

Transition Metal Oxynitrides for New Cathode of Polymer Electrolyte Fuel Cell

A. Ishihara^a, K. Lee^a, S. Doi^b, S. Mitsushima^b, N. Kamiya^b, and K. Ota^b

^a Japan Science and Technology Agency (JST)

^b Department of Energy and Safety Engineering, Yokohama National University
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501 Japan

Introduction

Polymer electrolyte fuel cells (PEFCs) are expected to be used to the transportable applications, especially to the automobile use, due to its high power density and low operating temperature. Although the theoretical efficiency is high, the actual efficiency is not so high due to large cathode overpotential. The cathode overpotential causes the large energy loss. An improvement of cathode materials should be needed to increase the energy conversion efficiency and to commercialize the fuel cell systems widely.

Highly dispersed platinum or platinum alloy on carbon powder are used as a conventional cathode catalyst at present. Though platinum is generally used as catalyst in many fields, its catalytic activity for ORR is not enough to obtain the sufficient energy efficiency. Furthermore, the estimated amount of the Pt resources was too small to make many fuel cell systems, especially fuel cell vehicles. Thus, in order to attain the popularity of the fuel cell systems in the future, the development of a non Pt catalyst is inevitable. We tried to apply transition metal oxynitrides such as TaON to cathode catalyst. TaON was known as visible light driven photocatalyst. However, the catalytic activities for oxygen reduction were unknown.

Experimental

TaON and Ta₃N₅ were prepared by heating Ta₂O₅ powder (Rare Metallic, purity: 99.9%) in alumina tube reactor under a flow of ammonia at 1123K for a certain hours. The crystallographic structure of the catalyst was analyzed by the XRD. Microanalysis of nitrogen content was performed using a Leco CHNS-932 elemental analyzer, and the surface analysis was performed by XPS.

After the 0.02g samples were added to 1 cm³ distilled water by ultrasonic treatment, the solution of 3 mm³ was picked up and dropped on the glassy carbon rod (Tokai carbon, diameter: 8mm). Then a diluted Nafion[®] solution was dropped on the samples to cover them and to keep them on the carbon surface.

The electrocatalytic activity for ORR and the stability in acid electrolyte (0.1mol dm⁻³ H₂SO₄) 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. The cyclic voltammetry (scan rate: 100mV s⁻¹) was performed under nitrogen atmosphere to investigate the stability of prepared catalysts, and the slow scan voltammetry (scan rate: 5mV s⁻¹) was performed under oxygen atmosphere to examine the catalytic activity of ORR. 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

Figure 1 shows X-ray diffraction patterns of Ta₂O₅

and the prepared samples. β -TaON is a yellow to yellowish-green oxynitride that has the same structure as baddeleyite, monoclinic ZrO₂. The structure of Ta₃N₅ consists of TaN₆ octahedra and is similar to Ti₃O₅ (ansovite). The XRD patterns corresponded to those of β -TaON and TaN₆, respectively. No impurity phase was observed in the XRD patterns.

Figure 2 shows the slow scan voltammogram under oxygen atmosphere. Ta₂O₅, Ta₃N₅ and TaON except TaO_{0.92}N_{1.05} (nitrogen content: 7wt%) had little catalytic activity for ORR. However, the reduction current of TaO_{0.92}N_{1.05} (nitrogen content: 7wt%) for ORR was observed below about 0.8V vs. RHE. Because under nitrogen atmosphere such a reduction current was not observed, the reduction current was responsible for oxygen reduction. It was shown that the catalytic activity was very sensitive to bulk composition and/or surface state, because only TaO_{0.92}N_{1.05} (nitrogen content: 7wt%) sample had some catalytic activity.

Acknowledgements

The authors wish to thank the Japan Science and Technology Agency (JST) and the New Industrial and Technology Development Organization (NEDO) for financial support.

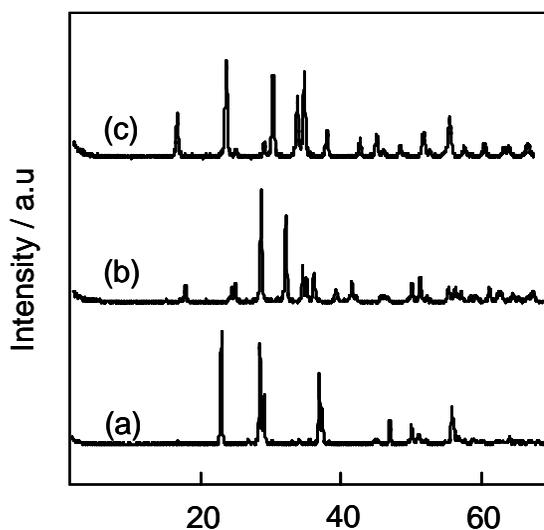


Fig.1 XRD patterns of: (a) Ta₂O₅; (b) sample prepared under NH₃ flow at 20 cm³ min⁻¹; (c) sample prepared under NH₃ flow at 1000 cm³ min⁻¹.

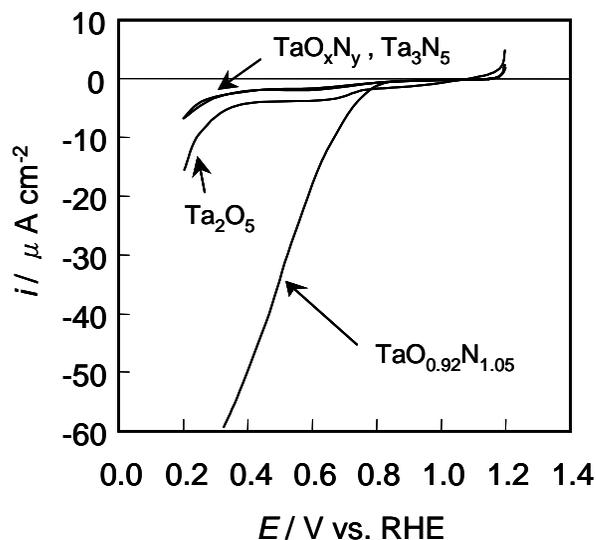


Fig.2 Potential-current curve for oxygen reduction reaction. Potential was cycled in the range of 0.05 – 1.2 V vs. RHE with the scan rate of 5mV s⁻¹.