Stabilization and activation of zirconium oxide based electrocatalysts as PEFC cathode by re-heat treatment

Yohei Okada[*], Akimitsu Ishihara[*], Masashi Matsumoto[‡], Masazumi Arao[‡], Hideto Imai[‡], Yuji Kohno[*], Koichi Matsuzawa[*], Shigenori Mitsushima[*], and Ken-ichiro Ota[*]

[*]Green Hydrogen Research Center, Yokohama Nat. Univ.
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501 JAPAN
[‡] NISSAN ARC Ltd.
1 Natsushima-cho, Yokosuka 237-0061 JAPAN

Introduction

Development of non-platinum electrocatalysts for oxygen reduction reaction (ORR) is required for real commercialization of polymer electrolyte fuel cells. We focused on group 4 and 5 transition metal oxides, because they have high chemical stability under acidic atmosphere even in high potential region, and are much less expensive than platinum. In our previous study, zirconium oxide based compounds made from oxyzirconium phthalocyanines by heat treatment under low oxygen partial pressure (LO_Zr-CNOs) showed high ORR activity[1-2)]. Therefore, their durability should be investigated.

In this study, we evaluated durability and activity of LO_Zr-CNOs with and without re-heat treatment for stabilization in order to develop high durable electrocatalysts.

Experimental

Oxyzirconium phthalocyanine (ZrOPc) is used as a starting material. The ZrOPc was mixed with multi-walled carbon nanotube (MWCNT) as a support. The mixture was immersed in *N*-methylpyrrolidone (NMP), and then evaporated to deposit the ZrOPc on the MWCNT. The MWCNT supported the ZrOPc was oxidized to LO_Zr-CNO by rotary electrical furnace at 900°C in 0.5%O_2 + 2%H_2/N_2 gas. The LO_Zr-CNO was heated in temperature range from 900 to 1200°C under nitrogen atmosphere as re-heat treatment for stabilization.

All electrochemical measurements were performed in 0.1 mol dm^{-3} H_2SO_4 at 30°C with a 3-electrode cell. A reversible hydrogen electrode (RHE) and a glassy carbon plate were used as a reference and a counter electrode, respectively. In order to evaluate the catalytic activity of the ORR, slow scan voltammetry (SSV) was performed with a scan rate of 5 mV s^{-1} from 0.2 to 1.2 V vs. RHE under O_2 and N_2 atmosphere. The ORR current density (i_{ORR}) which based on the mass of the whole catalyst included the carbon support was calculated from the difference between the current density under oxygen and nitrogen. The current density of the ORR at the potential of 0.8 V was defined as $i_{ORR\ at\ 0.8\ V}$ to evaluate the catalytic activity. Chronoamperometry (CA) at 0.6 V or 1.2 V vs. RHE for 5 to 15 h under oxygen atmosphere is used as degradation test. After the degradation test, the SSV was performed at the same condition.

Results and discussion

Figure 1 shows the potential – ORR current curves of the LO_Zr-CNO with and without the re-heat treatment. The ORR current densities of the LO_Zr-CNOs with the re-heat treatment in the range from 900 to 1000°C were larger than that without the re-heat treatment, and it was the largest for 1000°C of the re-heat treatment. The crystalline structure below 1100°C of the re-heat treatment was oxide. On the other hand, the re-heat treated LO_Zr-CNO above 1200°C had carbonitride structure and poor ORR activity.

Figure 2 shows the degradation of $|i_{ORR\ at\ 0.8\ V}|$ during the CA at 0.6 or 1.2 V for the LO_Zr-CNO with and without the re-heat treatment at 1000 and 1100°C. During the CA at the 0.6 V, the degradation slightly decreased by the re-heat treatment. On the other hand, during CA at the 1.2 V, the degradation of the LO_Zr-CNO without re-heat treatment was the largest among these three and the degradation obviously decreased by the re-heat treatment. In addition, the $|i_{ORR\ at\ 0.8\ V}|$ with the re-heat treatment at 1000°C was always largest among these three at both potential of 0.6 V and 1.2 V during the degradation test.

Zirconium oxide particles and deposited carbon on the zirconium oxide of the LO_Zr-CNO were found to be crystallized by the re-heat treatment according to XRD and TEM analysis. In the degradation of tantalum oxide-based catalyst, significantly surface carbon degradation was observed in high potential region[3)]. Therefore, the crystallization of both oxide and deposited carbon would be effective to the stabilization of oxide-based cathodes.

Acknowledgements

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Reference

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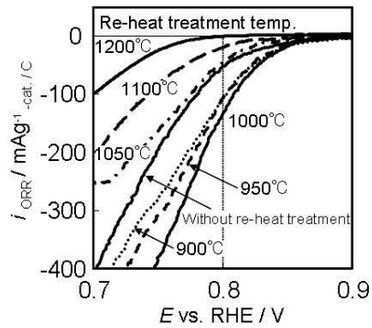

Fig. 1 Potential-current curves of ORR for LO_Zr-CNO with and without re-heat treatment under nitrogen atmosphere for 1 h.

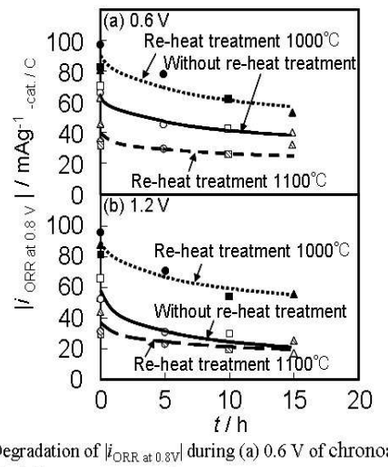

Fig. 2 Degradation of $|i_{ORR\ at\ 0.8V}|$ during (a) 0.6 V of chronoamperometry (b) 1.2 V of chronoamperometry.