



# Synthesis of carbon-supported titanium oxynitride nanoparticles as cathode catalyst for polymer electrolyte fuel cells



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## ABSTRACT

For use as the oxygen reduction reaction (ORR) catalyst in polymer electrolyte fuel cell cathodes, carbon-supported titanium oxynitride (TiO<sub>x</sub>N<sub>y</sub>-C) nanoparticles with a size of approximately 5 nm or less were synthesized without using NH<sub>3</sub> gas. A sol-gel route developed for the synthesis of pure rutile TiO<sub>2</sub> nanopowders was modified to prepare the carbon-supported titanium oxide nanoparticles (TiO<sub>x</sub>-C). For the first time, N atoms were doped into TiO<sub>x</sub> solely by heating TiO<sub>x</sub>-C under an inexpensive N<sub>2</sub> atmosphere at 873 K for 3 h, which could be due to carbothermal reduction. The TiO<sub>x</sub>-C powder was also heated under NH<sub>3</sub> gas at various temperatures (873–1273 K) and durations (3–30 h). This step resulted in the formation of a TiN phase irrespective of the heating conditions. Both N<sub>2</sub>- and NH<sub>3</sub>-treated TiO<sub>x</sub>N<sub>y</sub>-C did not crystallize well; however, the former showed a mass activity more than three times larger than that of the latter at 0.74 V versus the standard hydrogen electrode. Thus, titanium oxide nanoparticles doped with a small amount of N atoms are suggested to be responsible for catalyzing ORR in the case of N<sub>2</sub>-treated TiO<sub>x</sub>N<sub>y</sub>-C.

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## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) have long been considered to be promising candidates for power sources in vehicles, stationary applications, and compact portable devices. Performance and cost targets for PEFCs depend on the type of application. For example, reducing the loading of platinum-group metal catalysts in vehicles is an urgent requirement [1]. In 2011, the U.S. Department of Energy set technical targets for the use of platinum-group metal catalysts by the year 2017: the anode plus cathode loading should be reduced to 0.125 mg cm<sup>-2</sup> with a simultaneous increase in the platinum mass activity and durability [2]. Because oxygen reduction reaction (ORR) at the cathode is much slower than hydrogen oxidation reaction at the anode, reducing the loading of platinum-group metal catalyst in cathodes causes much more severe performance loss than reducing catalyst loading at anodes does [3]. Therefore, development of ORR catalysts with non-platinum-group metals is an attractive strategy to achieve the target.

As recently reported [4–6], some non-platinum-group metal catalysts composed of Fe, N, and C show remarkable initial-stage performance in a single cell. In particular, when all conditions

except for the catalyst loadings are identical, a membrane electrode assembly prepared using the catalyst developed by Proietti et al. [6] at the cathode showed cell voltages similar to those obtained using carbon-supported platinum (Pt-C) cathodes at low current densities. However, the cell voltages obtained using the catalyst developed by Proietti et al. started to drop at around 0.5 A cm<sup>-2</sup>, and the difference between them and the voltages obtained in cells with Pt-C cathodes increased with increasing current densities. As the particle size of the catalyst developed by Proietti et al. is generally several micrometers or more [7], the resulting catalyst layer thickness is ~100 μm [6], which is nearly 10 times larger than that of state-of-the-art Pt-C-based catalyst layers. Therefore, the cell voltage at higher current densities cannot be increased by simply increasing the catalyst loading. This leads to large mass-transportation losses, that is, ohmic losses and oxygen diffusion losses caused by the large catalyst layer thickness [7]. As pointed out elsewhere [1], a decrease in mass transportation losses is necessary not only for this type of catalysts but also for other types of non-platinum-group metal catalysts such as metal oxides, oxynitrides, and nitrides.

One of the strategies for reducing the catalyst layer thickness is decreasing the size of the constituent material, preferably to the nanometer scale, which is similar to the case of Pt in Pt-C catalysts. Nanosized non-platinum-group metal oxide, oxynitride, and nitride catalysts such as tantalum oxide [8,9], zirconium oxynitride [10], hafnium oxynitride [11–13], molybdenum nitride [14,15],

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chromium nitride [16], tungsten nitride [17], and titanium nitride [18] have been supported on carbon black for use in acidic PEFC cathode environments. Among them, oxides and oxynitrides of groups 4 and 5 metals are particularly stable because they are insoluble in acidic media, as confirmed by leaching tests conducted using inductively coupled plasma atomic emission spectroscopy. Further, we recently found that the presence of N atoms is necessary for maximizing the ORR activity of hafnium oxynitride nanoparticle catalysts [13] and titanium oxynitride catalysts of various particle sizes (~20–200 nm) [19]. Therefore, the development of nanosized oxynitride catalyst particles of groups 4 and 5 metals is an attractive option. However, only two types of materials, namely, zirconium, and hafnium oxynitride nanoparticles supported on carbon black, have been investigated so far; their synthesis includes heat treatment under an NH<sub>3</sub> atmosphere [10–13].

In the present work, we report an inexpensive synthesis route for carbon-supported titanium oxynitride (TiO<sub>x</sub>N<sub>y</sub>-C) nanoparticles without using NH<sub>3</sub> gas. Titanium is the most abundant among groups 4 and 5 metals [20]. The promising activity of titanium oxides or oxynitrides with particle sizes of several tens of nanometers or more has recently been reported by several authors, including us [19,21,22] and Lee's group [23]. A sol-gel route developed for the synthesis of nanosized unsupported rutile TiO<sub>2</sub> powder [24] was modified for the synthesis of TiO<sub>x</sub>N<sub>y</sub>-C. The crystal structures, morphologies, and surface chemical states of the TiO<sub>x</sub>N<sub>y</sub>-C catalysts were evaluated using X-ray diffraction (XRD), field emission transmission electron microscopy (FE-TEM), and X-ray photoelectron spectroscopy (XPS), respectively. The electrochemical stability and ORR activity was evaluated using cyclic voltammograms (CVs) and rotating disk electrode (RDE) voltammograms, respectively.

## 2. Experimental

### 2.1. Synthesis of catalysts

The TiO<sub>x</sub>N<sub>y</sub>-C catalysts were synthesized via a sol-gel route developed for rutile-TiO<sub>2</sub> nanopowders [24], with the following three modifications: (i) the addition of carbon supports, (ii) the use of different drying/heating conditions, and (iii) the use of different heating atmospheres in order to avoid oxidation of carbon supports at high temperatures and to dope N into the titanium oxides.

First, as-received carbon black powder (Vulcan XC-72, Cabot Co., Japan), hereafter denoted as C, was refluxed with nitric acid for 6 h, washed with water, and dried overnight at 363 K. Second, the refluxed C powder was stirred in 0.5 mol dm<sup>-3</sup> hydrochloric acid at 273 K; this was followed by the addition of cold titanium tetrachloride (TiCl<sub>4</sub>, Kishida Chemical Co., Japan). Third, the temperature of the dispersion was increased to ~330 K for 5 h with continuous stirring to evaporate the solvents. Fourth, the powder was washed with water and dried overnight in an oven at 363 K. Finally, the obtained precursor powder was placed in an alumina boat and heated in a horizontal quartz tube furnace that was slowly evacuated and purged with N<sub>2</sub> gas. The temperature was increased at a heating rate of 500 K h<sup>-1</sup> from room temperature to different high temperatures *T*; the *T* was then maintained for a variable time *t* and then reduced to room temperature without controlling the cooling rate. Below *T*, N<sub>2</sub> gas at a flow rate of 300 standard cubic centimeters per minute (sccm; 1 sccm = 1.67 × 10<sup>-8</sup> m<sup>3</sup> s<sup>-1</sup>) was used. At *T*, the following flowing gases were utilized to maintain different atmospheric conditions: N<sub>2</sub> introduced at 300 sccm or NH<sub>3</sub> introduced at 200 sccm. Under the fixed heating conditions of *T* = 873 K and *t* = 3 h, N<sub>2</sub> gas was used (hereafter referred to as N<sub>2</sub> treatment), whereas under the other conditions of *T* = 873–1223 K and *t* = 3–30 h, NH<sub>3</sub> gas was used (hereafter referred to as NH<sub>3</sub> treatment). The mass

of the catalyst sample was measured before and after NH<sub>3</sub> treatment, and the mass loss, Δ*m*, was calculated using the following equation:

$$\Delta m = \frac{100(m_i - m_f)}{m_i} \quad (1)$$

where *m<sub>i</sub>* and *m<sub>f</sub>* denote the sample mass before and after NH<sub>3</sub> treatment, respectively. Some of the precursor powder particles were oxidized in air above 973 K for 1 h to remove the carbon supports. By measuring the mass before and after oxidation and assuming that the remaining white powder after oxidation was composed of TiO<sub>2</sub>, the mass fraction of TiO<sub>x</sub> in the precursor powder was determined to be 4.4% (w/w).

### 2.2. Characterization

The morphology and crystal structure of the two catalysts heat-treated at 873 K for 3 h under the different gases were investigated by using a field emission transmission electron microscope (JEM-2100F, JEOL Co., Japan). The crystal structures were also analyzed by using an X-ray diffractometer (RINT-2200, Rigaku Co., Japan) with Cu Kα radiation generated at 40 kV and 30 mA in the 2θ range 10°–90° at a scan rate of 2° min<sup>-1</sup>. The chemical states of the catalysts were analyzed using an X-ray photoelectron spectrometer (Quantera SXM, ULVAC-PHI, Inc., Japan) with an Al Kα X-ray source (1486.6 eV).

### 2.3. Electrochemical stability and ORR activity measurements

To evaluate the electrochemical stability and ORR activity of the catalysts, CVs and RDE voltammograms were generated. The catalysts were dispersed in isopropyl alcohol by sonication for 1200 s to obtain a slurry. The mass fraction of the catalysts in the slurry was 2.5%. Aliquots of the slurry with volumes of 3.6 and 6.4 mm<sup>3</sup> were dropped onto glassy carbon (GC) disk electrodes with a geometrical surface area (*S*) of 0.0707 cm<sup>2</sup> (diameter, *φ*, of 3 mm) and 0.1257 cm<sup>2</sup> (*φ* = 4 mm), respectively, to obtain a TiO<sub>x</sub>N<sub>y</sub>-C catalyst loading (*mS*<sup>-1</sup>) of 1 mg cm<sup>-2</sup>. Subsequently, the electrodes were air-dried at 318 K for at least 600 s. To achieve a stable catalyst coating of the GC surface, 2.0 and 3.6 mm<sup>3</sup> of a 0.5% Nafion solution [prepared by diluting a 5% w/w Nafion solution (510211, Sigma-Aldrich Co., U.S.A.) in ethanol] was dropped onto the surface of the GC disk electrodes with *S* = 0.0707 and 0.1257 cm<sup>2</sup>, respectively. This step was followed again by air-drying at 318 K for at least 600 s. Prior to these catalyst coating treatments, the surface of the GC disk electrodes was polished with 1.0 and 0.05 μm alumina slurries, washed with water and acetone, and dried at 318 K in air.

Using a conventional three-electrode cell, electrochemical measurements were performed in 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at room temperature. The catalyst-coated GC disk electrode, carbon paper (TGP-H-120, Toray, Japan), and Ag/AgCl (3 mol dm<sup>-3</sup> NaCl) electrode (RE-1B, BAS Co., Japan) were used as the working, counter, and reference electrode, respectively. The working electrode was set in a rotator (RRDE-3A, BAS Co., Japan). All working electrode potentials were referenced to the standard hydrogen electrode (SHE). Using a potentiostat (Model 606A, ALS Co., U.S.A. or Model 2323, BAS Co., Japan), the RDE voltammograms were recorded by applying a disk potential, *E*, in the range of 0.05–1.2 V at a scan rate of 5 mV s<sup>-1</sup> and a rotation speed of 1500 rpm after bubbling with O<sub>2</sub> for 1800 s. CVs under a N<sub>2</sub> atmosphere were also recorded for identical *E* range at scan rates of 5 and 50 mV s<sup>-1</sup>. The current per unit geometrical area of the GC disk electrode obtained under the N<sub>2</sub> atmosphere (*i<sub>N</sub>*) subtracted from that under O<sub>2</sub> atmosphere (*i<sub>O</sub>*) was assumed to be responsible for the ORR.

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