TRANSITION METAL OXYNITRIDES FOR NEW CATHODE OF POLYMER ELECTROLYTE FUEL CELL

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ABSTRACT

Transition metal oxynitrides and nitrides such as tantalum oxynitrides (TaO\textsubscript{x}N\textsubscript{y}) and nitrides (Ta\textsubscript{3}N\textsubscript{5}) have been studied for application as a cathode catalyst of polymer electrolyte fuel cells without platinum. The nitride and oxynitrides in which Ta had the highest oxidation state showed the high stabilities in sulfuric acid. Samples were prepared by nitriding Ta\textsubscript{2}O\textsubscript{5} with NH\textsubscript{3} gas. TaO\textsubscript{0.92}N\textsubscript{1.05} (nitrogen content: 7.0wt\%) had a clear catalytic activity for the oxygen reduction reaction (ORR) in sulfuric acid (1mol/dm\textsuperscript{3}) at 30\textdegree C, although the nitride showed poor activity for the ORR. In addition, a Ta\textsubscript{x}Ny film prepared by sputtering Ta with N\textsubscript{2} also had a clear catalytic activity for the ORR after the surface of the sample was oxidized by potential cycling in sulfuric acid. The tantalum oxynitrides were clearly active for ORR, and the activity depended on the concentration of nitrogen in the oxynitride, although their activities are presently much lower than that of platinum.

INTRODUCTION

Fuel cells have been actively investigated since demonstrated by Sir William Grove (1) because they are theoretically highly efficient energy conversion systems of hydrogen or fossil fuels to electrical energy. Specific polymer electrolyte fuel cells, which use thin polymer membrane with protonic conduction, are expected to be used for the transportable applications, especially automobile use, due to their high power density and low operating temperature. Their theoretical efficiency is high. However, the actual efficiency is not very high due to the large overpotential of the oxygen reduction reaction (ORR) which is the cathode reaction of a fuel cell (2). This large overpotential should be reduced. Highly dispersed platinum on carbon powder is used as a commercial cathode catalyst at present. Though platinum is generally used as a catalyst in many industrial fields, its catalytic activity for oxygen reduction is not enough to obtain a sufficient efficiency (3). Platinum–transition metal alloys have been developed to enhance the catalytic activity of platinum (4–6). However, transition metals dissolve in acid electrolyte, so that the stability of alloy catalysts becomes a problem for long-term operation. In addition, the estimated amount of Pt deposits is too low to make a large number of fuel cell systems, especially for fuel cell powered vehicles. The required
platinum quantity for a 100kW fuel cell vehicle is presently estimated to be about 100 g. If all of the supplied platinum in the world (about 200 tons/year at 2003) is used to make fuel cell vehicles, only 200 thousand cars can be made per year. Therefore, in order to widely commercialize the fuel cell systems in the future, we have to develop a new catalyst without platinum. It is well known that tungsten carbide had the platinum-like electronic structure (7) and showed a similar hydrogen chemisorption property as Pt (8). However, most of the transition metal carbides including WC easily dissolve into the electrolyte under the cathodic conditions of polymer electrolyte fuel cells. They are unstable in acidic and oxidative atmospheres (9,10). Transition metal nitrides, which were used as refractory materials like carbides, are corrosion resistance materials (11). Recently, transition metal nitrides and oxynitrides are being studied for use as visible light driven photocatalysts (12-15). In this study, we have investigated the catalytic activity and the stability of tantalum oxynitrides for the ORR of polymer electrolyte fuel cells in order to develop a new catalyst without platinum.

**EXPERIMENTAL**

**Synthesis and characterization of TaON and Ta3N5 powder samples**

TaON and Ta3N5 were prepared by heating Ta2O5 powder (Rare Metallic, purity: 99.9%) in alumina tube reactor under a flow of ammonia gas (flow rate: 20-1000 cm3 min-1) at 1123K for a certain hours. The nitriding reactor was directly connected to a silicon oil bubbler made of Pyrex, and the effluent gas with entrained water generated during nitriding was passed into the bubbler at 420K, preventing contamination by water and O2 in air.

The crystallographic structure of the catalyst was analyzed by the XRD. Microanalysis of nitrogen content was performed using a Leco CHNS-932 elemental analyzer.

**Electrode preparation for powder samples**

After the 0.1g samples were added to 5 cm3 of distilled water by ultrasonic treatment, the20 mm3 solution was then placed on a glassy carbon rod (Tokai Carbon, diameter: 5mm). The glassy carbon with the oxynitride was heated at 80 °C to remove the water. Diluted Nafion® solution was then dropped on the specimens to cover and to keep the samples on the carbon surface. The material was heated to a temperature of 120 °C for several hours in nitrogen so that the coated Nafion® was recast.

**Synthesis of Ta3Ny film sample by sputtering**

Ta-N films were deposited using the sputter system. A tantalum target of 99.95% purity was sputtered in an argon/nitrogen plasma to produce tantalum nitride films. The flow of high-purity Ar and N2 gases was controlled using mass flow controllers. The base pressure of the chamber was 3*10^-5Pa. Glassy carbon rods were used as substrates. The film thickness was about 30nm.

**Electrochemical measurements**

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The electrocatalytic activity for ORR and the stability in acid electrolyte (0.1mol dm$^{-3}$ H$_2$SO$_4$) was evaluated by electrochemical measurements. A conventional 3-electrode cell was utilized, and the reversible hydrogen electrode (RHE) was the reference in the same solution. Cyclic voltammetry (scan rate: 100mV s$^{-1}$) was performed under nitrogen atmosphere to investigate the stability of prepared catalysts, and slow scan voltammetry (scan rate: 5mV s$^{-1}$) was performed under oxygen atmosphere to examine the catalytic activity of ORR.

The influence of the surface state on the catalytic activity for oxygen reduction was investigated by the potential control method and compared with that of platinum. A current density was expressed by geometric area. All experiments were performed at 303K (30°C) under the gas pressure of 1 atm.

**RESULTS AND DISCUSSION**

**Characterization of TaON and Ta$_3$N$_5$ powder samples**

Figure 1 (a) shows the X-ray diffraction patterns of Ta$_2$O$_5$ and the prepared samples. Nitriding of Ta$_2$O$_5$ at the NH$_3$ flow rate of 20 cm$^3$ min$^{-1}$ produced a yellow powder after 15 hours, and in the case of 1000 cm$^3$ min$^{-1}$, a scarlet powder appeared after 15 hours. β-TaON is a yellow to yellowish-green oxynitride that has the same structure as baddeleyite, monoclinic ZrO$_2$ (16). The structure of Ta$_3$N$_5$ consists of TaN$_6$ octahedra and is similar to Ti$_3$O$_5$ (anovite) (17). The XRD patterns of (b) and (c) corresponded to those of β-TaON and Ta$_3$N$_5$, respectively (16,17). No impurity phase was observed in the XRD patterns. The freshly prepared compounds were analyzed for N using the Leco CHNS-932 elemental analyzer. The oxygen content was calculated from the nitrogen content according to the electric neutral principle based on the assumption that the oxidation state of tantalum is 5+. Therefore, the elemental analysis revealed that the compositions of samples (b) and (c) were TaO$_{1.3}$N$_{0.8}$ and Ta$_3$O$_{0.3}$N$_{4.8}$, respectively. This indicated that the prepared tantalum oxynitrides and nitride were nonstoichiometric and had many defects in the crystals.

**Stability of powder samples in acid electrolyte**

Figure 2 shows the typical cyclic voltammogram of TaON under N$_2$ atmosphere. At first several cycles, the anodic peak at 0.9V and cathodic peak at 0.6V were observed and the anodic and cathodic currents decreased with potential cycling as shown in Fig.2. However, the current change was due to the Nafion$^\text{®}$ on the electrode surface. In case of the carbon rod with only Nafion$^\text{®}$, the similar current change was observed. After several potential cycles, the potential-current curve was not change to achieve the steady state so that the corrosion resistance of TaON is high in acid electrolyte. Because all of TaON, Ta$_2$O$_5$, and Ta$_3$N$_5$ had similar voltammogram, all samples had high corrosion resistance in acid solution. This is because the Ta in the samples had the highest oxidation state. This indicated that the semiconductors, whose metal had the highest oxidation state, were very stable in acid media at least in the potential range for oxygen reduction.
Catalytic activity of powder samples for ORR

Figs. 3 (A) and (B) show the potential-current curves of Ta$_3$N$_5$ and TaO$_{0.92}$N$_{1.05}$, respectively. The potential at which the reduction current with Ta$_3$N$_5$ under O$_2$ increased more than that under N$_2$ was about 0.4V. This indicated that Ta$_3$N$_5$ had a lower catalytic activity for the ORR. However, as shown in Fig. 2(B) the reduction current with TaO$_{0.92}$N$_{1.05}$ (N: 7.0wt%) under O$_2$ started at 0.8V. Because such a reduction current was not observed under the N$_2$ atmosphere, the reduction current might be due to the oxygen reduction. TaO$_{0.92}$N$_{1.05}$ (N: 7.0wt%) had a clear catalytic activity. The reduction current on Pt in 0.1 mol/dm$^3$ sulfuric acid takes place below 0.95V, indicating that the cathodic activity of TaO$_{0.92}$N$_{1.05}$ was presently much lower than that of Pt. The activity could be further improved by optimization of the catalyst composition and the electrochemical interface.

The catalytic activity of the active TaO$_{0.92}$N$_{1.05}$ decreased when the material was left under atmospheric conditions for 2,000 hours as shown in Fig.4. However, by applying multi-potential cycling at 50mV/s in the potential range of 0.05–1.2V, the catalytic activity for the ORR was perfectly recovered at about the 80$^{th}$ potential cycling as shown in Fig.4. This means that the activity could be easily recovered by potential cycling though the surface state of the TaO$_{0.92}$N$_{1.05}$ sample was gradually changed to inert under atmospheric conditions.

The influence of the surface state on the catalytic activity for oxygen reduction was investigated by the potential control method and compared with that of platinum. Slow scan voltammetry at scan rate of 1mV/s was performed under O$_2$ atmosphere at 30°C in 0.1 mol/dm$^3$ sulfuric acid. Before slow scan voltammetry, the potential was cycled between 1.2 and 0.05V (Scan rate: 50mV/s) to maintain the steady state. The potential was then slowly scanned from 1.2 to 0.4V, and increased up to 1.2V again. Figs. 5 (A) and (B) showed the results of the active TaO$_{0.92}$N$_{1.05}$ and platinum black, respectively. The reduction current in the cathodic direction was always lower than that in the anodic direction for the platinum group metal catalysts as shown in Fig. 5 (B). This was because the surface was oxidized at a higher potential to form a stable thin oxide layer whose catalytic activity was low. (18,19). In the anodic direction, the surface was maintained in the reduced state which had a good catalytic activity for the ORR. However, in the case of the active TaO$_{0.92}$N$_{1.05}$, the reduction current in the cathodic direction was greater than that in the anodic direction as shown in Fig. 5 (A). This result indicated that the oxidative surface had a higher catalytic activity than the reductive one. The dependence of the surface oxidation state on the reduction current at several constant potentials between the active TaO$_{0.92}$N$_{1.05}$ and platinum black was compared. The potential was cycled between 1.2 and 0.05V (Scan rate: 50mV/s) to maintain the steady state. The potential was then set the starting potential $E_s$ and scanned down at 1mV/s. The dependences of the starting potential $E_s$ on the reduction current at several constant potentials are shown in Figs. 5 (C) and (D). Since the oxide layer of Pt thickly formed at higher potentials, the reduction current on Pt at 0.9V nonlinearly decreased with the increasing starting potential of a slow scan. On the contrary, the reduction current on the active TaO$_{0.92}$N$_{1.05}$ at 0.65 and 0.7V linearly increased with the increasing starting potential. This remarkable behavior had never been observed for noble metals such as platinum. The catalytic activity of Pt decreased with the oxide formation. On the contrary, the catalytic activity of TaO$_{0.92}$N$_{1.05}$ was not
significantly affected by the oxide formation. Considering the cathode atmosphere in which oxygen is present, there is the possibility that this characteristic of the tantalum oxynitrides is favorable for oxygen reduction at higher potentials.

Catalytic activity of sputtered Ta<sub>3</sub>N<sub>y</sub> film for ORR

Ta<sub>3</sub>N<sub>y</sub> film on a glassy carbon rod was prepared by sputtering a Ta target in an N<sub>2</sub>(22%)/Ar gas mixture. The tantalum in the sample prepared by sputtering had a low oxidation state such as TaN and Ta<sub>2</sub>N (20,21). The low oxidation state Ta could be oxidized to the highest oxidation state, i.e., 5+. In fact, for the initial potential cycling, a small oxidation current was observed. The Ta<sub>3</sub>N<sub>y</sub> film might be partially oxidized to tantalum oxynitride. However, such an oxidation current rapidly decreased with continuous potential cycling and immediately reached the steady state in which the tantalum did not further dissolve. When the surface of Ta<sub>x</sub>N<sub>y</sub> was oxidized and became the suitable state for the oxygen reduction, the material was expected to have a clear catalytic activity for the ORR. Slow scan cyclic voltammograms at scan rate of 5mV/s in the potential range of 0.2-1.0V under N<sub>2</sub> and O<sub>2</sub> atmospheres at 30°C in 0.1 mol/dm<sup>3</sup> sulfuric acid. Before slow scan voltammetry, the potential was cycled between 1.2 and 0.05V (Scan rate: 50mV/s) to maintain the steady state. Figure 6 shows the slow scan cyclic voltammograms. The reduction current occurred below 0.8V the same as the active powder sample. Since the reduction current was not observed under the N<sub>2</sub> atmosphere, the reduction current was due to the oxygen reduction and this sample also had a clear catalytic activity for the ORR. The dependence of the potential scan direction on the reduction current was also the same as the powder sample.

CONCLUSIONS

To increase the catalytic activity of oxygen reduction reaction and to reduce the use of platinum which is utilized as a commercial cathode catalyst, non-platinum material such as tantalum oxynitride, TaON, was tried to apply to the cathode materials of polymer electrolyte fuel cell. Ta<sub>2</sub>O<sub>5</sub>, TaON, and Ta<sub>3</sub>N<sub>5</sub> had high stability in acid solution. TaO<sub>9</sub>N<sub>1.05</sub> (nitrogen content: 7wt%) had clear catalytic activity for ORR. The oxynitride might have the possibility to be a substitute material for the platinum cathode of polymer electrolyte fuel cells, although the activity should be further improved.

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Fig. 1  XRD patterns of samples: (a) Ta$_2$O$_5$; (b) sample prepared under NH$_3$ flow at 20 cm$^3$ min$^{-1}$; (c) sample prepared under NH$_3$ flow at 1000 cm$^3$min$^{-1}$.

Fig. 2  Potential-current curve of TaO$_{0.92}$N$_{1.05}$ under N$_2$ atmosphere. Potential was cycled in the range of 0.05 – 1.2 V vs. RHE with scan rate of 50mV s$^{-1}$. 

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Fig. 3. Potential-current curves of (A) Ta$_3$N$_5$ and (B) TaO$_{0.92}$N$_{1.05}$ under N$_2$ and O$_2$ atmospheres in 0.1 mol/dm$^3$ sulfuric acid. Potential was scanned from 1.2 V vs. RHE to 0.2 V with scan rate of 5 mV s$^{-1}$.

Fig. 4. Recovery of catalytic activity after the active catalyst left under atmospheric condition for ca. 2000 hours. Cyclic voltammograms of TaO$_{0.92}$N$_{1.05}$ at scan rate of 50 mV/s in the potential range between 0.05-1.2 V under O$_2$ at 30°C.
Fig. 5 Comparison of oxygen reduction behavior between TaO$_{0.92}$N$_{1.05}$ and Pt black. Slow scan voltammograms of (A) TaO$_{0.92}$N$_{1.05}$, and (B) Pt black (0.12mg). The dependence of the starting potential $E_s$ on the reduction current at several constant potentials (C) TaO$_{0.92}$N$_{1.05}$, (D) Pt black.
Fig. 6 Catalytic activity of sputtered TaON. Slow scan cyclic voltammograms at scan rate of 5mV/s in the potential range of 0.2-1.0V under N$_2$ and O$_2$ atmospheres. Before slow scan voltammetry, the potential was cycled between 1.2 and 0.05V (Scan rate: 50mV/s) to maintain the steady state.
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