

Development of Titanium Oxycarbonitride (TiCNO)-Based Electrocatalyst for Oxygen Reduction Reaction with High Activity and Stability

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With their efficiency, high power density, and low/zero emissions, proton exchange membrane fuel cells (PEMFCs) are recognized as promising energy converting system. However, high cost and insufficient durability currently hinder their commercialization. Especially, one of the major barriers is the high cost and low stability of platinum (Pt)-based catalysts [1]. Thus, developing alternative catalysts and/or Pt reducible catalysts with low cost and high stability has been strongly required for the commercialization of PEMFCs. In the effort to reduce the cost of PEMFCs, we have been developing novel non-noble metal catalysts and these composites with small amount of Platinum for alternative and/or Pt reducible PEMFCs catalysts. In this study, we synthesized novel titanium (Ti) based oxycarbonitride (TiCNO) catalyst analogues and tested their oxygen reduction reaction (ORR).

Sample 1 was synthesized by following; first, titanium carbonitride (TiCN) was synthesized by calcination of titanium carbide (TiC) and titanium nitride (TiN) at 1600 °C in nitrogen atmosphere. Then, the obtained powders were oxidized in the mixed gas of nitrogen, oxygen and hydrogen at 900 °C in order to synthesize TiCNO catalyst finally. Sample 2 was synthesized by following: titanium tetraisopropoxide was mixed with iron(II) acetate, acetylacetone and glycine in acetic acid aqueous solution and then evaporated. The obtained powder was calcinated in the mixed gas of hydrogen and nitrogen at 900 °C to synthesize iron-doped TiCNO.

Figure 1 shows the polarization curves of sample 1, sample 2 and Pt/C. Both of the TiCNO-based catalyst showed catalytic activity for ORR. Moreover, sample 2 had higher activity for ORR than sample 1 to follow Pt/C. First reason for higher activity with sample 2 is assumed to be the higher BET surface area. BET surface area of Sample 1 and sample 2 were 8.4 m²/g and 173.2 m²/g, respectively which indicated lower synthesis temperature caused higher BET surface area. Second reason for higher ORR activity is assumed to be electron conductivity. These samples and TiO₂ with rutile structure as reference was examined by the X-ray diffraction (XRD) measurements and the X-ray adsorption spectroscopy (XAFS). All of XRD patterns of samples (not shown) were identified as rutile structure. Figure 2 represents the X-ray adsorption near-edge structure (XANES) spectra of Ti K-edge for our samples and TiO₂. Pre-edge energies for both of our samples were lower than that for TiO₂ which indicated that the oxidation state was lower than Ti(IV) [2]. Titanium oxide analogues were reported to have high electron conductivity with defects of oxygen which caused the lower oxidation state than Ti(IV) [3]. Therefore, our samples are implied to have high ORR activity due to have high electron conductivity. In particular, catalytic activity of Sample 2 is assumed to be improved by enhanced electron conductivity on the rutile

type TiCNO structure doped with iron. Moreover, we have been also investigating TiCNO catalyst combined with a small amount of Pt to reduce the amount of Pt usage. Its catalytic activity towards ORR and stability in MEA test was found to be superior to commercial 50%Pt/C. These results indicate that practical use of this catalyst could be expected.

As non-noble metal electrocatalyst for the cost reduction of PEMFCs, We have been developing a novel titanium based oxycarbonitride (TiCNO) based catalyst for ORR. It was found that the enlargement of BET surface area and the addition of iron into the TiCNO dramatically promoted the ORR catalytic activity of TiCNO. It was also found that a possibility for reduction of the amount of Pt usage as a composite of TiCNO-based catalyst with small amount of Pt. We believe that the TiFeCNO and its composite with Pt for the ORR could be a promising non-noble metal and Pt-reducible catalyst for the commercialization of PEMFCs.

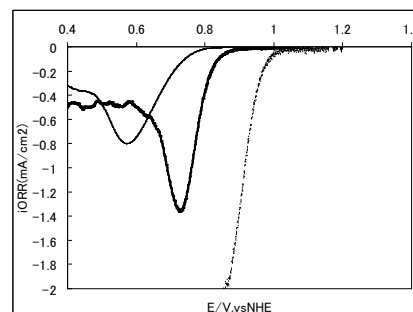


Figure 1. Polarization curve of sample 1 (solid line), sample 2 (bold line) and commercial 50%Pt/C (dashed line) in 0.5M H₂SO₄ under saturated oxygen at 30 °C. Potential scan rate: 5 mV/s. The current density was normalized to the geometric area. Reference electrode is normal hydrogen electrode (NHE).

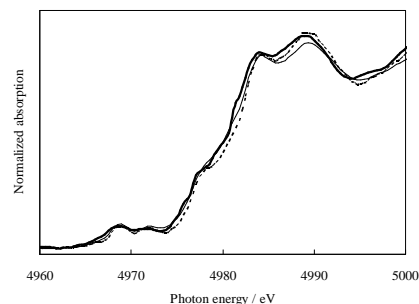


Figure 2. Comparison of XANES spectra of Ti K edge of sample 1 (solid line), sample 2 (bold line) and commercial TiO₂ (dashed line).

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