

## Co/N/C catalysts on a vertically aligned carbon support for oxygen reduction reaction

T. Kawasaki, R. Hinogami, M. Aizawa, and H. Gyoten

Advanced Technology Research Laboratories,  
Panasonic Corporation

3-4 Hikaridai, Seika-cho, Soraku-gun,  
Kyoto 619-0237, Japan

E-mail : kawasaki.takashi002@jp.panasonic.com

### Introduction

The oxygen reduction reaction (ORR) is one of the most crucial factors determining the performance of the proton exchange membrane fuel cell (PEMFC) because of its kinetic sluggishness. Although platinum-based materials have been investigated as active catalysts for the ORR, the noble metal catalysts and their alloys can hardly meet the demands for widespread commercialization of the fuel cells because of their high costs and limited supply. Therefore, lots of attentions have been paid to non-precious metal catalysts as an alternative to the platinum-based catalysts.<sup>1</sup>

To date, metal/nitrogen/carbon (M/N/C) catalysts obtained from the pyrolysis of their precursors are the most promising non-precious metal catalysts for the ORR.<sup>2-4</sup> However, PEMFCs with the M/N/C cathode catalysts have not yet shown sufficient power output to replace the platinum-based catalysts.

In order to improve the activity of the M/N/C catalysts, we focused on vertically aligned carbon nanotubes (VACNTs) as the catalyst support. It was reported that the Pt catalyst supported on VACNTs showed the superior PEMFC performance to that on carbon black.<sup>5</sup> The aligned support structure mainly improves the mass transport of oxygen to the Pt catalyst, leading to the reduction in the concentration overvoltage.

In this study, we fabricated cobalt/N/C catalysts on the aligned carbon support which possesses a vertically aligned carbon nanowall (CNW)-like structure. The fabrication method, structure, and ORR activities of the Co/N/C catalysts supported on the CNWs are discussed.

### Experimental

The CNWs were formed by annealing a 4H-SiC (0001) wafer at 1800°C in vacuum.<sup>6</sup> Each CNW is mutually supported and grown perpendicularly to the SiC substrate, as shown in Fig. 1. The aligned CNW layer has a typical thickness of ~1 μm and inter-wall distances of about several tens of nanometers.

The M/N/C catalysts were electropolymerized on the aligned CNWs. The aqueous solution used for the polymerization contains pyrrole and cobalt acetate. In the solution, cobalt ions are likely coordinated with nitrogen atoms of pyrrole. Therefore, the electropolymerization produces the cobalt-coordinated polypyrrole. The resulting cobalt-coordinated polypyrrole on the CNWs was heated at 800°C in the inert environment. Since this heat treatment causes the carbonization of the polypyrrole, the Co/N/C catalysts on the CNWs were obtained. The catalyst loadings were controlled by varying the accumulated charge density in the electropolymerization.

The ORR activities of the synthesized catalysts were evaluated by linear sweep voltammetry using a conventional three-electrode cell. 1 M HClO<sub>4</sub> (aq) was used as an electrolyte. The catalyst, a platinum wire, and reverse hydrogen electrode (RHE) were utilized for the working, counter, and reference electrodes, respectively. The cur-

rent density measurements were carried out both in O<sub>2</sub>- and N<sub>2</sub>-saturated solutions. The ORR current density was calculated by subtracting the current measured in the N<sub>2</sub>-saturated solution from that in the O<sub>2</sub>-saturated solution. As a comparison, the current density measurements were also performed for the CNWs without the catalysts and the Co/N/C catalysts on a planar glassy carbon (GC).

### Results and discussion

Fig. 2 summarizes the ORR activities obtained for different samples. Since catalysts on the CNWs and GC themselves showed negligible ORR activity, the observed activity is due to the Co/N/C catalysts. Irrespective of the carbon supports (e.g., CNWs and GC), the ORR occurred from about 0.7 V for the Co/N/C catalysts. However, the catalysts on the CNWs showed larger current densities than those on the GC below a potential of 0.7 V. This result indicates that the aligned CNW support enhances the ORR activity of the Co/N/C catalysts. Although the large surface area of CNWs contributes the enhancement, the effective transport of oxygen by the vertically aligned structure also would affect it.

We have preliminary shown that the formation of non-precious metal catalysts on an aligned carbon support is effective to enhance the catalytic activity. Further improvements will be described on the fabrication and performance of the M/N/C catalysts on the CNWs.

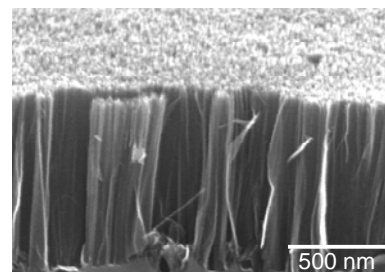


Fig. 1 SEM image of CNWs derived from annealing SiC

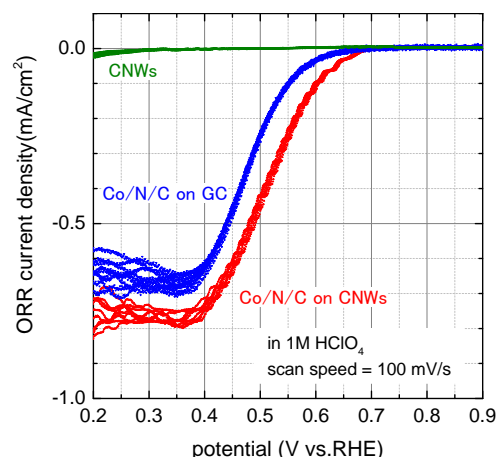


Fig. 2 ORR catalytic activity in 1 M HClO<sub>4</sub> (aq)

### References

- <sup>1</sup> R. Othman, A. L. Dicks, and Z. Zhu, *Int. J. Hydrog. Energy* **37**, 357 (2012).
- <sup>2</sup> E. Proietti, F. Jaouen, M. Lefevre, N. Larouche, J. Tian, J. Herranz, and J. P. Dodelet, *Nat. Commun.* **2** (2011).
- <sup>3</sup> M. Lefevre, E. Proietti, F. Jaouen, and J. P. Dodelet, *Science* **324**, 71 (2009).
- <sup>4</sup> G. Wu, K. L. More, C. M. Johnston, and P. Zelenay, *Science* **332**, 443 (2011).
- <sup>5</sup> Z. Q. Tian, et al., *Adv. Energy Mater.* **1**, 1205 (2011).
- <sup>6</sup> M. Kusunoki and H. Kato, *Appl. Surf. Sci.* **254**, 257 (2007).