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Catalytic Activity of Zirconium Oxynitride Prepared by Reactive Sputtering for ORR in Sulfuric Acid

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Zirconium oxynitride (ZrO_xN_y) prepared by the reactive sputtering method under O_2 and N_2 atmosphere was evaluated as a nonplatinum cathode catalyst for polymer electrolyte fuel cells. The ZrO_xN_y prepared at $p_{Ar} = 0.886$ Pa, $p_{N_2} = 0.41$ Pa, and $p_{O_2} = 1.7$ mPa with a substrate temperature of 800°C during the film formation had a superior catalytic activity for the oxygen reduction reaction (ORR) in sulfuric acid. The onset potential for the ORR had a maximum of 0.8 V vs a reversible hydrogen electrode. The thin-film X-ray diffraction analysis and ionization potential measurement revealed that the ZrO_xN_y with a high catalytic activity for the ORR contained the Zr_2ON_2 crystalline structure.
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Polymer electrolyte fuel cells (PEFCs) are expected as power sources for residential cogeneration systems and transportation applications due to their high theoretical energy efficiency and lower emission of pollutants. However, PEFCs have some serious problems to be solved before their commercialization. In particular, a large overpotential of the oxygen reduction reaction (ORR) must be reduced in order to obtain a higher energy efficiency. A large amount of platinum is generally used as a cathode catalyst in present PEFCs to decrease the overpotential of the ORR. However, Pt is expensive and its resources are limited, so that Pt usage will be limited for future commercialization of PEFCs. Many methods have been studied to reduce use of the Pt catalyst, such as a greater dispersion of Pt particles and/or alloying with transition metals.[1,2] However, because the dissolution and deposition of highly dispersed Pt particles proceeds during long-term operation,[3] a drastic reduction of Pt usage would be difficult. Therefore, development of a new nonplatinum catalyst is strongly recommended.

We have examined the applicability of transition metal oxynitrides to the cathode catalysts.[4-6] In particular, zirconium oxynitride films prepared using the reactive sputtering method had a definite catalytic activity for the ORR. In addition, as the heating temperature of a substrate during the sputtering increased to 800°C, the catalytic activity for the ORR increased.[4] In this study, the dependence of the catalytic activity of ZrO_xN_y prepared by reactive sputtering at 800°C for the ORR on the gas atmosphere during the sputtering was investigated.

Experimental

Thin-film specimens were prepared using reactive sputtering and were expressed as ZrO_xN_y in this study. The ZrO_xN_y thin films were prepared on the surface of a substrate (a polished glassy carbon rod with $\phi = 5.2$ mm, Tokai Carbon) with radio frequency magnetron sputtering (MUE-ECO-EV, Ulvac). The metal Zr (99.9%, Furuchi Chemical) was used as a target. The chamber was evacuated to less than 1.0×10^{-3} Pa, and then argon, oxygen, and nitrogen gases were introduced. The N_2 flow rate was changed from 0 to 29 $cm^3\ min^{-1}$, and the O_2 flow rate was changed from 0.01 to 0.30 $cm^3\ min^{-1}$. The Ar flow was balanced and the total gas flow rate was 29 $cm^3\ min^{-1}$. The heating temperature of the substrate was always kept at a constant temperature of 800°C during sputtering. Partial pressures of N_2 (p_{N_2}) and O_2 (p_{O_2}) were calculated by multiplying the ratio of the flow rate of each gas and the total pressure in the chamber. A sputtering power and a sputtering time were fixed at 150 W and 80 min, respectively.

The electrochemical measurements were carried out using a three-electrode cell at 30°C in 0.1 M H_2SO_4. A reversible hydrogen electrode (RHE) and a carbon plate were used as a reference and a counter electrode, respectively. The electrode potential was referred to the RHE in the present study. In order to evaluate the catalytic activity for the ORR, a slow scan voltammetry (SSV) was performed under N_2 and O_2 atmospheres. The scan rate and the potential range of the SSV were 5 mV s^{-1} and 0.2–1.0 V. Current density was based on the geometric surface area of the working electrode. The current difference between O_2 and N_2 corresponds to the oxygen reduction current (i_{ORR}). The electrode potential at the current density of the ORR of -0.2 μA cm^{-2} was defined as an onset potential of the ORR, E_{ORR} (Fig. 1), to evaluate the catalytic activity. Slow scan cyclic voltammetry was also performed under a N_2 atmosphere to examine the electrochemical stability of the electrode. The scan rate and potential range were 5 mV s^{-1} and 0.2–1.0 V, respectively.

The thickness of the films was determined by the cross-sectional transmission electron microscopy (TEM) images of the films. The cross-sectional TEM images revealed that the film thickness was ca. 70 nm. Therefore, the crystalline structure was analyzed using thin-film X-ray diffraction (XRD; X'Pert PRD MRD, PANalytical). The angle of the X-ray incidence was kept constant at 0.40°. The chemical composition of ZrO_xN_y was analyzed using Rutherford backscattering spectrometry (RBS; 1 MV Tandem Accelerator, NEC Corp.). The ionization potential was measured using a photoelectron spectroscopic analyzer (AC-2, Riken Keiki).

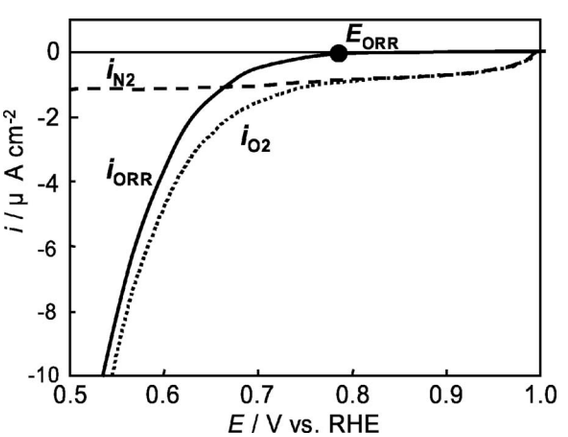

Figure 1. SSVs of ZrO_xN_y under a N_2 (i_{N_2}) or O_2 (i_{O_2}) atmosphere and the potential vs ORR current (i_{ORR}) curve in 0.1 M H_2SO_4 at 30°C with a scan rate of 5 mV s^{-1}.

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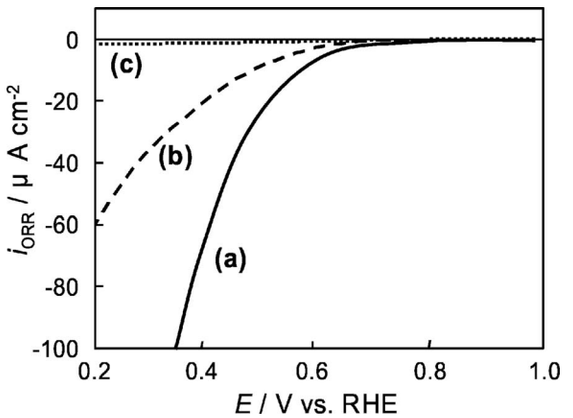

Figure 2. Potential vs i_{ORR} curves of the ZrO_xN_y prepared under different p_{N_2} and p_{O_2} in 0.1 M H_2SO_4 at 30°C with a scan rate of 5 mV s^{-1}: (a) p_{N_2}/p_{O_2} = 240, (b) p_{N_2}/p_{O_2} = 2400, and (c) p_{N_2}/p_{O_2} = 0.

Results and Discussion

Figure 2 shows the potential i_{ORR} curves of ZrO_xN_y prepared under different p_{N_2} and p_{O_2}. As shown in Fig. 2a, when the N_2 and O_2 flow rates were 24 and 0.1 cm^3 min^{-1}, (p_{Ar} = 0.086 Pa, p_{N_2} = 0.41 Pa, p_{O_2} = 1.7 mPa), where the gas ratio was p_{N_2}/p_{O_2} = 240. The i_{ORR} was started at ca. 0.8 V, indicating that the ZrO_xN_y prepared under p_{N_2}/p_{O_2} = 240 had a high catalytic activity for ORR. When the O_2 flow rate was one-tenth of that at (a), that is, p_{N_2}/p_{O_2} = 2400, the catalytic activity was slightly lower, as shown in Fig. 2b. The i_{ORR} of the ZrO_xN_y prepared under Ar + O_2 without N_2, namely, p_{N_2}/p_{O_2} = 0, hardly showed the ORR activity as shown in Fig. 2c. The results indicated that the catalytic activity of ZrO_xN_y for the ORR significantly depended on the gas atmosphere during the sputtering, and the presence of N_2 in the atmosphere is very important for the ORR activity.

Following these results, the relationship between the catalytic activity for the ORR and p_{N_2} or p_{O_2} during the sputtering was investigated. Figure 3a shows the relationship between the onset potential (E_{ORR}) and the O_2 partial pressure during sputtering with an N_2 flow rate of 10, 24, and 29 cm^3 min^{-1}. The E_{ORR} had a maximum of ca. 0.78 V at approximately 2 mPa of p_{O_2}. Therefore, the existence of a moderate amount of O_2 during the film formation was essential to enhance the catalytic activity for the ORR. Figure 3b shows the relationship between E_{ORR} and N_2 partial pressure during sputtering with an O_2 flow rate from 0.01 to 0.30 cm^3 min^{-1}. The E_{ORR} value in this figure was saturated at ca. 0.7 V above 0.2 Pa of p_{N_2}. In contrast, when no N_2 was introduced in the chamber, the E_{ORR} was 0.2–0.5 V, indicating that the ZrO_xN_y prepared under no N_2 had a poor catalytic activity. The existence of N_2 during the sputtering was required to increase the catalytic activity, and the p_{N_2} above 0.2 Pa slightly affected the catalytic activity for the ORR. Thus, the ZrO_xN_y thin films, which were prepared by reactive sputtering under N_2 and a moderate O_2 atmosphere, have high catalytic activities for the ORR. These results imply that both the nitridation and oxidation of Zr are necessary to produce the catalytic activity for ORR. However, the E_{ORR} of the platinum-supported carbon catalyst was ca. 1.05 V. The catalytic activity of the ZrO_xN_y films for the ORR was insufficient. Therefore, the catalytic activity of the ZrO_xN_y films should be enhanced by optimization of the catalyst design.

Figures 4a-c show the thin-film XRD patterns of ZrO_xN_y films prepared under conditions corresponding to Fig. 2a-c, respectively. As shown in Fig. 4a, the ZrO_xN_y with the highest catalytic activity among all specimens prepared under these experimental conditions showed the crystal structure of Zr_2ON_2 (JCPDS 50–1170). This result indicated that at a flow ratio of p_{N_2}/p_{O_2} = 240, the nitridation as

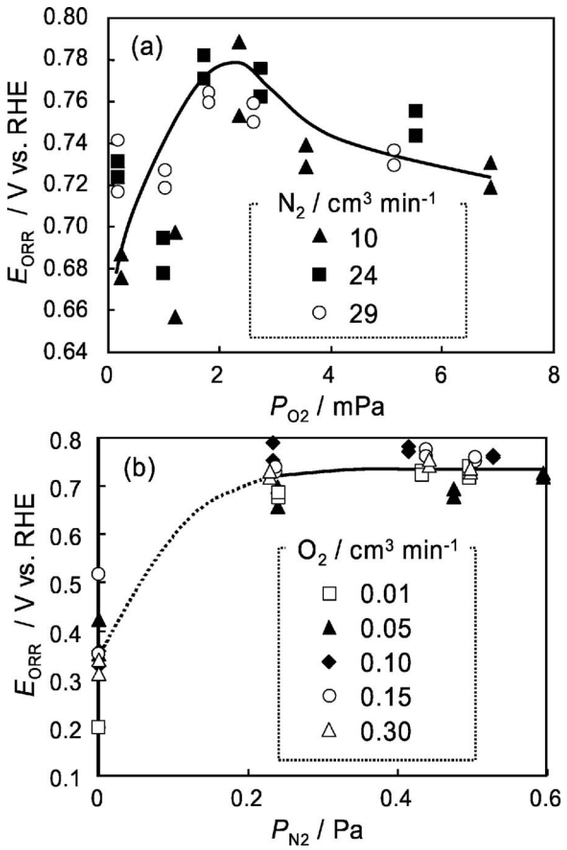

Figure 3. Relationships between the E_{ORR} and (a) p_{O_2} or (b) p_{N_2} in 0.1 M H_2SO_4 at 30°C. Scan rate 5 mV s^{-1}.

well as the oxidation of Zr took place to form Zr_2ON_2. The ZrO_xN_y with a slightly lower ORR activity, which was prepared at p_{N_2}/p_{O_2} = 2400, had ZrN (JCPDS 35–0753) and $Zr_7O_8N_4$ (JCPDS 50–1172) structures as shown in Fig. 4b. The ratio p_{N_2}/p_{O_2} was 10 times larger; therefore, the nitridation proceeded more than the oxidation to form ZrN. However, O_2 is so much more active than N_2 that the oxynitride, $Zr_7O_8N_4$, formed as well as ZrN. Liu et al. prepared the ZrO_xN_y/C powder by the ammonolysis of carbon-supported zirconia at 950°C. They revealed that the ZrO_xN_y/C consisted of the β-phase $Zr_7O_8N_4$, and the monoclinic phase ZrO_2 had a definite catalytic activity for the ORR.[7] However, our results suggested that the ZrO_xN_y having a Zr_2ON_2 structure on the surface had a higher catalytic activity for the ORR than that having a $Zr_7O_8N_4$ structure. As shown in Fig. 4c, when no N_2 gas was included in the sputtering atmosphere, i.e., p_{N_2}/p_{O_2} = 0, two kinds of peaks were observed. One was identified as ZrO (JCPDS 20–0684), and another peak lay between the peaks of metallic Zr (JCPDS 05–0665) and $ZrO_{0.35}$ (JCPDS 17–0385). This pattern indicated that the supply of O_2 was not enough to form the Zr oxide, although O_2 was included in the sputtering atmosphere. Following the catalytic activity shown in Fig. 2c, both the metallic Zr, ZrO, and $ZrO_{0.35}$ had poor catalytic activities for ORR. Thus, we found that the ZrO_xN_y with Zr_2ON_2 crystalline structures, which were prepared under N_2 and moderate O_2 atmosphere, had a superior catalytic activity for ORR.

RBS analysis was performed to confirm the formation of Zr_2ON_2. The Zr, O, and N atomic percentages of the ZrO_xN_y, which were identified as Zr_2ON_2 by the thin-film XRD, were 36, 25, and 39, respectively. These percentages are close to the theoretical values of Zr_2ON_2 where the percentages of Zr, O, and N are 40, 20, and 40, respectively. The crystallization of the film was incomplete;

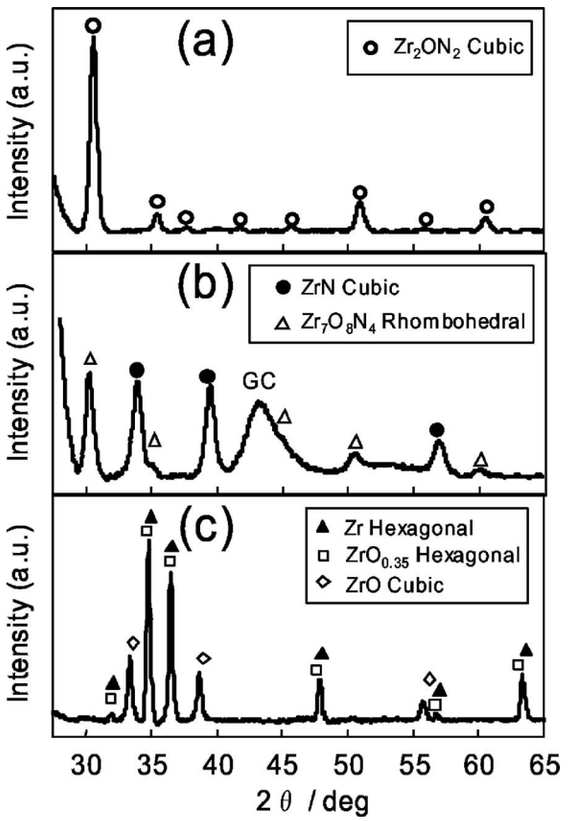

Figure 4. Thin-film XRD patterns of ZrO_xN_y prepared at (a) p_{N_2}/p_{O_2} = 240, (b) p_{N_2}/p_{O_2} = 2400, and (c) p_{N_2}/p_{O_2} = 0.

therefore, the O content was a little larger than that of the theoretical value. Both the thin-film XRD and RBS analyses supported the formation of Zr_2ON_2 in the thin film with a high catalytic activity.

Figure 5 shows the slow scan cyclic voltammograms (SSCVs) in the steady state of the ZrO_xN_y films prepared at conditions corresponding to Fig. 2a-c under a N_2 atmosphere. The SSCV of ZrO_xN_y, which was prepared at p_{N_2}/p_{O_2} = 240, had no specific peaks. In addition, the anodic electric charge was almost equal to the cathodic one. These results indicated that the ZrO_xN_y with Zr_2ON_2 structures

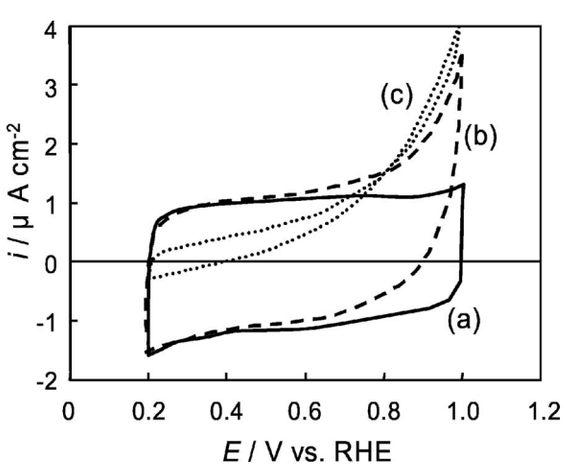

Figure 5. Steady-state SSCVs of ZrO_xN_y under a N_2 atmosphere in 0.1 M H_2SO_4 at 30°C with a scan rate of 5 mV s^{-1}: (a) p_{N_2}/p_{O_2} = 240, (b) p_{N_2}/p_{O_2} = 2400, and (c) p_{N_2}/p_{O_2} = 0.

had high electrochemical stability in 0.1 M H_2SO_4 at 30°C. Large anodic currents were observed at the SSCV of ZrO_xN_y prepared at p_{N_2}/p_{O_2} = 2400 (ZrN and $Zr_7O_8N_4$ by thin-film XRD) and ZrO_xN_y prepared at p_{N_2}/p_{O_2} = 0 (metallic Zr and zirconium oxides with low oxidation state of Zr by thin-film XRD). In particular, the metallic Zr, ZrO, and $ZrO_{0.35}$ were unstable in acid solution because the anodic current was observed even at the cathodic potential scan. Zirconium nitrides, Zr, ZrO, and $ZrO_{0.35}$, had poor electrochemical stabilities.

Both an adsorption of oxygen molecules and a desorption of water molecules are required to continue the ORR smoothly. When the oxidation state of Zr in the catalyst was close to the metallic state, that is, the Zr had a lower oxidation number, the interaction between Zr and oxygen was so strong that the oxygen stuck on the surface strongly and the desorption of the water molecules barely occurred. When the Zr had a higher oxidation number, the interaction was too weak for the adsorption of the O_2 molecules to proceed. Therefore, an intermediate oxidation number of Zr in the catalyst was suitable for the moderate interaction between the Zr and oxygen, and the ORR proceeded smoothly on the active site.

Mishima et al. have investigated the Zr_2ON_2 as a visible-light photocatalyst.[8] The bandgap of Zr_2ON_2 was 2.6 eV. Although the upper energy level of the electron in the valence band of Zr_2ON_2 was unknown, it was lower than −5.6 eV, because no oxygen gas evolved when the upper energy level was higher than −5.6 eV. That is, the ionization potential of the Zr_2ON_2 was expected to be higher than 5.6 eV. We measured the ionization potential of the ZrO_xN_y with Zr_2ON_2 structure using a photoelectron spectroscopic analyzer to estimate the electronic structure of the specimen. The ionization potential of the ZrO_xN_y with a Zr_2ON_2 structure was determined to be 5.06 eV. This value was lower than that expected on the Zr_2ON_2, 5.6 eV. In general, the ionization potential of the oxides decreases with an increase in the surface defect density.[9-12] The low ionization potential of the ZrO_xN_y suggested that although the ZrO_xN_y prepared using reactive sputtering had the Zr_2ON_2 structure, it had some surface defects which created the donor levels close to the edge level of the conduction band, that is, close to the Fermi level. The electrons in the donor level due to the surface defects probably participate in the ORR, although the structure of the defect was not clear.

Conclusions

We investigated the dependence of the catalytic activity of ZrO_xN_y prepared by reactive sputtering for the ORR on the gas atmosphere during film formation at a substrate temperature of 800°C. The ZrO_xN_y prepared at p_{Ar} = 0.886 Pa, p_{N_2} = 0.41 Pa, and p_{O_2} = 1.7 mPa had the highest catalytic activity, and the onset potential for the ORR was ca. 0.8 V vs RHE. The thin-film XRD analysis revealed that the ZrO_xN_y with the highest catalytic activity for the ORR had a Zr_2ON_2 crystalline structure. However, the ionization potential of ZrO_xN_y with a Zr_2ON_2 structure was 5.06 eV, which was lower than the expected value of Zr_2ON_2 (>5.6 eV). This result indicates that the Zr_2ON_2 structure with some surface defects could be very important toward production of a highly active catalyst for ORR.

Acknowledgments

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