



A Carbon-Support-Free Titanium Oxynitride Catalyst for Proton Exchange Membrane Fuel Cell Cathodes



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ABSTRACT

Cathode catalysts without platinum group metals (PGMs) or carbon supports can reduce the price of proton exchange membrane fuel cells in automobiles, making them commercially competitive. In this paper, an inexpensive and PGM-free catalyst—amorphous nitrogen-doped TiO₂-shell on TiN-core—was synthesized without carbon support. While existing PGM-free all-oxide catalysts without carbon support have shown moderate current densities (at the order of $\mu\text{A}/\text{cm}^2$), the current density of this new catalyst is three orders of magnitude higher. Replacing commercial carbon support by hydrothermally synthesized Ti₄O₇ significantly enhanced the activity to be close to that of carbon-supported platinum. Although its conductivity and surface area were not sufficient for an accurate evaluation of its activity, these new results demonstrate the possibility of high-performance non-PGM catalysts without carbon supports.

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1. Introduction

Due to concerns of pollution and global warming, there is an urgent need to reduce the emission from automobiles on the global scale, and some countries have implemented nearly zero emission limits. While the lithium-ion battery and other energy storage/conversion devices can eliminate emission in smaller vehicles, the proton exchange membrane fuel cell (PEFC) is more suitable for “high-load vehicles” such as trucks, buses and vehicles that operate over long distances (>500 kilometres) [1]. The PEFC-powered vehicles have been commercialized recently, yet their prices remain high due to the scarce and expensive platinum group metals (PGMs) in the catalysts, as well as the need to protect carbon-black supports from corrosion [2,3]. In PEFC, the PGM loading required for oxygen reduction reaction (ORR) at the cathode is an order of magnitude higher than that for hydrogen oxidation reaction at the anode. At potentials above 0.207 V versus the standard hydrogen electrode, the carbon support corrodes. The corrosion rate is especially high during the startup/shutdown of the cell, due to the so-called reverse-current decay mechanism which increases the potential up to ~ 1.5 V [4]. Therefore, non-PGM

cathode catalysts [5–17] and/or PGM catalysts on carbon-free supports [18–25] have been extensively developed to reduce the cost of PEFC.

Most known non-PGM catalysts utilize graphitic carbon materials as conductive supports and/or the catalyst itself [7–14,16,17]. Exceptions include sputtered thin-films, [5] plates [6], and micron-sized powders [15] of group IV/V metal oxides. These metal oxide catalysts are stable against leaching in acidic media [5,6]. However, their poor conductivity leads to very moderate current density, with the geometric current density on the order of $\mu\text{A}/\text{cm}^2$ in the practical potential range [5,6,15]. To increase the active surface area and the current density, conductive agents have been utilized to connect the oxide nanoparticles to the carbon supports [14,16].

Oxides [18–22], nitrides [23,24], borides [25], and other carbon-free compounds have been used to support PGM catalysts. Some platinum catalysts on conductive oxide supports have shown better ORR activity than conventional carbon-supported platinum (Pt–C) or platinum-cobalt (PtCo–C) catalysts [21]. The conductive PGMs can show ORR activity when supported on non-conductive oxides, such as dopant-free TiO₂ [19,21]. On the other hand, all-oxide non-PGM catalysts on oxide supports remain a challenge due to the poor conductivity of the oxides.

Here we developed a new PGM-free oxynitride catalyst without carbon support. The moderate ORR activity of a previously developed carbon-supported titanium oxynitride (TiO_xN_y–C) [17] was significantly improved by replacing commercial carbon black

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support by hydrothermally synthesized Ti_4O_7 fibers. In acidic media, this catalyst achieved the highest activity among the ever reported carbon-support-free oxide catalysts and a limiting current density similar to Pt–C. This new record demonstrated the potential of all-oxide catalysts in PEFC cathodes.

2. Experimental

2.1. Synthesis of Ti_4O_7 supports

0.6 g of TiO_2 powder (P25, Japan Aerosil Co., Shinjuku-ku, Tokyo, Japan) was hydrothermally treated at 423 K for 72 h in 10 M NaOH solution using a Teflon-lined autoclave. The autoclave was set in an aluminium block placed on a hot stirrer to continuously stir the dispersion. After the hydrothermal treatment, the autoclave was allowed to cool and opened after stopping the stirring. The obtained powder was washed with HNO_3 solution until $\text{pH} \leq 1$, then washed with distilled water until the pH became neutral. The washed powder was dried in a convection oven at 380 K for at least overnight. The absence of trace sodium was verified by XPS (Supplementary material). The dried powder was placed in an alumina boat which was then set in a horizontal quartz tube furnace. The furnace was slowly evacuated and purged with 5% H_2 in Ar. The support samples were heated from room temperature to 1323 K at a rate of 10 K min^{-1} , then the temperature was maintained for 6 h, and the samples were cooled to room temperature. The flow rate of H_2/Ar was 500 standard cubic centimetres per minute (sccm, $1 \text{ sccm} = 1.67 \times 10^{-8} \text{ m}^3 \text{ s}^{-1}$) during the pyrolysis.

2.2. Catalyst synthesis

The catalysts were synthesized by modifying the solution-phase combustion route [17] to replace carbon black with Ti_4O_7 , or even without any support. Their structure which is shown later in section 3 is TiN-core covered with amorphous nitrogen-doped TiO_2 -shell and we call this as TiO_xN_y for the sake of simplicity. A given mass of Ti_4O_7 support was dispersed in distilled water in a polytetrafluoroethylene (PTFE) beaker by stirring at room temperature. The bottom of the beaker was coated with a PTFE-carbon composite on the outside to facilitate heating within via a hot stirrer. Next, titanium tetrafluoride powder (TiF_4 , Sigma-Aldrich Co., St. Louis, Missouri, U.S.) and urea powder ($(\text{NH}_2)_2\text{CO}$, Wako Chemical Industries Ltd., Osaka, Osaka, Japan) were added to the dispersion with continuous stirring to achieve a mass ratio of Ti_4O_7 : TiF_4 -derived TiO_2 :urea = R :1:100, where R ranged from 0–2. Unless otherwise noted, R was fixed at 1. Then, 35% (w/w) hydrochloric acid solution (HCl, Kishida Chemical Co., Osaka, Osaka, Japan) was added to the resulting dispersion till $\text{pH} \leq 1$, in order to hydrolyze TiF_4 and generate titanium hydroxides [17]. The PTFE beaker was placed on another stirrer pre-heated to 523 K, stirred continuously until the water evaporated, and then dried in a convection oven at least overnight at 380 K. Subsequently, each precursor powder was placed in an alumina boat and inserted into another horizontal quartz-tube furnace (different from that used for the synthesis of Ti_4O_7). The tube was slowly evacuated, purged with N_2 gas, then the powder samples were heated from room temperature to various temperatures, T , at a rate of 10 K min^{-1} and maintained for 2 h. Then the samples were 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. Note that some solid by-products became attached to the inner wall of the quartz tube during pyrolysis. Such by-products can stop the gas flow if they block the narrow opening of the quartz tube, and thus can be dangerous. We used a long quartz tube with a length that was more than three times longer than the

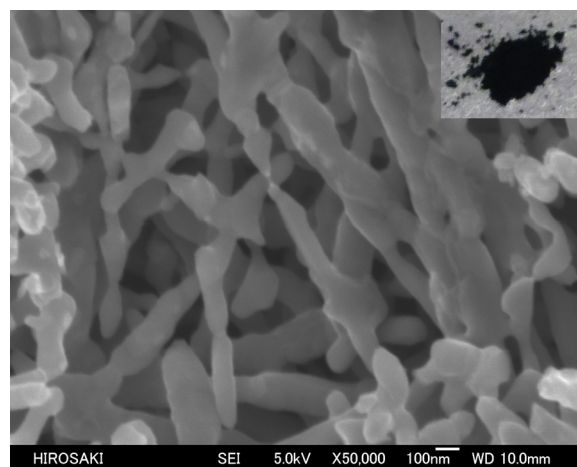


Fig. 1. FE-SEM image of the Ti_4O_7 fibers and their photograph (inset).

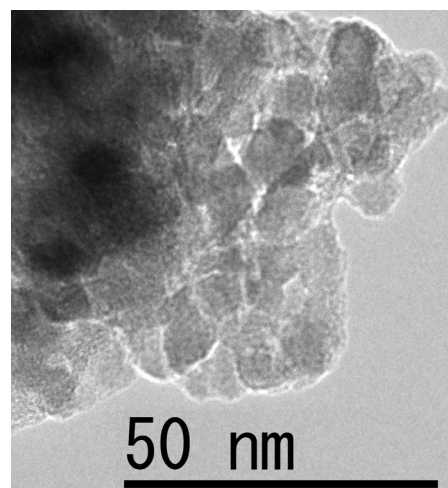


Fig. 2. TEM image of TiO_xN_y catalyst prepared by pyrolysis at 1273 K for 2 h under flowing N_2 gas. The mass ratio (R) of Ti_4O_7 to TiF_4 -derived TiO_2 was 1.

heating zone to allow sufficient space for the accumulated by-products inside the tube and avoid blockage. After pyrolysis and the ejection of the alumina boats, the by-products were easily removed by washing the tube with water.

2.3. Characterization

The morphology of the TiO_xN_y catalysts was investigated using a field emission-scanning electron microscope (JSM-7000F, JEOL, Akishima, Tokyo, Japan) and transmission electron microscope (JEM-2100, JEOL, Akishima, Tokyo, Japan). The electrical conductivity, σ , of Ti_4O_7 support and TiO_2 precursor were measured by a four-probe method with compressed pellets using a powder resistivity measurement system (MCP-PD51, Mitsubishi Chemical Analytech Co., Chigasaki, Kanagawa, Japan). The bulk crystal structures of the catalysts were analyzed using an X-ray diffractometer (M18XHF, Mac Science Co., Hachioji, Tokyo, Japan) with $\text{Cu-K}\alpha$ radiation generated at 30 kV and 50 mA (scan range 10 – 80° , step size 0.02° , and scan rate 2° min^{-1}). The surface crystal structures were analyzed using a Raman spectrometer (LabRAM HR Evolution, Horiba Co., Kyoto, Kyoto, Japan) with a 532-nm (visible) or 325-nm (UV) laser. The chemical states of the catalysts were determined using X-ray photoelectron spectroscopy (Quantera SXM, ULVAC-PHI, Inc., Chigasaki, Kanagawa, Japan) with an Al-

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