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Effects of transition metal doping in Pt/M-TiO_2 (M = V, Cr, and Nb) on oxygen reduction reaction activity

Jun-Hyuk Kim [a, b], Gihan Kwon [c], Hankwon Lim [d], Chenhui Zhu [e, f], Hoydoo You [e], Yong-Tae Kim [a, *]

[a] School of Mechanical Engineering, Pusan National University, Busan 609-735, Republic of Korea
[b] Hybrid Materials Solution National Core Research Center (NCRC), Pusan National University, Busan 609-735, Republic of Korea
[c] Chemical Science and Engineering Division, Argonne National Laboratory, IL 60439, USA
[d] Department of Chemical Systematic Engineering, Catholic University of Daegu, Daegu 712-702, Republic of Korea
[e] Materials Science Division, Argonne National Laboratory, IL 60439, USA
[f] Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

HIGHLIGHTS

- Various transition metals were doped to TiO_2 support for Pt-based electrocatalyst.
- Dopants resulted in a marked enhancement of ORR specific activity.
- Compressive strain and increased conductivity led to the performance enhancement.
- Pt/V-TiO_2 shows a far superior durability than conventional Pt/C.

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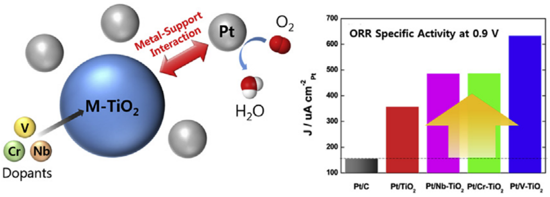
GRAPHICAL ABSTRACT



ABSTRACT

High cost and low durability are unresolved issues that impede the commercialization of proton exchange membrane fuel cells (PEMFCs). To overcome these limitations, Pt/TiO_2 is reported as an alternative electrocatalyst for enhancing the oxygen reduction reaction (ORR) activity and/or durability of the system. However, the low electrical conductivity of TiO_2 is a drawback that may be addressed by doping. To date, most reports related to Pt/doped-TiO_2 focus on changes in the catalyst activity caused by the Pt-TiO_2 interaction (metal-support interaction), instead of the effect of doping itself; doping is merely considered to enhance the electrical conductivity of TiO_2. In this study, we discuss the variation in the electronic fine structure of Pt caused by the dopant, and its correlation with the ORR activity. More extensive contraction of the Pt lattice in Pt/M-TiO_2 (M = V, Cr, and Nb) relative to Pt/TiO_2 and Pt/C leads to outstanding ORR specific activity of Pt/M-TiO_2. Notably, a fourfold increase of the specific activity is achieved with Pt/V-TiO_2 relative to Pt/C. Furthermore, an accelerated durability test (ADT) of Pt/V-TiO_2 demonstrates that this system is three times more durable than conventional Pt/C due to the metal-support interaction.

Abbreviations: PEMFC, Proton exchange membrane fuel cell; ORR, oxygen reduction reaction; ADT, accelerated durability test; ECSA, electrochemical surface area; TEM, transmission electron microscopy; XRD, X-ray diffraction; EXAFS, extended X-ray absorption fine structure; ICP-OES, inductively coupled plasma optical emission spectrometer; XAS, X-ray absorption spectroscopy; PAL, Pohang accelerator laboratory; CV, cyclic voltammogram; FWHM, full-width at half-maximum; TF-RDE, thin film rotating disk electrode.

[*] Corresponding author.
E-mail address: yongtae@pusan.ac.kr (Y.-T. Kim).

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) has been intensively studied due to its low-temperature stability, high energy conversion efficiency, and eco-friendly characteristics. Platinum on carbon support (Pt/C) is considered to be one of the most promising electrocatalysts for use in the PEMFC; however, commercialization of this system is still limited by unresolved issues such as high platinum cost and low carbon durability.

During the past decade, Pt usage in the electrode has been successfully reduced by two orders of magnitude [1]; however, this is not sufficient and further cost-cutting is still required. Efforts to reduce the cost involve improving the catalyst efficiency to accelerate the sluggish oxygen reduction reaction (ORR). The currently employed strategies for developing highly active ORR electrocatalysts generally involve the use of Pt-M alloys (M = Cr, Mn, Fe, Co, Ni, Cu, and Ru) [2–7], catalysts with a core/shell structure (Co@Pt [8], Ni@Pt [8], Pt@Pt-Cu [9], and Pd@Pt [10]), or shape/size control of Pt nanoparticles [11,12]. TiO_2 reportedly shows strong metal-support interaction with Pt [13,14], and efforts to enhance the catalyst performance by using Pt-TiO_2 have been reported [15,16]. However, the insulator characteristics of TiO_2 are believed to hinder the transfer of electrons [17,18]. Therefore, most previous studies have focused on the catalyst stability rather than catalyst performance. Attempts have been made to augment the ORR performance by enhancing the electrical conductivity via doping [19–23]. DiSalvo et al. [24] indicated that the ORR rates of Pt/$Ti_{0.7}W_{0.3}O_2$ are comparable to that achieved with conventional Pt/C. Sun and Cai et al. [25] also demonstrated that Pt/Nb-TiO_2 exhibits higher activity than Pt/C. However, since most reports related to Pt/doped-TiO_2 discuss changes in the activity due to Pt-TiO_2 interaction rather than caused by the doping effect itself, doping is generally regarded to serve the singular function as an electrical conductivity enhancer.

Interestingly however, the present research confirms changes in the electronic structure of Pt when the Pt/TiO_2 system is used. Furthermore, the dopant may not only increase the electrical conductivity of TiO_2 but also modify the Pt fine structure, resulting in the modification of the ORR activity.

Herein, three different dopants are introduced into Pt/M-TiO_2 (M = V, Cr, and Nb) in order to confirm the effect of doping on the ORR activity. It is demonstrated that the most significant enhancement of the ORR activity is achieved with vanadium-doped titania (Pt/V-TiO_2) that exhibits the strongest strain effect; this sample also exhibits long-term stability. Various high-resolution analysis techniques such as X-ray absorption fine structure (EXAFS) using a synchrotron beam are employed herein for strain investigation, and the accelerated durability test (ADT) is utilized to evaluate the durability of the catalysts. Transmission electron microscopy (TEM), X-ray diffraction (XRD), electrochemical tests, and density functional theory (DFT) calculation are also used for the characterization of Pt/M-TiO_2.

2. Materials and methods

2.1. Preparation of TiO_2 and M-TiO_2

All M-TiO_2 (M = V, Cr, and Nb) nanopowders were fabricated by sol-gel and/or hydrothermal synthesis and all of the precursors were precisely measured to adjust the dopant ratio to 5 mol%.

Titanium butoxide (97%, Sigma Aldrich), ammonium metavanadate (99%, Kanto Chemicals), and nitric acid solution were selected to obtain V-TiO_2 nanopowders with some modification of the synthesis method reported by Liu et al. [26] The appropriate amount of ammonium metavanadate required to adjust the dopant ratio to 5 mol% was completely dissolved in distilled water, and nitric acid was then added until the pH of the solution became 2–3. After stirring for 30 min, titanium butoxide was slowly added to the solution with constant stirring for 24 h. Preparation of the Cr-TiO_2 nanopowders has been described elsewhere [27]. Titanium isopropoxide (97%, Sigma Aldrich) and chromium nitrate (99%, Sigma Aldrich) were selected as the starting materials by reference to a previous report [28]. Titanium isopropoxide was dispersed in acetic acid with stirring for 15 min and the solution was then poured into an appropriate amount of distilled water with vigorous stirring for an hour. Nitric acid was subsequently added and the solution was left undisturbed at 78 °C for 40 min, followed by 75 min of stirring at the same temperature. After this process, hydrothermal synthesis was conducted. Specifically, the solution mixed with distilled water was poured into an autoclave and the temperature was maintained at 250 °C for 12 h. After completion of the hydrothermal synthesis, the solution was mixed with nitric acid and was stirred for 30 min. For the synthesis of Nb-TiO_2, titanium isopropoxide and niobium ethoxide (99.95%, Sigma Aldrich) were used as precursors. The measured titanium isopropoxide was added to 0.5 M isopropanol solution with stirring for 30 min. Distilled water was then slowly added to the solution with stirring for 24 h. TiO_2 nanoparticles were synthesized using the same method employed for Cr-TiO_2 without the doping process.

The prepared sample was fully filtered with distilled water followed by drying at 80 °C for 24 h. The sample was then heat-treated to achieve crystallization at 500 °C over 4 h in an air atmosphere, and continuously calcined for dopant activation [29] at 300 °C for 2 h under H_2 atmosphere.

2.2. Preparation of Pt/TiO_2 and Pt/M-TiO_2

Chloroplatinic acid hexahydrate (99.95%, Sigma Aldrich) was used as a precursor for the supported Pt samples, and Pt nanoparticles were deposited on the surface of the support using sodium borohydride. First, the requisite amount of Pt precursor was dissolved in distilled water. The support material was then dispersed in distilled water for 20 min using sonication and vigorously mixed with the Pt precursor solution for 15 min. The mixture of the Pt metal salt and support was subsequently reduced by the addition of the sodium borohydride solution. The precipitate was filtered and washed with distilled water, and then dried in an oven at 80 °C for 24 h. For comparison, a Pt/C (Premetek, 20 wt% on Vulcan XC-72) electrocatalyst was used.

2.3. Characterization

The amount of Pt was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Ultima 2 CHR, KBSI PN317), and the TiO_2 phase was confirmed by X-ray diffraction (XRD, Philips PANalytical) using Cu Kα radiation ($\lambda = 1.5406$ Å). The morphology of the powders was observed using transmission electron microscopy (TEM, Tecnai G2 F20); the electrocatalyst nanopowders were dispersed in ethanol by sonication for use in TEM specimen preparation. XPS (ESCALAB 250 Busan Center, KBSI) was used to confirm the presence of the dopant (dopant core level spectra were represented in Supporting Information) also Pt 4*f* spectra for all samples. All the obtained spectra were calibrated with the C 1*s* peak (284.6 eV). The X-ray absorption spectroscopy (XAS) Pt L_3-edge data were recorded in the transmission mode at the Pohang Accelerator Laboratory (PAL) using the 7D XAFS beam line with a ring current of 100 mA at 3.0 GeV. The beam source was a bending magnet (1.4557 T), and the monochromator was a Si (111) double crystal with an energy resolution ($\Delta\lambda/\lambda$) of 2×10^{-5} at 10 keV. The background absorption spectra were removed using