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1   Introduction

Polymer electrolyte fuel cells (PEFCs) are expected to be as power sources for residential cogeneration systems and transportation applications due to their high theoretical energy efficiency and less emission of pollutants. However, PEFCs have some serious problems to be solved for their commercialization. In particular, a large overpotential of the oxygen reduction reaction (ORR) must be reduced in order to obtain 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 the Pt usage will be limited in the future commercialization of PEFCs. Many researches have been tried to reduce the use of 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 dispersion Pt particles proceeds during long-term operation [3], the drastic reduction of Pt usage would be difficult. Therefore, the development of a new non-platinum catalyst is strongly required.

We have reported that tungsten carbide with tantalum addition [4], tantalum oxynitride [5-8], zirconium oxide [9, 10], titanium oxide [11], zirconium oxynitride [12, 13], chromium carbonitride [14] and tantalum carbonitride [15] were stable in an acid solution and had a definite catalytic activity for the ORR.

In particular, we found that the partially oxidized $TaC_{0.58}N_{0.42}$ powder had a good catalytic activity for the ORR and the mixture with the carbon black was useful to increase the ORR current [16, 17]. However, the characterization of the specimens and the discussion of the correlation between the physical properties and the catalytic activity for the ORR had not been elucidated yet.

In the present paper, the characterization of the specimens such as the measurement of the ionization potential was performed and the correlation between the physical properties of the specimens and the catalytic activity for the ORR was discussed.

2   Experimental

Tantalum carbonitride (TaC_xN_y) powder was used as a starting material. Ta_2O_5 powder and carbon black were uniformly mixed, and the mixture was heat-treated at 1600 °C under flowing N_2 to make carbonitride. The composition of the TaC_xN_y was controlled by a quantity of the carbon black. In the present study, $TaC_{0.58}N_{0.42}$ powder was used as a starting material.

The $TaC_{0.58}N_{0.42}$ powders were heat-treated at 1000 °C for a holding time from 3 to 32 h under a flow rate of 20 cm^3 min^{-1} of the 2 % - H_2/N_2 gas containing 0.25 % oxygen to obtain

powder specimens with different oxidation state. Crystalline structure of the specimens was analyzed using X-ray diffraction (XRD-6000, SHIMADZU) with Cu Kα radiation. Ionization potential of partially oxidized $TaC_{0.58}N_{0.42}$ was measured using Photoelectron Spectrometer Surface analyzer Model AC-2 (Riken Keiki).

Both TaC and TaN have a same crystalline structure (Rock-Salt type) and form a complete solid solution. The XRD pattern did not change from TaC (JCPDS: 35-0801) to TaN (JCPDS: 32-1283), and an each peak shifts to higher angle with the increase in the nitrogen content, which known as Vegard's law. In the present paper, the compounds with XRD peaks which existed between TaC and TaN were expressed as TaC_xN_y. The peak intensity of the Ta_2O_5 increased with the increase in the holding time of the heat treatment, while the intensity of the TaC_xN_y decreased.

In order to quantify the degree of oxidation of the $TaC_{0.58}N_{0.42}$, the peak intensity at $2\theta = 35°$ of TaC_xN_y (1 0 0), which was expressed as I (TaC_xN_y), and the peak intensity at $2\theta = 28.3°$ of Ta_2O_5 orthorhombic (1 11 0), which was expressed as I (Ta_2O_5), were utilized to calculate the ratio, I (Ta_2O_5)/{I (TaC_xN_y) + I (Ta_2O_5)}. The ratio, I (Ta_2O_5)/{I (TaC_xN_y) + I (Ta_2O_5)}, was designated the degree of the oxidation of the $TaC_{0.58}N_{0.42}$ and expressed as DOO (Degree Of Oxidation).

A partially oxidized specimen was mixed with carbon black (7 wt.-%), Ketjen Black, and the mixed powder (2.8 mg cm^{-2}) was dropped onto a glassy carbon rod ($\Phi = 5.2$ mm). A 0.5 wt.-% Nafion® solution, then, was dropped onto the surface to cover the mixed powder.

All electrochemical experiments were conducted in a three-electrode cell under nitrogen or oxygen atmosphere in 0.1 mol dm^{-3} H_2SO_4 at 30 °C. A reference electrode was a reversible hydrogen electrode (RHE) in the same solution. Cyclic voltammetry (CV) (scan rate: 50 mV s^{-1}, 0.05 - 1.0 V) was performed under nitrogen atmosphere to investigate an electrochemical stability of the specimens. Slow scan voltammetry (SSV) (scan rate: 5 mV s^{-1}, 1.0 - 0.2 V) was performed under nitrogen or oxygen atmosphere to evaluate the catalytic activity for the ORR. A current difference between under O_2 and under N_2 might be due to the oxygen reduction. Therefore, the oxygen reduction current density (i_{ORR}) was defined as the difference in the current densities between under the O_2 atmosphere (i_{O2}) and the N_2 atmosphere (i_{N2}). The current density was based on the geometric surface area of the working electrode. An onset potential for the ORR, E_{ORR}, was defined as the electrode potential at the $i_{ORR} = -0.2$ µA cm^{-2} to evaluate the catalytic activity for the ORR.

3   Results and Discussion

3.1   Degree of oxidation of $TaC_{0.58}N_{0.42}$
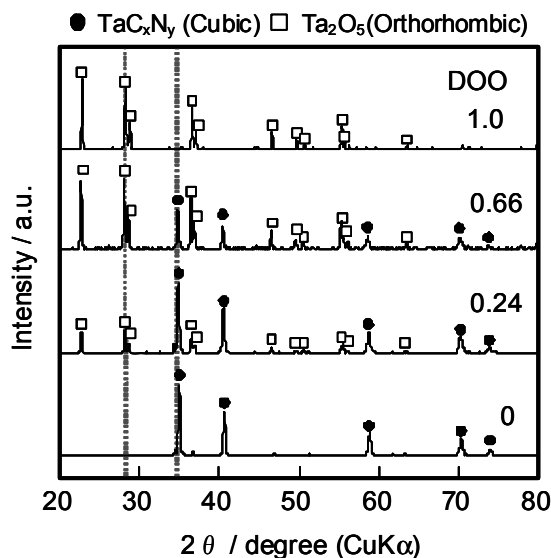

Figure 1:   XRD patterns of the powder specimens with the different holding time of heat treatment. The holding time of the upper specimen was longer, and the lowest specimen was the starting material, $TaC_{0.58}N_{0.42}$.

Figure 1 shows the XRD patterns of the powder specimens with the different degree of oxidation (DOO). The DOO of the specimen with no heat treatment was zero, that is, $TaC_{0.58}N_{0.42}$. Although the surface of the $TaC_{0.58}N_{0.42}$ was probably oxidized, no peaks of the Ta_2O_5 were observed because the surface oxide layer was very thin. The DOO of the specimen with completely oxidized was unity, that is, Ta_2O_5. However, this completely oxidized powder was not prepared using the heat treatment in the present paper because of the low oxygen concentration. Therefore, a commercial reagent, Ta_2O_5 (Kojundo Kagaku), was used as the powder with DOO of unity.

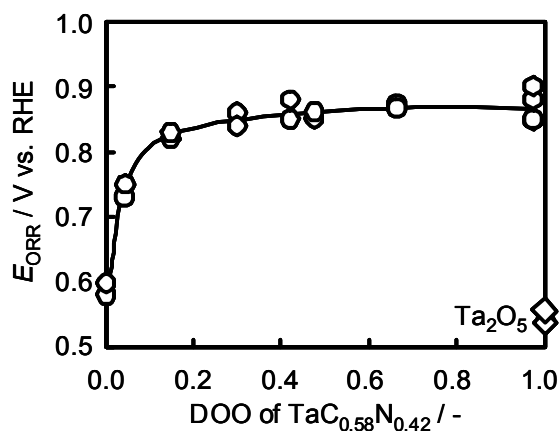### 3.2 Dependence of the degree of oxidation of $TaC_{0.58}N_{0.42}$ on the catalytic activity for the ORR

Figure 2: Relationship between the DOO and the E_{ORR}. E_{ORR} was defined as the electrode potential at the i_{ORR} = -0.2 µA cm^{-2}. 0.1 mol dm^{-3} H_2SO_4, 30°C, scan rate = 5 mV s^{-1}.
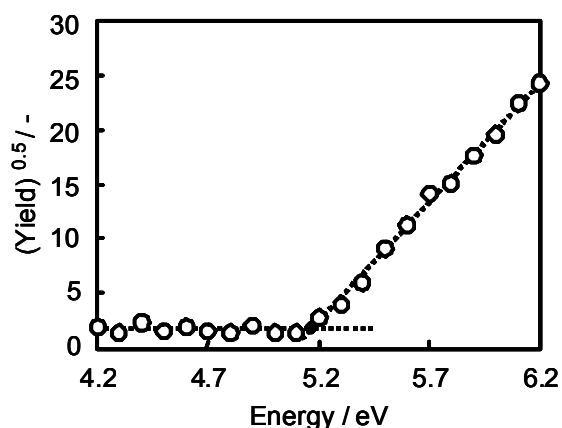

Figure 3: Relationship between the square root of the photoelectric quantum yield $Y^{1/2}$ and the photon energy.

Figure 2 shows the relationship between the DOO and the E_{ORR}. The E_{ORR} abruptly increased with the increasing DOO up to 0.2. Then, the E_{ORR} had high value over 0.85 V above the DOO of 0.3. The maximum of the E_{ORR} is approximately 0.9 V. The starting material (DOO = 0) and the completely oxidized material (DOO = 1) had a poor catalytic activity. This result indicated that an appropriate oxidation of $TaC_{0.58}N_{0.42}$ was essential to obtain the large oxygen reduction current.

3.3 Ionization potential of the partially oxidized $TaC_{0.58}N_{0.42}$

The ionization potential of the specimens was measured using Photoelectron Spectrometer Surface analyzer to discuss the electronic structure of the specimens. Figure 3 shows the relationship between the square root of the photoelectric quantum yield $Y^{1/2}$ and the photon energy, that is, the photoelectron spectra of the partially oxidized $TaC_{0.58}N_{0.42}$ with the DOO

of 0.42. A linear relation was obtained in the range from 5.2 to 6.2 eV. The intersection between the straight line and the background line provided a threshold energy. The threshold energy corresponded to a photoelectric ionization potential. The ionization potential of the partially oxidized $TaC_{0.58}N_{0.42}$ with the DOO of 0.42 was estimated to be 5.10 eV as shown in Figure 3. The highest energy level of electrons in the valence band of Ta_2O_5 is -7.83 ~ -7.93 eV [18], that is, the ionization potential of Ta_2O_5 is 7.83 ~ 7.93 eV. However, the ionization potential of the partially oxidized $TaC_{0.58}N_{0.42}$ with the DOO of 0.42 was 2.7 eV lower than that of Ta_2O_5. The work function of metal Ta was 4.25 eV [19]. For titanium, Henrich et al. investigated the relationship between the work function, that is, the ionization potential, of reduced TiO_2 (1 1 0) and the density of defect states on the surface [20]. They found that the work function decreased with increasing the density of defects. The similar behavior is expected to occur in case of the partially oxidized $TaC_{0.58}N_{0.42}$. Ta_2O_5 had the band gap of 3.9 eV [18]. Lattice defects and impurities introduce localized electron levels in the band gap of metal oxides. Vacancies of oxide ion give donor levels close to the edge level of the conduction band [21]. The conduction band edge level of Ta_2O_5 is -3.93 ~ -4.03 eV [18]. These values are close to the ionization potential of partially oxidized $TaC_{0.58}N_{0.42}$ with the DOO of 0.42. Therefore, the partially oxidized $TaC_{0.58}N_{0.42}$ with the DOO of 0.42 probably had some vacancies of oxide ion.

Figure 4 shows the relationship between the DOO and the ionization potential. The ionization potential of the $TaC_{0.58}N_{0.42}$ was 4.8 eV, and the completely oxidized, commercial Ta_2O_5 had 5.4 eV. The ionization potential of the partially oxidized $TaC_{0.58}N_{0.42}$ powder had almost the same value, 5.2 eV. The ionization potential of pure TaON and Ta_3N_5 were 6.6 and 6.0 eV, respectively [18]. The ionization potentials obtained in the present study were much lower than those of TaON and Ta_3N_5. This low ionization potential suggested that the partially oxidized $TaC_{0.58}N_{0.42}$ had some surface defects. Lattice defects and impurities introduce localized electron levels in the band gap of metal oxides. Vacancies of oxide ion give donor levels close to the edge level of the conduction band. We expected that the partially oxidized $TaC_{0.58}N_{0.42}$ probably had some vacancies of oxide ion.
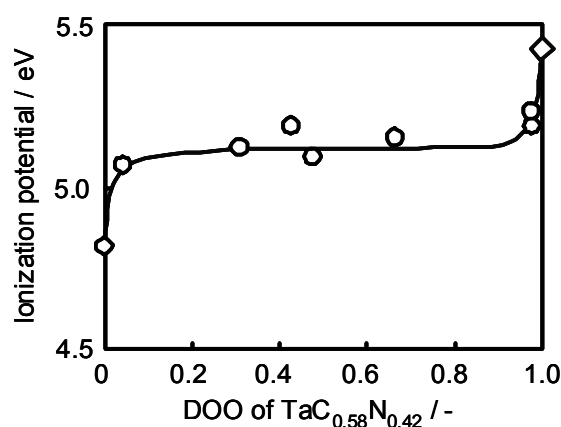

Figure 4:   **Relationship between the DOO and the ionization potential.**
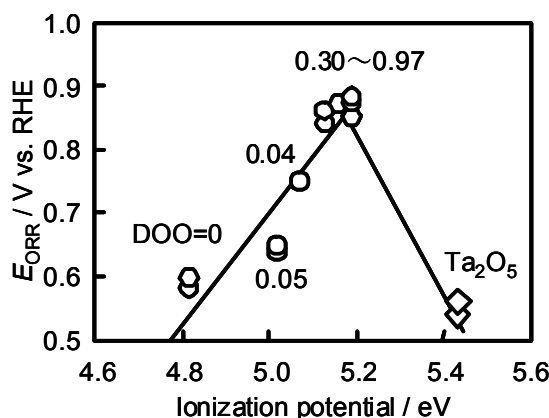
Figure 5:   Relationship between the ionization potential and the onset potential of the ORR.

Figure 5 shows the relationship between the ionization potential and the E_{ORR}. The volcano plot was obtained. The adsorption of oxygen molecules on the surface was required as the first step to proceed the ORR. Many researches revealed that the presence of surface defects sites was required to adsorb the oxygen molecules on the surface of the oxides such as TiO_2 (1 1 0), ZnO, NiO (1 0 0), $Ce_xZr_{(1-x)}O_2$, V_2O_5, and MoO_3 [22-27]. The increase in the surface defects on the partially oxidized $TaC_{0.58}N_{0.42}$ yielded the increase in the adsorption sites of oxygen molecules. In addition, the interaction of oxygen with the catalyst surface is essentially important because both the adsorption of oxygen and the desorption of water on the surface is necessary to continue the fluent progress of the ORR. When the interaction of oxygen with the catalyst surface is strong, the desorption of water is restrained. On the other hand, when the interaction of oxygen with the catalyst surface is weak, few adsorption of oxygen molecules proceeds. There might be a most suitable strength of the interaction between the oxygen and the catalyst surface. Metallic Ta atom strongly adsorbed oxygen because of the large adsorption energy of oxygen (887 kJ mol⁻¹) and calculated bond energy of Ta-oxygen atoms (715 kJ mol⁻¹) [28]. In case of Pt, the adsorption energy of oxygen and the calculated bond energy of Pt-oxygen atoms were 280 kJ mol⁻¹ and 397 kJ mol⁻¹, respectively [28]. These values of Ta were much larger than those of Pt. As the oxidation of Ta metal proceeded, the interaction of oxygen with Ta of the catalyst surface became weak because the oxide ions attracted the electrons of the highest occupied molecule orbital of Ta to be Ta charged positively. Because the ionization potential was related to the strength between the surface of the specimen and oxygen, the volcano plot shown in Figure 5 suggested that there was a suitable interaction between the surface of the specimen and oxygen. Therefore, the oxidization could control the strength of the interaction between the oxygen and the Ta, and as the interaction became suitable the catalytic activity for the ORR increased.

4   Conclusions

The partially oxidized $TaC_{0.58}N_{0.42}$ was investigated as non-platinum cathode for PEFC. In order to quantify the degree of oxidation, the DOO was defined using the XRD peaks of Ta-CN and Ta_2O_5. The onset potential for the ORR had high value, that is, 0.9 V vs. RHE, at

higher oxidation state of the $TaC_{0.58}N_{0.42}$. We found that the partial oxidation of $TaC_{0.58}N_{0.42}$ was greatly useful to enhance the catalytic activity for the ORR. The volcano plot of the ionization potential vs. the E_{ORR} suggested that there was a suitable interaction between the surface of the partially oxidized $TaC_{0.58}N_{0.42}$ and oxygen.

Acknowledgments

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