi, *Thin Solid Films*, **259**, 70 (1995)
- [13] L.-B. Xiong, J.-L. Li, B. Yang and Y. Yu, *J. Nanomater.*, **2012**, 13 (2012)
- [14] T. Hanawa, *J. Periodontal Implant Sci.*, **41**, 263 (2011)