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Supplementary Information

Creation of Oxygen Reduction Reaction Active Sites on Titanium Oxynitride *Without* Increasing the Nitrogen Doping Level

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S1. Experimental details.

Synthesis of the catalysts: Support-free TiO_xN_y catalysts were synthesised using the solution-phase combustion route with optimised conditions for the activity.[15] First, 0.31 g of TiF_4 powder (Sigma-Aldrich Co., St. Louis, Missouri, U.S.) and 20.00 g of urea powder ($(NH_2)_2CO$, Wako Chemical Industries Ltd., Osaka, Osaka, Japan) were dissolved in 370 cm^3 of distilled water by stirring using a polytetrafluoroethylene (PTFE)-coated magnetic bar at room temperature in a PTFE beaker. The external part of the beaker's bottom was coated with a PTFE–carbon composite to facilitate heating on a hot stirrer. The resulting mass ratio of urea to TiF_4-derived TiO_2 was 100. Next, 36 ml of 35% (w/w) HCl solution (Kishida Chemical Co. Ltd., Osaka, Osaka, Japan) was added dropwise to the solution via continuous stirring to reduce the pH value to less than 1. The HCl concentration in the solution was 1 mol dm^{-3}. Then, the PTFE beaker was placed on another stirrer pre-heated to 523 K, stirred continuously until the solvent evaporated and then dried in a convection oven overnight at 380 K. The dried powders were ground using an agate mortar. Subsequently, each precursor powder was set on an alumina boat and placed in a horizontal quartz tube furnace. The tube was slowly evacuated and purged with N_2 gas. Then, the powder samples were heated from room temperature to 1123 K at a rate of 10 K min^{-1}; this temperature was maintained constant for 2 h. The samples were then cooled to room temperature at an uncontrolled rate. The N_2 flow rate was 100 sccm during pyrolysis. After pyrolysis, the powders were ground in an agate mortar. This catalyst is denoted as as-synthesised TiO_xN_y. Note that some solid by-products were found to have attached to the inner wall of the quartz tube during pyrolysis. Such solid by-products can stop the gas flow if they block the narrow opening of the quartz tube, which can be extremely dangerous. Therefore, a quartz tube more than three times longer than the heating zone was used to provide sufficient space for by-product accumulation inside the tube in order to prevent any blockage. The tube part outside the heating zone was not lagged by thermal insulators. After pyrolysis and ejection of the alumina boats, the by-products were easily removed by washing the tube with water. Some as-synthesised TiO_xN_y catalysts were annealed under a mixed gas containing 10% H_2 (v/v) in Ar. They were set on an alumina

boat, placed in another horizontal quartz tube furnace and slowly evacuated. Then, the H_2/Ar gas mixture was introduced into the tube and heated from room temperature to the target temperature between 623 K and 1023 K at a rate of 10 K min^{-1}. This temperature was maintained for 3 h, followed by cooling at an uncontrolled rate. The flow rate of the gas mixture was 500 sccm during annealing.

Characterisation: The morphology of the TiO_xN_y catalysts was investigated using a field-emission scanning electron microscope (JSM-7000F; JEOL, Akishima, Tokyo, Japan) and a transmission electron microscope (JEM-2100; JEOL, Akishima, Tokyo, Japan). The bulk crystal structures of the catalysts were analysed using an X-ray diffractometer (MiniFlex600; Rigaku Co., Akishima, Tokyo, Japan) with Cu Kα radiation generated at 40 kV and 15 mA (scan rage = 20°–80°, step size = 0.02° and scan rate = 2° min^{-1}). The surface crystal structures of the catalysts and commercial rutile TiO_2 powder (MPT-881; Ishihara Sangyo Co., Osaka, Osaka, Japan) were evaluated using a Raman spectrometer (NRS-5100; JASCO Co. Ltd., Hachioji, Tokyo, Japan) with a 532-nm laser. The chemical states of the catalysts were determined using an X-ray photoelectron spectrometer (PHI 5000 VersaProbe; ULVAC-PHI, Inc., Chigasaki, Kanagawa, Japan) with an Al Kα X-ray source (1486.6 eV). The peak shifts due to surface charge were corrected using the binding energy of C 1s (284.8 eV), originated from the hydrocarbon contaminants from the spectrometer. The spectra were acquired at three different points for all the catalysts. Then Ti 2p and N 1s spectra were analysed by fitting six and four symmetric peaks, respectively, after subtracting Shirley-type background then the average area fraction of each peaks was calculated.

ORR activity and selectivity measurements: Rotating disk electrode (RDE) and rotating ring–disk electrode (RRDE) voltammograms were obtained to evaluate the ORR activity and selectivity, respectively, of the catalysts. The TiO_xN_y catalyst, 5% w/w Nafion® ionomer solution (510211; Sigma-Aldrich Co., St. Louis, Missouri, U.S.) and isopropyl alcohol were sonicated together for 1200 s and further mixed using a planetary mixer (Mazerustar KK-250S; Kurabo Co., Osaka, Osaka, Japan) for 180

s to obtain a homogeneous catalyst ink. The mass fraction of Nafion in the catalyst layer was set to 0.05, and the catalyst loading on glassy carbon (GC) disk (4 mm diameter)–platinum ring (5 mm inner diameter and 7 mm outer diameter) electrode (BAS Co., Sumida-ku, Tokyo, Japan) was set to 2.0 mg cm^{-2}. The density of TiO_xN_y catalysts was considerably high and the surface area was small because they are free from carbon supports. Therefore, the GC surface was observed to form so-called catalyst islands when the catalyst loading was low. A high loading value of 2.0 mg cm^{-2} was thus necessary for uniform coating of the GC surface. Prior to coating the catalyst layer by dropping the catalyst ink, the GC surface was polished with 1.0- and 0.05-μm alumina slurries, washed with water and air dried at 320 K for at least 600 s. A conventional three-electrode cell was used for the room-temperature electrochemical measurements performed in 0.1-mol dm^{-3} H_2SO_4. The catalyst-coated GC disk electrode, a carbon rod (Nilaco Co., Chuo-ku, Tokyo, Japan) and an Ag/AgCl (3-mol dm^{-3} NaCl) electrode (BAS Co., Sumida-ku, Tokyo, Japan) were used as the working, counter and reference electrodes, respectively. The working electrode was set on a rotator (RRDE-3A, BAS Co., Sumida-ku, Tokyo, Japan). All working electrode potentials were referenced to the reversible hydrogen electrode (RHE). After sequentially bubbling O_2 and N_2 for 1800 s, the RDE voltammograms were recorded by applying a disk potential (E) from 1.26 to 0.11 V (cathodic) at a scan rate of 5 mV s^{-1} and a rotation speed of 1500 rpm using a bi-potentiostat (Model 2323 or 704B; BAS Co., Sumida-ku, Tokyo, Japan). The ring potential was set constant at 1.26 V to obtain the RRDE voltammograms. The ORR activity was measured by background-corrected current density, $j_O - j_N$, which is the difference in the current per unit geometrical area of the GC disk electrode that was obtained in O_2 (j_O) and in N_2 (j_N). For measuring the selectivity, the number of electrons transferred per oxygen molecule, n, was calculated by analysing RRDE voltammograms with a following equation;

$$n = -4I_d / (-I_d + I_r / N)$$

where I_d and I_r are the disk and ring currents, respectively, and both of these currents were background-corrected as described above. The N is the collection efficiency (0.424) provided by the manufacturer (BAS Co.). An accelerated degradation test in a load cycle mode was performed for the best catalyst using

a protocol for automotive PEFCs.[4] The disk potential was cycled with a rectangular wave between 0.6 V (3 s) and 1.0 V (3 s) for 10,000 times using a potentiostat (SP-150; BioLogic Co., Seyssinet-Pariset, Grenoble, France). After the 10,000 cycles, the activity was evaluated with a protocol identical to the initial one. The background-corrected current density after the 10,000 cycles divided by the initial one, $j(10\mathrm{k})\cdot j(0)^{-1}$, was used to measure the degradation of active sites by the test.

S2. Morphology of TiO_xN_y catalysts.

The morphology of the TiO_xN_y catalysts before and after the annealing under 10% H_2 (v/v) in Ar was investigated using field-emission scanning electron microscopy (FE-SEM). The annealing did not significantly change the morphology, as shown in Fig. S1. As the temperature of the annealing was lower in comparison with that of the first pyrolysis under N_2, i.e. 1123 K, no drastic aggregations were found after the second annealing.

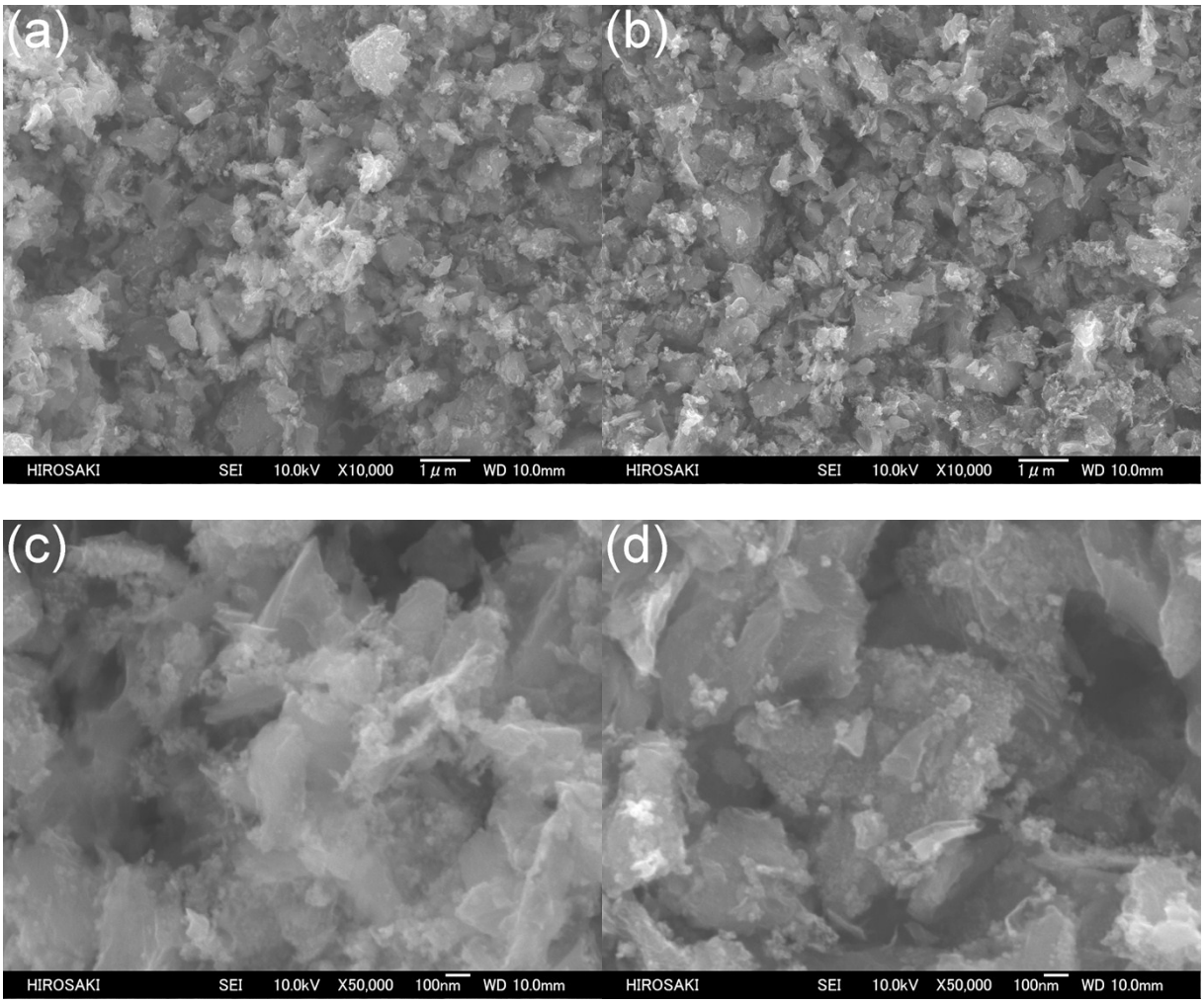

Fig. S1 Field-emission scanning electron microscopy (FE-SEM) images of titanium oxynitride (TiO_xN_y) catalysts (left) before and (right) after annealing at 923 K for 3 h under 10% H_2 (v/v) in Ar. The images were acquired under two different magnifications: (a and b) 10,000× and (c and d) 50,000×.

S3. ORR kinetics of TiO_xN_y catalysts.

Table S1. ORR kinetic data of catalysts shown in Fig. 4; (i) as-synthesised TiO_xN_y catalysts and of those after annealing at (ii) 623 K, (iii) 723 K, (iv) 823 K, (v) 923 K and (vi) 1023 K under 10% H_2 (v/v) in Ar.

Catalyst label	$E_{1/2}$ vs. RHE *1	$j_k\|_{E = 0.7\ V}$ *2	$n\|_{E = 0.6\ V}$ *3
(i)	0.63 V	1.40 mA cm^{-2}	3.9
(ii)	0.59 V	0.72 mA cm^{-2}	3.9
(iii)	0.62 V	1.32 mA cm^{-2}	3.9
(iv)	0.64 V	1.74 mA cm^{-2}	3.9
(v)	0.65 V	1.97 mA cm^{-2}	3.9
(vi)	0.64 V	1.64 mA cm^{-2}	3.9

*1 Half-wave potential; the potential at which half of the limiting current density after background-correction, j_l, was obtained.

*2 Kinetic current density; $|j| \cdot |j_l| / (|j_l| - |j|)$ at $E = 0.7$ V.

*3 Number of electrons transferred per oxygen molecule at $E = 0.6$ V.