

Oxygen Reduction Reaction Activity of Nitrogen-Doped Titanium Oxide in Acid Media

Mitsuharu Chisaka,¹ Akimitsu Ishihara,² Kazuaki Suito,² Ken-ichiro Ota² and Hirokazu Muramoto³

¹Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan

²Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan

³Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku, Toyohashi, Aichi 441-8580, Japan

Groups 4 and 5 metal-oxide compounds have been regarded as promising candidates for polymer electrolyte fuel cell (PEFC) cathode catalysts because they are insoluble in acid media [1]. One of the synthesis routes, oxidation of metal carbonitrides, produced the highest oxygen reduction reaction (ORR) activity levels among catalysts developed by Ishihara and Ota et al. [2]. The surfaces of these carbonitride-derived catalysts were almost free from nitrogen and it was revealed that oxygen defects were essential for achieving high ORR activity [2]. Recently, using several heat-treatment steps under H₂/Ar (5% H₂) gas, NH₃ gas, or both, Chisaka et al. showed that carbon-supported hafnium oxide with oxygen defects was active toward ORR; however, doping of nitrogen atoms into the oxides was necessary for maximizing the activity [3]. These findings from two different groups suggest that the doping of nitrogen into metal-carbonitride-derived, almost nitrogen-free metal-oxide catalysts should increase their ORR activities. We report here our collaboration results: partially oxidized titanium carbonitride catalysts were doped for the first time with nitrogen by heating them under NH₃ gas to increase their ORR activity.

Titanium carbonitride powders with the elemental composition TiC_{0.82}N_{0.23}O_{0.06} (Japan New Metals Co., Japan) were oxidized by heating at 1173 K for 4 h under a mixed gas containing 2% H₂, 0.5% O₂, and 97.5% N₂. The composition of the resulting catalysts was TiC_{0.21}N_{0.01}O_{1.88}. They were further heated at various temperature, *T*, for 3 h under NH₃ gas. The effects of the *T* on ORR activity were investigated by obtaining cyclic voltammograms (CVs). The catalyst morphologies, bulk and surface crystal structures, and surface chemical states were evaluated using field-emission transmission electron microscopy (FE-TEM), X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) to clarify the key factors affecting ORR activity.

Figure 1 shows FE-TEM images of as-synthesized TiC_{0.21}N_{0.01}O_{1.88}. Black plates and small gray spherical particles aggregated between the plates are observed in Fig. 1(i), indicating that at least two different phases were present in the TiC_{0.21}N_{0.01}O_{1.88} catalyst. The size of the black plates varied between ~20 and 200 nm. Energy-dispersive X-ray spectroscopy analyses revealed that titanium atoms were present and absent in the black plates and gray aggregated particles, respectively. Only carbon atoms were observed in the gray particles. A high-magnification FE-TEM image of the black plates is shown in Fig. 1(ii). They were well crystallized and the lattice distance was 3.2 Å.

Figure 2 shows the XRD patterns of as-synthesized TiC_{0.21}N_{0.01}O_{1.88} and TiC_{0.21}N_{0.01}O_{1.88} heat-treated at six *T* values, ranging from 773 to 1273 K under NH₃ gas. A single tetragonal rutile-TiO₂ phase was observed for as-synthesized TiC_{0.21}N_{0.01}O_{1.88} and TiC_{0.21}N_{0.01}O_{1.88} NH₃-treated at *T* < 873 K. The lattice

distance calculated from the strongest peak, the rutile (110) plane of the XRD pattern of the as-synthesized TiC_{0.21}N_{0.01}O_{1.88}, was 3.25 Å, which agrees well with the results obtained from the black plates in the FE-TEM image shown in Fig. 1(ii). A mixture of the tetragonal rutile-TiO₂ phase and a cubic TiN phase was observed in TiC_{0.21}N_{0.01}O_{1.88} catalysts NH₃-treated at 873 K ≤ *T* ≤ 1073 K, whereas those NH₃-treated at *T* ≥ 1173 K exhibited only the cubic TiN phase.

Figure 3 shows the ORR mass activity versus potential [(*I*_O - *I*_N)*m*_T⁻¹ - *E*] curves for as-synthesized TiC_{0.21}N_{0.01}O_{1.88} and TiC_{0.21}N_{0.01}O_{1.88} heat-treated at six different *T* values under NH₃ gas. The as-synthesized TiC_{0.21}N_{0.01}O_{1.88} showed a clear (*I*_O - *I*_N)*m*_T⁻¹ at a high *E* of ~0.8 V. The activity increased with increasing *T* up to 1073 K, but decreased with further increases in *T*. Raman spectra and XPS analyses revealed that the improved activity observed in the *T* range of 873–1073 K shown in Fig. 3(c)–(e) was not attributed to the electronic conductivity of graphitic layers, but to the oxygen defects and/or doped nitrogen in rutile-TiO₂ lattice.

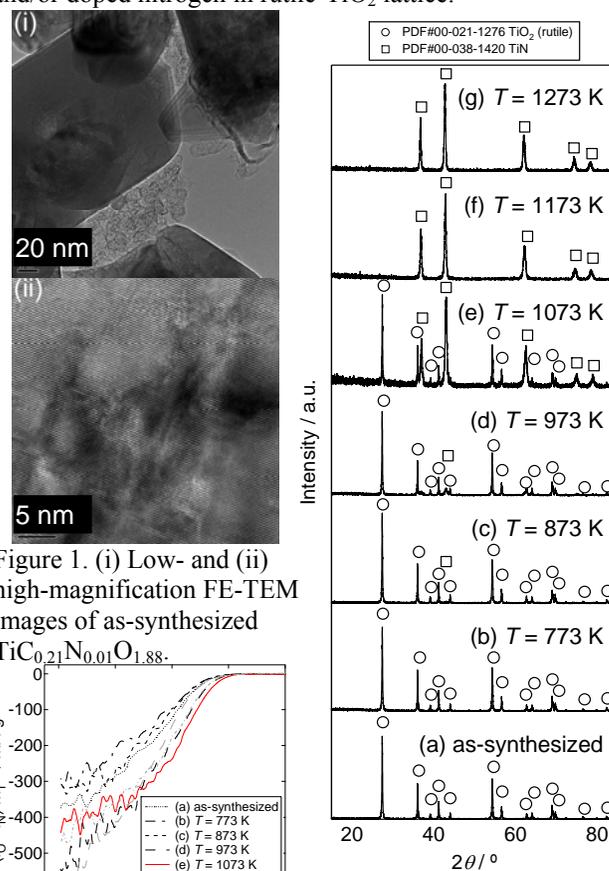


Figure 1. (i) Low- and (ii) high-magnification FE-TEM images of as-synthesized TiC_{0.21}N_{0.01}O_{1.88}.

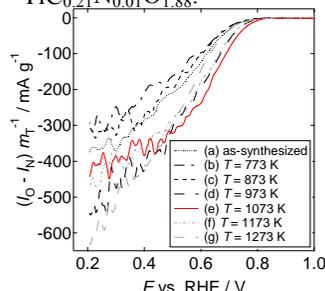


Figure 3. (*I*_O - *I*_N)*m*_T⁻¹ - *E* curves of catalysts (a)–(g) shown in Figure 2. The scans were performed in 0.1 M H₂SO₄ at 5 mV s⁻¹.

References

1. A. Ishihara, Y. Ohgi, K. Matsuzawa, S. Mitsushima, and K. Ota, *Electrochim. Acta*, **55**, 8005 (2010).
2. K. Ota, Y. Ohgi, K. D. Nam, K. Matsuzawa, S. Mitsushima, and A. Ishihara, *J. Power Sources*, **196**, 5256 (2010)
3. M. Chisaka, Y. Suzuki, T. Iijima, Y. Ishihara, R. Inada, and Y. Sakurai, *ECS Electrochem. Lett.*, **1**, F4 (2012).

Acknowledgments

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