CARBON 2019
LEXINGTON, KY

NANOSCOPIC COMBINATION OF EDGE AND FLAT PLANES IN ACTIVE SITE FOR OXYGEN REDUCTION AND EVOLUTION

Jun Maruyama[1*], Shohei Maruyama[1], Tomoko Fukuhara,[1] Yuko Takao[2], Kohei Miyazaki[3]

[1]*Research Division of Environmental Technology, Osaka Research Institute of Industrial Science and Technology, 1-6-50, Morinomiya, Joto-ku, Osaka 536-8553, Japan*
[2]*Research Division of Organic Materials, Osaka Research Institute of Industrial Science and Technology, 1-6-50, Morinomiya, Joto-ku, Osaka 536-8553, Japan*
[3]*Graduate School of Global Environmental Studies, Kyoto University, Kyoto Daigaku Katsura, Nishikyo-ku, 615-8510 Kyoto, Japan*

*Presenting author's e-mail: maruyama@omtri.or.jp

Introduction

There is an increasing demand for a catalyst with high activity and durability for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) at the cathode of Zn-air batteries, which have recently attracted much attention due to its high energy density, high safety, and low production cost. We attempted to realize the high activity by forming iron-phthalocyanine (FePc)-derived carbonaceous thin film and the high stability by using the graphite basal plane as a substrate for the thin film coating. We also attempted the further activity enhancement by fine-etching of the graphite basal plane. In this study, we fundamentally examined a possibility of forming a nanoscopic three-dimensional active site for the ORR and OER by using highly-oriented pyrolytic graphite (HOPG) basal plane as a nearly ideal flat surface.

Materials and Methods

HOPG with its basal plane finely etched (HOPG-e),[1] and a commercially-available grid for transmission electron microscopy (TEM) with graphene supported on porous Si_3N_4 were used as a substrate. The FePc powder and the substrate were put inside of a crucible with a cap and heat-treated at atmospheric pressure in an Ar atmosphere at 800 ºC for 1 h to form the FePc-derived carbonaceous thin film (CFePc) on the substrate surface.[2] The HOPG and HOPG-e surfaces loaded with CFePc are labeled HOPG-CFePc, and HOPG-e-CFePc, respectively.

Results and Discussion

The TEM image of CFePc formed on graphene is shown in **Figure 1**. The black spots corresponded to iron atoms and a 2-dimensional lattice-like ordered structure was observed. Clear images were obtained particularly in the regions marked with white rectangles. The N *K*-edge X-ray absorption near-edge structure (XANES) and its simulation by the density functional theory suggested the fused FePc with the peripheral benzene ring detached, as shown in **Figure 2**. The atomic force microscope image of HOPG-e-CFePc is shown in **Figure 3**. The generation of nano- to sub-micrometer streaky and hole-like concaves were observed for the etched surface. It is reasonable to assume that the surface was homogeneously coated with the CFePc layer. Both the ORR and OER currents were increased by the CFePc coating and further increased by the surface fine-etching followed by the CFePc coating. In particular, the onset of OER occurred at a potential close to the standard electrode potential, i.e., at a very low overpotential (η). The low-η OER was

experimentally confirmed by the evolved O_2 detection and theoretically supported by simulation based on the density functional theory involving nanoscopic combination of planar Fe–N_4 unit shown in **Figure 2** and edge-oriented Fe–N_2 unit, which were detected in the Fe *K*-edge (XANES) of HOPG-e-CFePc.

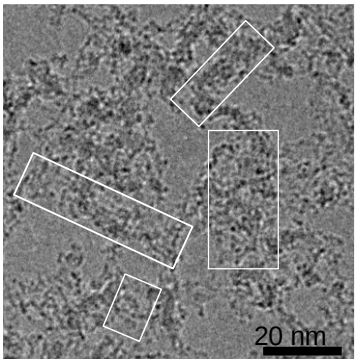

Fig.1 TEM image of CFePc on graphene

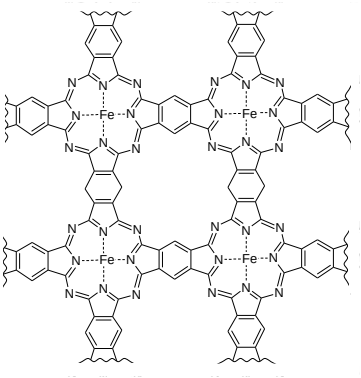

Fig. 2. Possible 2-dimensional model for CFePc based on DFT calculation results.

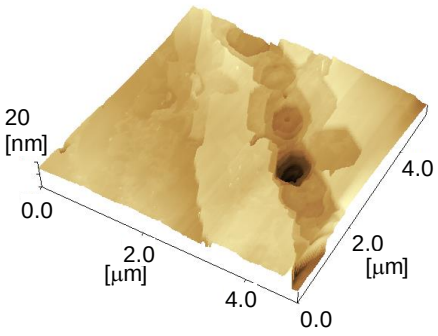

Fig. 3. AFM images of HOPG-e-CFePc.

Conclusions

The nanoscopic combination of the edge and flat planes at the active site for the ORR and OER was generated on the HOPG surface by the surface etching of the basal plane, followed by the FePc-derived carbonaceous thin film coating, which substantially enhanced both the ORR and OER. This three-dimensional active site thus showed the potential to improve the Zn-air battery efficiency and the stability, in particular, by a lower voltage for the OER.

Acknowledgment

A part of this study was conducted in the project "Advanced Research Program for Energy and Environmental Technologies," undertaken by New Energy and Industrial Technology Development Organization, Japan.

References

1. Maruyama, J., Maruyama, S., Fukuhara, T., Hanafusa, K. (2017). Efficient edge plane exposure on graphitic carbon fiber for enhanced flow-battery reactions. *J. Phys. Chem. C* 121, 24425-24433
2. Maruyama, J., Amano, T., Inoue, S., Muramatsu, Y., Yoshizawa, N., Gullikson, E.M. (2018). Carbonaceous two-dimensional lattice with FeN_4 units. *Chem. Commun.* 54, 8995-8998