# Enhancement of oxygen reduction activity of zirconium oxide-based cathode for PEFC

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## Introduction

In order to popularize PEFCs widely, we have developed the non-precious metal catalysts for oxygen reduction reaction (ORR). Our researches are focused on the oxide-based compounds of group 4 and 5 metals. We have reported that the oxide-based compounds, in particular, partially oxidized carbonitrides of $Zr$[1] $Nb$[2], and $Ta$[3] had high stability and high catalytic activity for the ORR in acidic solution. However, it is hard to prepare the fine oxide-based particles, because of the large particle size of the carbonitrides. We have already reported that it is possible to prepare the nano particles using organic complexes as the starting materials[4]. In this study, the effect of preparing conditions such as heat treatment temperature and atmosphere on the ORR activity of zirconium oxide-based compounds was investigated.

## Experimental

Precursors were oxy-zirconium phthalocyanine (ZrOPc) supported on multi-walled carbon nanotube (MWCNT). The precursors were heat-treated in the temperature range from 800 to 1000°C for 0 to 400 min under $N_2$ containing 2% $H_2$ + 0.05% $O_2$, that is, low $P_{O2}$ atmosphere to prepare the zirconium oxide-based catalysts (designated as LO_Zr-CNO (Pc)). On the other hand, the same precursors were heat-treated at 900°C under $N_2$ containing 2% $H_2$ to prepare the thermal decomposition catalysts (designated as TD_Zr-CNO (Pc)).

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. A slow scan voltammetry was performed at a scan rate of 5 mV s$^{-1}$ from 0.2 to 1.2 V under $O_2$ and $N_2$ atmosphere. The ORR current density ($i_{ORR}$) was estimated from difference between the current density under oxygen and nitrogen. A current density was based on the amounts of supported catalysts.

## Results and Discussion

Fig.1 shows the relationships between the heat-treatment time and $i_{ORR}$ at 0.8 V vs. RHE of LO_Zr-CNO(Pc) prepared under different temperatures. It was found that there was an optimal heat treatment time at each temperature, and the optimal time increased with heat treatment temperature. In the temperature range from 900 to 1000°C, the LO_Zr-CNO(Pc) prepared at 900°C shows the highest ORR activity.

Fig.2 shows the comparison of the potential – ORR current density curves for the Zr-CNO(CN), the TD_Zr-CNO (Pc), and LO_Zr-CNO (Pc). The Zr-CNO(CN) means that zirconium oxide-based catalyst made by oxidizing the zirconium carbonitride. The Zr-CNOs in Fig.2 showed best ORR activity in each preparation condition. The ORR current density, $i_{ORR}$, of the LO_Zr-CNO(Pc) was twice larger than that of the TD_Zr-CNO(Pc), and almost 300 times larger than that of the Zr_CNO(CN) at 0.8 V vs. RHE. Among these conditions, the LO_Zr-CNO(Pc) showed the largest $i_{ORR}$ at 0.8 V, that is, about 300 mA g$^{-1}$.

From these results, it was concluded that the LO_Zr-CNO(Pc) showed the largest $i_{ORR}$ at 0.8 V vs. RHE which meant low $P_{O2}$ oxidation was useful to enhance the ORR activity.

## Reference

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[2] K.-D. Nam, A. Ishihara, K. Matsuzawa, S. Mitsushima, M. Matsumoto, H. Imai, and K. Ota, *Electrochim. Acta*, **55**, 7290 (2010).
[3] A. Ishihara, M. Tamura, K. Matsuzawa, S. Mitsushima, and K. Ota, *Electrochim. Acta*, **55**, 7581 (2010).
[4] S. Yin, A. Ishihara, K. Matsuzawa, S. Mitsushima, and K. Ota, *ECS Trans.*, **50** (2) 1785 (2012)

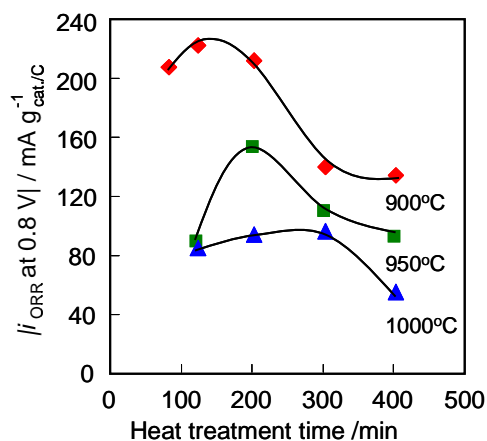Fig.1 Relationships between the heat treatment time and $i_{ORR}$ at 0.8 V of LO_Zr-CNO(Pc) prepared at different temperatures.
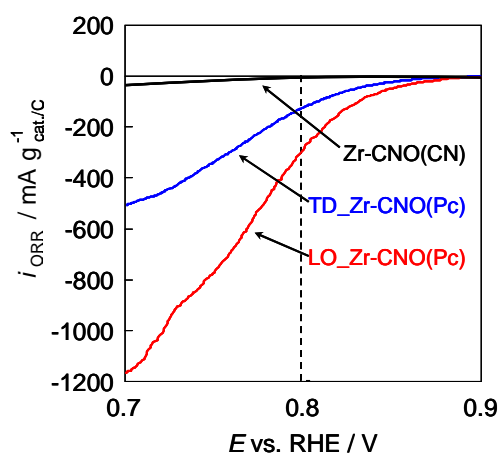


Fig.2 $i – E$ curves of Zr-CNO(CN), TD_Zr-CNO(Pc), and LO_Zr-CNO(Pc) for ORR.