The Oxygen Reduction Reaction on Nb-doped Titanium Dioxide Single Crystal Electrodes

Natsumi KAMEDA, Masashi NAKAMURA, and Nagahiro HOSHI*

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University,
1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

* Corresponding author: hoshi@faculty.chuiba-u.jp

ABSTRACT

Structural effects on the oxygen reduction reaction (ORR) have been studied on the low index planes of rutile TiO_2 doped with Nb (0.05–1 wt%) in 0.1 mol L^{-1} HClO_4 . The order of the ORR activity at 0.20 V (vs. RHE) is $\text{TiO}_2(100) < \text{TiO}_2(111) < \text{TiO}_2(110)$, and the activity increases with increasing Nb concentration. The activity of $\text{TiO}_2(110)$ is 5.6 times as high as that of $\text{TiO}_2(100)$ at Nb concentration 1 wt%. The order of the ORR activity does not correlate with the amount of oxygen vacancy defects that are known as the active sites of the ORR of TiO_2 nanoparticles. The ORR activity of 1 wt%Nb-doped $\text{TiO}_2(100)$ modified with melamine is 2.1 times higher than that of the unmodified one. The activity of 1 wt%Nb-doped $\text{TiO}_2(110)$ modified with melamine is the highest in the low index planes of TiO_2 . Modification by tetra-*n*-hexylammonium cation (THA^+) affects the ORR activity slightly.

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1. Introduction

Polymer electrolyte fuel cell (PEFC) is a clean energy conversion system because water is the only reaction product. However, the oxygen reduction reaction (ORR), which is a reaction of the air electrode of a fuel cell, has high overvoltage and slow reaction rate; large amount of Pt is used as catalysts of fuel cells at present. Reduction of Pt loading is necessary for expanding practical use of fuel cells, because the number of national resources of Pt is limited and the cost of Pt is high.

The current operating temperature of PEFC is from 80 to 90 °C. Higher operating temperature is required for PEFC to increase the efficiencies of power generation and heat exhaust. The next-generation PEFC targets the operation above 100 °C. Pt is not durable at the operation above 100 °C. We must find materials that have high durability and high activity for the ORR above 100 °C. Hamazaki et al. reported that the electrode using Ti_4O_7 is superior to the conventional electrode using carbon in durability and stability.¹ Groenenboom et al. revealed that the overvoltage of the ORR on Nb-doped TiO_2 is lower than that of undoped TiO_2 and the durability is as high as that of TiO_2 .² Yamamoto et al. predicted that the onset potential of the ORR of TiO_2 doped with Pd or Rh equals to the equilibrium potential of the ORR.³ These results suggest that TiO_2 electrodes have great potential of new cathode catalysts of fuel cells in the next generation. Many papers reported the ORR on Pt nanoparticles supported on TiO_2 particles.^{4,5} However, there have been few reports on the ORR activity of Nb-doped TiO_2 without Pt nanoparticles.^{2,6}

In this study, we have adopted the following three methods to improve the ORR activity of Nb-doped TiO_2 : (1) control of the surface in atomic level using single crystal electrodes, (2) modification of the surface with hydrophobic species, and (3) improvement of the conductivity by changing Nb concentration. An electrochemical reaction depends on a surface structure of the electrode;^{7–10} study on the ORR activity using single crystal electrodes is effective for the elucidation of the active sites of the catalytic activity. Marković et al. reported that the ORR activity increases as $\text{Pt}(100) < \text{Pt}(111) < \text{Pt}(110)$.¹¹ However, structural

effects on the ORR have not been studied on single crystal electrodes of Nb-doped TiO_2 except the report of Ota et al.¹² We have evaluated the ORR activity using Nb-doped rutile $\text{TiO}_2(100)$, $\text{TiO}_2(110)$, and $\text{TiO}_2(111)$ single crystal electrodes of which surfaces are regulated in atomic level. Previous study uses the double layer charge to estimate the relative ORR activity,¹² whereas we use real surface area of TiO_2 single crystal electrode to obtain the absolute value of the ORR activity. Figure S1(a) shows the hard sphere models of TiO_2 single crystal surfaces examined.

Jinnouchi et al. predicted that the change of the adsorbed water structure destabilizes Pt oxides (blocking species of the ORR) to increase the ORR activity on stepped surfaces of Pt.¹³ Hydrophobic organic species can also change the water structure, increasing the ORR activity. Asahi et al. and Miyabayashi et al. successfully increase the ORR activity of Pt nanoparticles by the modification with melamine and alkyl amines, respectively.^{14,15} Alkyl amines, melamine and tetra-*n*-hexylammonium cation (THA^+) also enhance the ORR activity of Pt single crystal electrodes.^{16–18} Especially, melamine and THA^+ increase the activity of the stepped surfaces of Pt as well as Pt(111). Thus we have adopted melamine and THA^+ as modification species of Nb-doped TiO_2 single crystal electrodes. There has been no study on the effects of hydrophobic species on the ORR of TiO_2 . The structures of melamine and THA^+ are shown in Fig. S1(b).

TiO_2 is a semiconductor; it has almost no electrical conductivity without doping. Nb doping improves the electrical conductivity markedly. We have measured the ORR of TiO_2 single crystal electrodes with the following three weight percentage of Nb: 0.05 wt%, 0.5 wt%, and 1 wt%.

In this communication, we have studied the ORR on Nb-doped TiO_2 single crystal electrodes with and without hydrophobic organic species in 0.1 M HClO_4 . Previous studies show that the oxygen vacancy defects are the active sites of the ORR of TiO_2 nanoparticles.^{19,20} Thus we have also estimated the amount of oxygen vacancy defects on TiO_2 single crystal electrodes using X-ray photoelectron spectroscopy (XPS) to elucidate whether the change of the activity is due to the surface structure or the amount of oxygen vacancy defects.

Figure 1. Ti 2p XPS spectra of 1 wt% Nb-doped TiO₂ single crystals after the chemical polishing and the annealing. (a) TiO₂(100), (b) TiO₂(110), (c) TiO₂(111).

2. Experimental

Perchloric acid (ultrapure) and hydrofluoric acid (ultrapure) were purchased from Kanto Chemical Co. Inc. Melamine and THA⁺ were obtained from Wako Pure Chemical Industries, Ltd. and Sigma-Aldrich, respectively. All the electrolytic solutions were prepared with ultrapure water produced using Milli-Q Advantage A10 (Millipore). Rutile type TiO₂ single crystal plates (10 mm × 10 mm × 0.50 mm) doped with Nb were purchased from Shinkosha Ltd.

Surface treatment method by Imanishi et al. was used to prepare atomically flat TiO₂ surfaces.²¹ Chemical polishing was done by immersing TiO₂ single crystals in 30 wt% hydrofluoric acid aqueous solution for 6 hours, and then the TiO₂ single crystals were annealed at 600 °C for 1.5 hours in air. The flatness of the surface was estimated using atomic force microscope (AFM) (Multi Mode 8, Bruker) in air.

The amount of oxygen vacancy defects was estimated using XPS (JPS-9030, JEOL Ltd.) in ultra-high vacuum (2.0×10^{-8} Pa). XPS spectra were obtained using an MgK α line (1253.6 eV) as the X-ray source.

Modification with hydrophobic species was done as follows. Aqueous solutions of melamine (0.7 mmol L⁻¹ (mM)) and THA⁺ (0.01 mM) were prepared. Atomically flat TiO₂ single crystals were immersed in the solution for 10 minutes. Excess hydrophobic species was removed by rinsing the electrode three times with ultrapure water.

We measured voltammograms using electrochemical analyzer (ALS 701D, BAS) and rotating ring disc electrode (RRDE-3, BAS). Linear sweep voltammogram (LSV) was measured from 0.05 to 1.0 V (vs. RHE) at scanning rate of 0.010 V s⁻¹ in 0.1 M HClO₄ saturated with O₂. The rotation speed was 1600 rpm. IR drop was corrected in all the voltammograms. The ORR activity was evaluated using cathodic current density at 0.20 V (vs. RHE). We use a geometric area of the electrode as a real surface area because the surface of the single crystal electrode is atomically flat. A Pt plate was adhered to the back of TiO₂ single crystal plate using In/Ga alloy to improve the electrical conductivity with RRDE-3.²¹ The resistance values of the Nb-doped TiO₂ single crystal electrodes were 12–18 Ω . The TiO₂ single crystal electrode with Pt plate was set to homemade Teflon holder, and connected to RRDE-3. Only well-defined surface of TiO₂ electrode has contact with the electrolytic solution using this holder.

3. Results and Discussion

Figure S2 shows AFM images of single crystal surfaces of 1 wt% Nb-doped TiO₂ electrodes after the surface treatment. The surfaces are composed of wide terraces and monoatomic steps. Roughness of the terrace is within 0.2 nm. Ionic radii of Ti⁴⁺ and O²⁻ are 0.075 nm and 0.14 nm, respectively; the roughness of the terrace is within one atom. Thus we have judged that the surfaces were smooth in atomic level.

Figure 1 shows XPS spectra of Nb doped TiO₂ single crystal electrodes. The peaks around 458 eV and 459 eV are assigned to 2p_{3/2} orbitals of Ti³⁺ and Ti⁴⁺, respectively. The peaks around 464 eV and 465 eV are due to 2p_{1/2} orbitals of Ti³⁺ and Ti⁴⁺, respectively. Larger 458 eV peak indicates that more oxygen vacancy defects exist on the surface.²² Table S1 shows the ratio of the peak area around 458 eV to the total peak area. There is no significant difference in the amount of oxygen vacancy defects as shown in Table S1. The amount of oxygen vacancy defects does not correlate with that of the ORR activity as shown later.

Figures 2(a–c) show the voltammograms of Nb-doped TiO₂ single crystal electrodes in 0.1 M HClO₄ saturated with Ar. When the Nb concentration increases, the conductive carrier density in the electrode also increases, resulting in higher current density. Redox peaks appear around 0.3 V (vs. RHE) on all surfaces at Nb concentration 0.05 and 1 wt%. The origin of these redox peaks is not known at present. No remarkable structural effect is found in the voltammograms. Voltammograms of 1 wt% Nb-doped TiO₂ modified with melamine and THA⁺ were almost identical with those of the unmodified ones.

Figure S3 shows LSV of the low index planes of Nb-doped TiO₂ in 0.1 M HClO₄ saturated with O₂. Cathodic currents depend on the surface structure significantly. The ORR activity is improved with increasing Nb concentration. The activity increases as TiO₂(100) < TiO₂(111) < TiO₂(110) regardless of the Nb concentrations. Figure 2(d) illustrates the ORR activity at 0.20 V (vs. RHE). The ORR activity of TiO₂(110) (1 wt% Nb) is 5.6 times as high as that of TiO₂(100) (1 wt% Nb), whereas the amount of oxygen vacancy defects does not depend on the surface structure significantly (Table S1). These results clearly show that surface structures rather than oxygen vacancy defects govern the activity for the ORR on well-defined TiO₂ single crystal electrodes.

We estimated the onset potential of the ORR (E_{onset}) using the potential at which cathodic current density reaches 0.1 $\mu\text{A cm}^{-2}$ in O₂ saturated solution. Table S2 summarizes the values of E_{onset} . E_{onset} shifts to higher potential with the increase of Nb concentration. E_{onset} gets higher as TiO₂(100) < TiO₂(111) < TiO₂(110) at any Nb concentration, giving the same activity series as that estimated using cathodic current density at 0.20 V (vs. RHE).

The highest activity of TiO₂(110) may be related to the surface energy. Previous studies show that the rate-determining steps of the ORR on TiO₂ surface are OH formation and H₂O desorption.^{23,24} If OH is easily generated or H₂O is desorbed quickly, the ORR will become active. The surface energy of TiO₂(110) is the smallest in the low index planes, giving the weakest bonding force between the surface and molecules.²⁵ Therefore, H₂O molecules on TiO₂(110) are most easily desorbed in the low index planes, giving the highest ORR activity.

LSVs are also measured on 1% Nb-doped TiO₂ single crystal electrodes modified with hydrophobic species. Figure S4 shows LSV of the Nb-doped TiO₂ electrodes in 0.1 M HClO₄ saturated with

Figure 2. Voltammograms of Nb-doped TiO₂ single crystals in 0.1 M HClO₄ saturated with Ar: (a) TiO₂(100), (b) TiO₂(110), (c) TiO₂(111). (d) Structural and Nb-doping effects on the ORR activity in 0.1 M HClO₄ at 0.20 V (vs. RHE). (e) The ORR activity of 1 wt% Nb-doped TiO₂ modified with hydrophobic species.

O₂. The order of E_{onset} (Table S2) is equal to that of the ORR activity at 0.20 V (vs. RHE) of bare surfaces, but the order was changed by the modification with the hydrophobic species. Melamine/TiO₂(111) has the highest E_{onset} (0.41 V (vs. RHE)) in the surfaces examined. Figure 2(e) shows the ORR activity at 0.20 V (vs. RHE) on bare and modified 1% Nb-doped TiO₂ electrodes. Melamine increases the ORR activity of all the TiO₂ single crystal electrodes. Melamine/TiO₂(110) has the highest ORR activity (2.7 $\mu\text{A cm}^{-2}$) in the surfaces examined. Melamine/TiO₂(100) gives the highest activity improvement ratio: the ORR activity of melamine/TiO₂(100) is 2.1 times higher than that of bare TiO₂(100). Enhancement ratio of the ORR by THA⁺ is smaller than that of melamine. The order of the activity of the ORR after the modification is identical with that of bare surfaces: TiO₂(100) < TiO₂(111) < TiO₂(110).

At present, we do not have the solid evidence of the mechanism of the structural effects and the enhancement of the activity by hydrophobic organic species on TiO₂ single crystal electrodes. Studies on the structural effects on the carrier density and the adsorbed species are now on progress using impedance measurement and vibrational spectroscopy in our laboratory.

4. Conclusion

The order of the ORR activity on Nb-doped single crystal electrodes of TiO₂ is TiO₂(100) < TiO₂(111) < TiO₂(110) at 0.20 V (vs. RHE) regardless of the Nb concentration, and the activity is improved by increasing the Nb concentration. The ORR activity of 1 wt% Nb-doped TiO₂(110) is 5.6 times higher than that of 1 wt% Nb-doped TiO₂(100). Melamine modification increases the ORR activity of all the TiO₂ single crystals. The ORR activity of melamine modified TiO₂(100) is 2.1 times as high as that of unmodified one. Melamine modified TiO₂(110) gives the highest activity for the ORR. Enhancement ratio of the ORR by THA⁺ is much smaller than that by melamine.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-00105>.

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