Catalytic Activity of Partially Oxidized Transition-metal Carbide–Nitride for Oxygen Reduction Reaction in Sulfuric Acid

Yoshiro Ohgi,* Akimitsu Ishihara, Yohei Shibata, Shigenori Mitsushima, and Ken-ichiro Ota
Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501

(Received February 28, 2008; CL-080229; E-mail: ken-ota@ynu.ac.jp)

In order to commercialize polymer electrolyte fuel cells (PEFCs) widely, partially oxidized transition-metal carbide–nitride (TM-C–N; TM = Ti, Zr, and Ta) have been investigated as new cathodes without platinum. The specimens were prepared by the electrophoretic deposition of the transition-metal carbide–nitride on titanium plate and were heat-treated at 1000 °C under flowing 2%-H_2/N_2 gas containing ca. 0.25% oxygen. Partially oxidized Ta-based catalysts had highest catalytic activity, followed by Ti- and Zr-based catalysts.

Polymer electrolyte fuel cells (PEFCs) are expected as an alternative to conventional combustion engines for transportation, residential, and portable applications owing to their high efficiency of energy conversion, low pollutant emission, and high power density. There are, however, some technological and economical problems before the commercialization of PEFCs. One of the technological problems is a large overpotential of oxygen reduction reaction, though platinum is utilized as an electrocatalyst. The large overpotential of the oxygen reduction reaction should be reduced to obtain high energy efficiency. One of the economical problems is the high cost of platinum catalysts due to the limitation of its amount of resources. Although many attempts have been made to reduce platinum usage, the cost of electrodes still remains high.[1] Therefore, development of new cathode catalysts without platinum is vital.

We have mainly studied the stability and electrocatalytic activity for the oxygen reduction reaction of group 4 and 5 transition-metal oxide and oxynitride thin films prepared by reactive sputtering.[2,3] However, in case of powder sample, a sufficient reproducibility of the electrochemical measurements was not obtained because electrical contact between the oxides and oxynitrides, and the current collector was poor owing to their low electric conductivity. We found that an electrophoretic deposition of Ta_3N_5 powder using a titanium plate and partial oxidation treatment gave a sufficient reproducibility.[4] In this study, we applied the electrophoretic deposition and heat treatment to some transition-metal carbide–nitride powders (TM-C–Ns) to compare the catalytic activity for the oxygen reduction reaction with high reproducibility. In this paper, TM represents Ti, Zr, and Ta.

A mixture of TM oxides and carbon powder was heat-treated at 1600–1800 °C under nitrogen atmosphere to produce the TM-C–N powders used as starting materials. A TM-C–N (100 mg) and iodine (20 mg) were dispersed in 50 cm^3 of acetone. Each TM-C–N powder was electrophoretically deposited on a Ti plate ($10 \times 10 \times 0.4\,mm^3$) by applying of 150 V for 200 s.[5] Each TM-C–N on Ti plate was partially oxidized with heat treatment at 1000 °C for an hour under flowing 100 $cm^3 \cdot min^{-1}$ of 2%-H_2/N_2 gas mixture containing ca. 0.25% oxygen in a tube furnace (Koyo Thermo Systems).

All TM-C–N/Ti plates with and without heat treatment were characterized using an X-ray diffractmeter (XRD; XRD-6000, Shimadzu) with Cu Kα radiation in the range from 10 to 90°. The ionization potential of partially oxidized Ta-C–N was measured using a photoelectron spectrometer surface analyzer (model AC-2, Riken Keiki).[6]

All electrochemical experiments were conducted in a three-electrode glass cell under nitrogen and oxygen atmosphere in 0.1 $mol \cdot dm^{-3}$ H_2SO_4 at 30 °C using a potentiostat PS08 (Toho Technical Research). A working, a reference, and a counter electrode were TM-C–N/Ti with heat treatment, a reversible hydrogen electrode (RHE), and a carbon plate, respectively. Slow scan voltammetry with a scan rate of 5 $mV \cdot s^{-1}$ from 0.05 to 1.0 V was performed under N_2 and O_2 atmosphere to evaluate the catalytic activity for the oxygen reduction reaction. A current difference between under O_2 and under N_2 might be due to the oxygen reduction reaction (i_{ORR}). The current density was based on the geometric surface area of the working electrode.

Figure 1 shows the XRD patterns of TM-C–N/Ti with (B) and without heat treatment (A). An intensity of each specimens was normalized using the maximum intensity of each pattern, and the peaks were identified using the ICDD database. As shown in Figure 1a, all of the TM-C–N/Ti without heat treatment showed carbide–nitride peaks. Both transition-metal carbides (TM-Cs) and transition-metal nitrides (TM-Ns) have the same crystalline structure (rock-salt type) and form a complete solid solution. Each peak shifts to a higher angle with the increase in nitrogen content, which is known as the Vegard's law. In this paper, the compounds with the XRD peaks which existed between TM-C and TM-N were expressed as TM-C–N. Ti-C–N/Ti without heat treatment had hexagonal Ti peaks (ICDD #44-1294) which was due to the substrate, indicating that the amount of the Ti-C–N electrodeposited on Ti was lower than that of the Ta-C–N and Zr-C–N even though the condition of the electrophoretic deposition was the same. All of the TM-C–N/Ti with heat treatment had tetragonal TiO_2 peaks (ICDD #21-1276). These TiO_2 peaks were probably due to the oxidation of the surface of the Ti substrate with which the catalyst powder was imcompletely covered. Ti-C–N/Ti and Ta-C–N/Ti with heat treatment had both carbide–nitride and oxide (tetragonal TiO_2: ICDD #21-1276, orthorhombic Ta_2O_5: ICDD #25-0922) peaks. This result indicated that the oxidation was incomplete and that the partially oxidized Ti-C–N and Ta-C–N powder were obtained on the Ti plate, because the TM-C–N peaks were remained. On the other hand, only oxide peaks was observed in the patterns of the Zr-C–N/Ti with heat treatment. Zr-C–N was oxidized to form ZrO_2 (ICDD #50-1089).

Figure 2 shows the Tafel plots for the oxygen reduction reaction on the (partially) oxidized Ti-C–N/Ti, Zr-C–N/Ti, and Ta-C–N/Ti in 0.1 M H_2SO_4 at 30 °C. The partially oxidized Ta-C–N/Ti had a highest activity toward the oxygen reduction

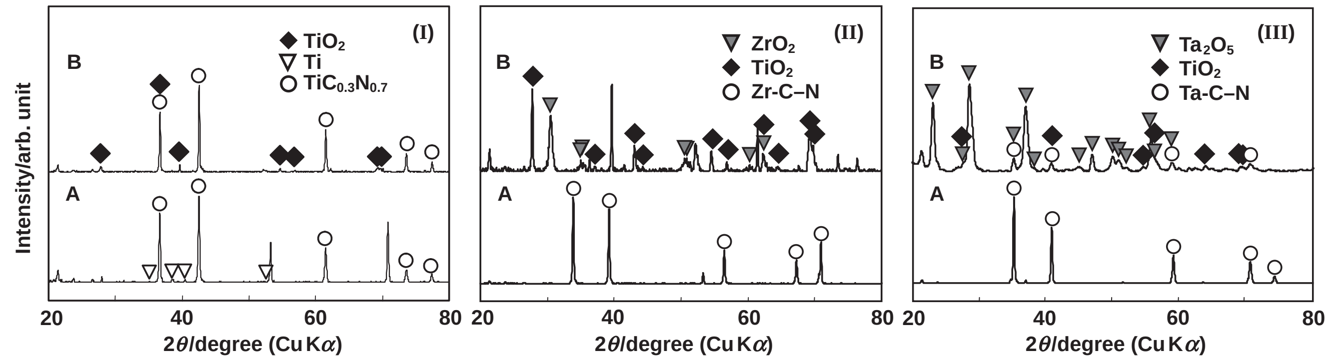

Figure 1. XRD patterns of (I) Ti-C–N/Ti, (II) Zr-C–N/Ti, and (III) Ta-C–N/Ti without heat treatment (A); with heat treatment at 1000 °C for 1 h in 2%H_2–0.25%O_2–N_2 (B).

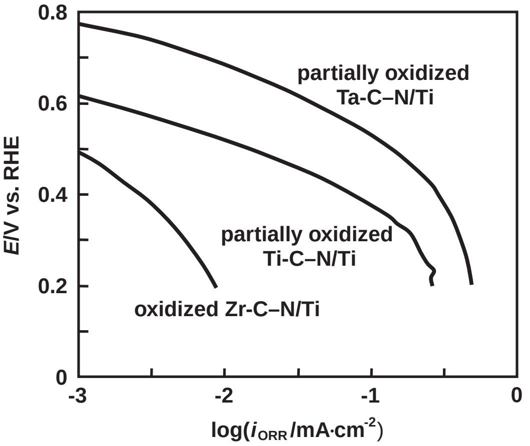

Figure 2. Tafel plots of Ti-C–N/Ti, Zr-C–N/Ti, and Ta-C–N/Ti with heat treatment for the ORR in 0.1 M H_2SO_4 at 30 °C under N_2 and O_2. Scan rate: 5 mV·s^{-1}, scan range: 0.2–1.0 V.

reaction, followed by the partially oxidized Ti-C–N/Ti and the oxidized Zr-C–N/Ti. The onset potential on the partially oxidized Ta-C–N for the oxygen reduction reaction (at $i_{\mathrm{ORR}} = -0.2\,\mu\mathrm{A\,cm^{-2}}$) was ca. 0.81 V vs. RHE. This value was higher than that of TaO_xN_y/Ti, i.e., 0.75 V. Therefore, the partially oxidized Ta-C–N/Ti had higher catalytic activity for the oxygen reduction reaction than TaO_xN_y/Ti. The Tafel slopes of the partially oxidized Ta-C–N/Ti and Ti-C–N/Ti were ca. -90 mV·decade^{-1} in the range of i_{ORR} from 10^{-3} to 10^{-2} mA·cm^{-2}. On the other hand, the Tafel slope of the oxidized Zr-C–N/Ti was approximately -300 mV·decade^{-1}, which was much larger than that of Ta and Ti-based compounds. The effect of the Ti plate used as a substrate on the catalytic activity for the oxygen reduction reaction needed to be considered because TiO_2 plate had some catalytic activity for the oxygen reduction reaction.[7] However, the catalytic activity of TiO_2 plate was lower than that of the partially oxidized Ta-C–N/Ti, and the contact area between the Ti substrate and the electrolyte was very small.[4] Therefore, the contribution of Ti substrate to the oxygen reduction reaction current of the partially oxidized Ta-C–N/Ti was considered to be negligible.

The ionization potentials of the starting material, Ta-C–N, and partially oxidized Ta-C–N/Ti were 4.92 and 5.14 eV, respectively. The ionization potential of the Ta_2O_5 is 7.83–7.93 eV.[8] The ionization potential of the partially oxidized Ta-C–N was no less than ca. 2.7 eV lower than that of Ta_2O_5. Henrich et al. reported that the ionization potential of TiO_2(110) decreased with increasing the density of surface defects.[8] Similar behavior is expected to occur in the case of the partially oxidized Ta-C–N. The partially oxidized Ta-C–N probably had some oxide ion vacancies on the surface. Many researches revealed that the presence of surface defect sites was required to adsorb the oxygen molecules on the surface of the oxides,[9,10] which was the first step to proceed with the oxygen reduction reaction. Therefore, the partially oxidized Ta-C–N with some surface defects had a definite catalytic activity for the oxygen reduction reaction.

Considering the catalytic activity for the oxygen reduction reaction, the heat-treated Ta-C–N/Ti has highest performance among the heat-treated Ti-C–N/Ti and Zr-C–N/Ti. The Ta-C–N/Ti was partially oxidized during the heat treatment by the trace amount of oxygen. The catalytic activity of the partially oxidized Ta-C–N/Ti might be increased by controlling the partial oxidation state.

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