Bottom-up design of ORR catalyst using pyridinic nitrogen containing molecules and carbon nanotubes

Moeko Furukawa [a], Riku Shibuya[a], Kotaro Takeyasu[b,c], Junji Nakamura [b,c]*

[a]*Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan*
[b]*Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan*
[c]*Tsukuba Research Center for Energy Materials Science (TREMS), University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan*
**Corresponding author: nakamura@ims.tsukuba.ac.jp*

Abstract: Nitrogen containing carbon materials have been reported to show catalytic activities such as an oxygen reduction reaction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work. In the present study, we prepared bottom-up catalysts composed of pyridinic nitrogen-containing aromatic molecules and carbon supports such as carbon nanotubes and carbon blacks. It is found that the bottom-up catalysts show ORR activities, particularly for a 1,10-phenantroline type local structure.

Keywords: oxygen reduction reaction, carbon electro-catalyst, pyridinic nitrogen

1. Introduction

Nitrogen containing carbon materials have been reported to show catalytic activities such as an oxygen reduction reaction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work [1]. We then try to prepare catalytically active carbon surfaces covered with pyridinic nitrogen-containing aromatic molecules with high density. To assemble the active sites, we have recently demonstrated that the pyridinic-N contained molecules can be used for the bottom up synthesis for the ORR catalysts [2]. That is, bottom-up catalysts composed of pyridinic nitrogen-containing molecules and carbon supports. They have identical local structures in the vicinity of pyridinic nitrogen so that one can evaluate specific activity of the molecules. In the present study, we measured the ORR activity of pyridinic nitrogen-containing molecules supported on carbon nanotubes and carbon blacks.

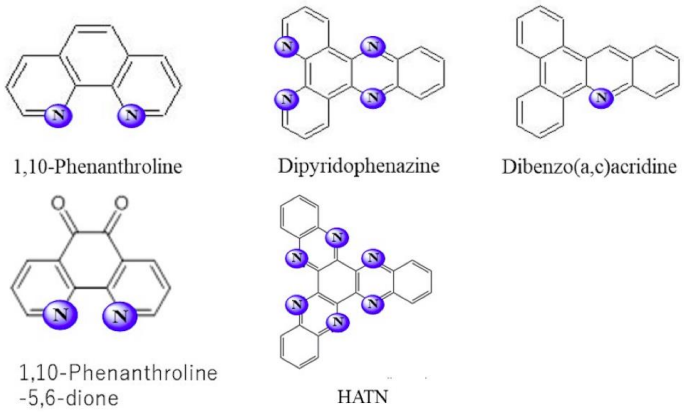

Fig. 1 Pyridinic nitrogen-containing molecules adsorbed on CNT or CB.

2. Experimental

Pyridinic nitrogen-containing molecules used were 1,10-phenanthroline, 1,10-phenanthroline-5,6-dione, dipyridophenazine, dibenzo(a,c)acridine, and HATN, as shown in Fig. 1. The bottom-up catalysts were prepared by simply immersing the carbon support materials into a catalyst solution. Solvent used was 0.1 % Nafion solution. The catalytic performances for oxygen reduction reactions (ORR) of the prepared catalysts were measured by rotating ring disc electrode (RRDE) method in acidic electrolyte (0.1 M H_2SO_4) at room temperature. The prepared catalysts were characterized by X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

Fig. 2 shows typical ORR activities for molecules adsorbed on CNT and CB. Among the molecules, 1,10-phenanthroline and dipyridophenazine on CNT showed highest activities, whose onset potentials (potentials versus RHE at a current density of 20 μA cm^{-2}) were 0.37 V and 0.35 V, respectively. On the other hand, ~ 0.15 V lower onset potentials were observed for dibenzo (a,c) acridine and HATN. This tendency suggested that 1,10-phenanthroline type local structure showed high ORR activities because dipyridophenazine also contains the local structure. The accretion of oxo group on 1,10-phenanothroline did not shift the onset potential more than 0.02 V. In terms of support materials, CNT made a greater contribution to the ORR activities than CB. The detail of the effect of the local structure in the adsorbed molecules and the support materials will be discussed.

References

[1] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Science, 2016, 351, 361-365.

[2] R. Shibuya, T. Kondo, J. Nakamura, ChemCatChem, 2018

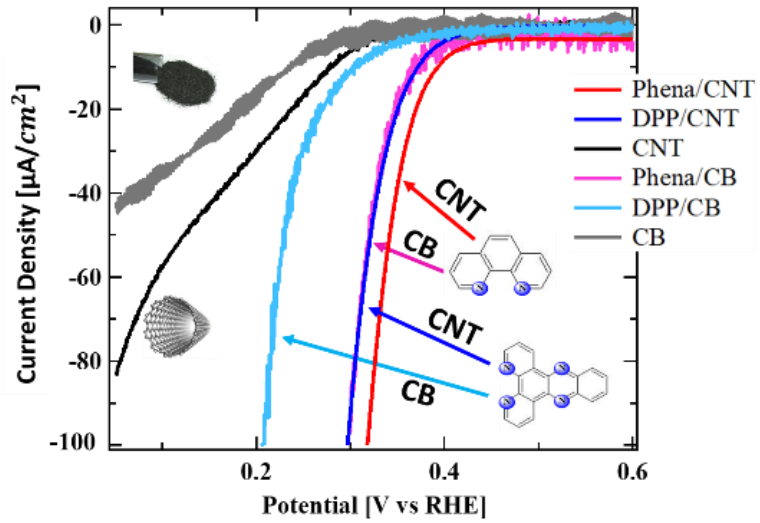

Fig. 2 ORR activities for the bottom-up synthesized catalysts using CNT or CB.