



Bifunctional Catalyst

Nanoscopic Combination of Edge and Flat Planes in the Active Site for Oxygen Reduction and Evolution

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Abstract: An iron-containing carbonaceous flat plane was enriched with edges by substrate fine etching and metal oxide loading, resulting in substantial enhancement of the catalytic activity for the oxygen reduction and evolution, which was fundamentally shown using the highly oriented pyrolytic graphite basal plane as the substrate. The evolution close to the standard electrode potential was elucidated by a mechanism involving the nanoscopic edge-flat plane combination.

Introduction

The electrochemical oxygen reduction (ORR) and evolution (OER) reactions are essential reactions involved in major energy conversion devices between chemical and electrical energies, such as fuel cells, water electrolysis, and metal-air batteries. Both ORR and OER are involved as the discharge and charge reactions, respectively, in secondary metal-air batteries, typically exemplified by Zn-air batteries, which have recently attracted much attention due to their safety, low production cost, and high energy-density.^[1] An alkaline electrolyte is typically used^[2] and the ORR and OER are expressed as follows.

$$O_2 + 2H_2O + 4e^{-} \frac{\text{discharge}}{\text{charge}} 4OH^{-}$$

Both are slow reactions and cause a high overpotential (η) leading to the low energy efficiency of the Zn-air battery. Bifunctional catalysts for both reactions with a high activity and low cost are therefore required to enhance the reactions and have been studied for decades.^[3] There are a wide variety of materials that show the bifunctional catalysis; i.e., the transition metal oxides, such as MnO_x and Co₃O₄, La_{1-x}Sr_xMnO₃, NiCo₂O₄, carbon materials, and their composites with metal oxides.^[4] Most of the studies have focused on the development of new materials by introducing additional elements and changing their composition; however, little is known about the fundamental effect of the nanoscopic surface structure on the bifunctional catalysis.

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One of the earliest studies of the Zn-air batteries used carbon materials as the bifunctional catalyst.^[5] The advantages of the carbon materials are a high electron conductivity, chemical stability, and feasibility to form various structures based on various types of carbons, such as fullerene, carbon nanotubes, and graphene, which are also applicable to design the surface structure. The doping of N, P, and S atoms, and metal ions is also possible, imparting the function as catalysts. In particular, it has long been known that the metal ion coordinated by N and embedded in the carbon surface with a planar configuration (metal–N_x unit) functions as the active site for the ORR.^[6] Quite recently, the application as the OER catalyst was reported;^[7–9] however, the microscopic three-dimensional surface structure was not considered.

This study thus highlights the effect of the surface structure on both the ORR and OER by exploiting the potential of the carbon materials to form various structures. We used the basal plane of the highly-oriented pyrolytic graphite and generated nanoscopic etched structures on it. The basal plane is assumed to be an almost ideal flat surface suitable for fundamental investigations and for enhanced durability for the OER as the substrate for the metal-N_x unit by imparting a planar configuration and reducing the structural disorder.^[10,11] We found a substantial enhancement effect of the nanoscopic combination of the basal and edge planes on both reactions, as well as on the onset of the OER at a very low η , which was clarified and confirmed for the first time in this study using an O₂ detecting technique.

Results and Discussion

The surface etching of the HOPG basal plane was enabled by coating with a carbonaceous thin film derived from cobalt phthalocyanine (CoPc) and thermal oxidation based on our recent study.^[12] Co oxide nanoparticles were generated during the thermal oxidation and functioned as a catalyst for the fine carbon surface etching, which were easily removed by an acid treatment afterwards. The Fe–N_x unit was imparted by coating

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the FePc-derived carbonaceous thin film and treating it with an acid to remove the soluble Fe species. MnO_x was deposited to form another type of edge at the periphery of the deposited particle. The low- η OER was then observed for the combination of the Fe–N_x unit on the basal and edge planes and the MnO_x edge, which also showed a synergetic effect for the ORR as well.

The surface etching (treatment A, denoted by "–e"), FePcderived thin film coating (treatment B, denoted by "–CFePc"), and MnO_x loading (treatment C, denoted by "–Mn") were carried out in this order and all of the eight combinations of execution and non-execution of each treatment were investigated as an ORR-OER bifunctional electrode. Table 1 lists the serious of HOPG electrodes and their surface compositions measured by X-ray photoelectron spectroscopy.

Table 1. Combination of HOPG surface treatment displayed in label and surface composition. $^{[a,b]}$

	Surface concentration [atom %]			
	С	0	Ν	Mn
HOPG	98.74	1.26		
HOPG-Mn	94.97	4.08		0.95
HOPG-CFePc	96.92	1.98	0.99	
HOPG-CFePc-Mn	92.66	5.76	0.23	1.33
HOPG-e	98.13	1.77	0.10	
HOPG-e-Mn	96.87	2.40	0.21	0.52
HOPG-e-CFePc	96.16	3.21	0.61	
HOPG-e-CFePc-Mn	94.35	4.11	0.33	1.18

[a] The XPS spectra are shown in Figure S2. [b] Although Fe 2p peaks were detected, their intensities were low and insufficient for reliable determination of the surface concentration.

Figure 1 shows typical atomic force microscopy (AFM) images of the electrode surface. The generation of nano- to sub micrometer streaky and hole-like concaves was observed for the etched surface. Almost no change in the Raman spectrum after the etching (Figure S1) indicated that the accompanying edge plane generation occurred only in the vicinity of the surface and the D band intensity was below the detection limit. Treatment B formed a FePc-derived carbonaceous flat film



Figure 1. AFM images of HOPG-CFePc, HOPG-CFePc-Mn, HOPG-e-CFePc, and HOPG-e-CFePc-Mn. AFM images of all the samples are shown in Figure S3.

(CFePc) on the basal plane of the HOPG with a step structure, which was retained due to the sufficient thinness of the film. Small bright dots in the AFM images were caused by the Fe aggregates, which were generated by the FePc decomposition and present below the carbonaceous thin film blocking the acid access. Particulate or sheet-like MnO_x was generated by the treatment C.

The local structures around Fe and Mn were investigated by measurements of the X-ray absorption fine structures. Figure 2 shows the Fe and Mn *K*-edge X-absorption near edge fine structure (XANES) spectra for HOPG-e-CFePc-Mn. In spite of the insufficient peak intensity of the Fe 2p XPS spectrum, a clear absorption peak was obtained for the Fe *K*-edge spectrum measured at a low X-ray incident angle and a fluorescence mode. The experimentally obtained Fe *K*-edge XANES spectrum well fit the simulated curve including those for the Fe–N₄ and Fe–N₂ models. The Fe–N₂ structure was previously proposed^[13] and probably present at the end of the basal plane, i.e., at the immediate vicinity of the edge plane.^[14] Further detailed experimental results to show the Fe–N₂ structure are being obtained and will be reported in another paper.



Figure 2. (a) Fe and (b) Mn *K*-edge XANES spectra for HOPG-e-CFePc-Mn. The simulated Fe *K*-edge XANES curve was obtained by the weighted addition of those for FePc, Fe foil, and those calculated by using FEFF8.2 for the five and three-atom models consisting of a Fe atom surrounded by four nitrogen atoms in a square-planar coordination (Fe–N₄ model) and two nitrogen atoms in an isosceles right triangle configuration (Fe–N₂ model). The simulated Mn *K*-edge XANES curve was obtained by the weighted addition of those for MnOOH and Mn(CH₃CO₂)₂.

The experimentally obtained Mn K-edge XANES spectrum well fit the curve obtained by the weighted addition of the spectra for MnOOH and Mn(CH₃CO₂)₂, indicating that the ox-





ides generated through oxidation of $Mn(CH_3CO_2)_2$ adsorbed on the HOPG surface by $KMnO_4$ was MnOOH.

The relationships between the ORR current and electrode potential for these series of electrodes are shown in Figure 3a. The CFePc on the HOPG substantially decreased η to enhance the catalytic activity for the ORR. The MnOOH loaded on it further enhanced the peak current, which was attributed to the synergetic effect of the CFePc and MnOOH because almost no enhancement was observed at HOPG-Mn. The effect was explained by the catalytic effect of MnOOH for the electrochemical reduction or the decomposition of the ORR intermediate, HO₂⁻, generated on the CFePc to increase the overall number of electrons involved in the ORR per O₂ molecule.^[15] The effect of the surface etching on the ORR enhancement was observed, in particular, in the low potential region. The enhancement was attributed to the capture and reduction of HO_2^- at the edge plane,^[16] implying the significant effect of the surface structure on the ORR.



Figure 3. Relationships between currents and electrode potential for (a) ORR and (b) OER in O_2 -saturated 1 mol dm⁻³ KOH at 25 °C. The potential scan rate was 10 mV s⁻¹. The sign of the reduction (cathodic) current was taken as negative. The reference electrode was Hg/HgO/1 mol dm⁻³ KOH.

Figure 3b shows the relationships between the OER current and the electrode potential. The OER current was clearly observed at HOPG-Mn, in particular, in the high potential region, which was in agreement with previous reports.^[17,18] It should be noted that the onset of the OER was 0.3 V for HOPG-e-CFePc, indicating the occurrence of the OER at a significantly low η , because the standard electrode potential in a solution of pH = 14 is 0.401 V vs. standard hydrogen electrode, i.e., 0.28 V vs. Hg/HgO/1 mol dm⁻³ KOH. This low- η OER phenomenon was also observed at HOPG-CFePc-Mn and the OER current in the low η region was enhanced by the etching (HOPG-e-CFePc-Mn). The essential role of Fe was indicated by the lower activities for the ORR and OER at the HOPG coated with the metal-free-Pc-derived carbonaceous thin film than those containing Fe (Figure S4).

The low- η OER has been reported;^[19–22] however, it has not been fully clarified whether the current was caused by the OER, or by electric double-layer charging and oxidation of the electrode itself; i.e., the carbon surface oxidation and the MnOOH oxidation and dissolution.^[23] We thus attempted to electrochemically detect the evolved O₂ by placing a Pt wire over the HOPG-CFePc-Mn electrode for the reduction of O₂ diffused from the electrode surface (Figure S5a, Figure S5b). In this combinedelectrode system, the low- η OER phenomenon was reproduced (Figure S5c). A reduction current at the Pt wire was observed in accordance with the OER current (Figure S5d). Because the potential setting of the Pt wire (0 V) and the electrolyte concentration excluded the possibilities of the reduction of the oxidized carbon species and the Mn dissolution in the low- η OER region, respectively, the reduction current was related to the O₂ evolved at the HOPG-CFePc-Mn electrode. This result indicated that the oxidation current observed in the low- η region in Figure 3b was caused by the OER, which was confirmed for the first time. It should be noted here that this study was focused on the clear demonstration of the effect of the surface structure using the HOPG basal plane as an almost ideal flat surface that was suitable for the fundamental study in spite of the low specific surface area leading to the low current density.

In the series of electrodes examined in this study, the low- η OER was observed for HOPG-e-CFePc, HOPG-CFePc-Mn, HOPG-e-CFePc-Mn, and not for the other electrodes. The requirement for the low- η OER occurrence was therefore the combinations of the CFePc coating–surface etching or CFePc–MnOOH. The nearly equivalent OER current at HOPG-e-CFePc and HOPG-CFePc-Mn suggested a similar OER mechanism. The structure in common for the two combinations was the presence of the flat CFePc plane and the edge. The latter was derived from the step of the HOPG surface or the MnOOH particle loaded on the CFePc thin film.

Quite recently, a two-dimensional lattice-like π -conjugated structure parallel to the graphene plane was found in CFePc using transmission electron microscopy, measurement of the N K-edge X-ray absorption near-edge structure (XANES), and its simulation using the density functional theory (DFT).^[24] The experimental N K-XANES characteristics were well explained by the simulation based on the FePc fused dimeric model. It would be reasonable to assume that a part of the structure was chipped in CFePc at the edge of the HOPG surface to generate the Fe-N₂ unit based on the Fe K-XANES spectrum. We thus formulated a model to represent the structure close to the edge by the chipped FePc dimer with the Fe-N₂ unit, which was superimposed on the FePc dimer representing the flat plane of the lower part of the step (Figure 4, C1). The energy profile of the OER was then evaluated based on the DFT calculation (Supporting information) using the model and a newly postulated mechanism to explicate the low- η OER phenomenon.







Figure 4. (a) Energy profiles obtained by DFT calculations based on conventional reaction pathway involving planar active site (b, blue line) and reaction pathway involving combination of edge and planar active sites (c, red line). The number near the intermediate structure model indicates the corresponding reaction step in the energy profile.

A favorable energy profile was obtained with a lower η for the reaction pathway involving both the Fe–N₄ and the Fe–N₂ units than for the conventional pathway involving only the planar active site (Figure 4). Because the combination of the CFePc flat plane and the edge of the loaded MnOOH was the similar situation to the combination of the flat and edge plane on HOPG-e-CFePc, HOPG-CFePc-Mn was anticipated to enable the low- η OER, although the detailed structure of the edge is unclear at present and its investigation would require further extensive studies.

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, the FePc-derived carbonaceous thin film coating, and the MnOOH deposition, which substantially enhanced both the ORR and OER. The XANES spectrum showed the Fe–N₄ and Fe–N₂ units on the step-enriched surface; the latter structure of which was assumed to be present at the edge. The low- η OER was experimentally confirmed by the evolved O₂ detection and theoretically supported by the DFT calculations based on the new

mechanism involving the three-dimensional active site. The combination of the edge and flat planes thus showed the potential to improve the Zn-air battery efficiency and the stability, in particular, by a lower voltage for the OER.

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^[1] Y. Li, H. Dai, Chem. Soc. Rev. 2014, 43, 5257-5275.

^[2] Z.-L. Wang, D. Xu, J.-J. Xu, X.-B. Zhang, Chem. Soc. Rev. 2014, 43, 7746– 7786.





- [3] K. Kinoshita, Electrochemical Oxygen Technology, John Wiley & Sons, New York, 1992.
- [4] D. U. Lee, P. Xu, Z. P. Cano, A. G. Kashkooli, M. G. Park, Z. Chen, J. Mater. Chem. A 2016, 4, 7107–7134.
- [5] A. J. Appleby, G. Crepy, G. Feuillade, Power Sources 1977, 6, 549-568.
- [6] M. Shao, Q. Chang, J.-P. Dodelet, R. Chenitz, Chem. Rev. 2016, 116, 3594– 3657
- [7] H. Fei, J. Dong, Y. Feng, C. S. Allen, C. Wan, B. Volosskiy, M. Li, Z. Zhao, Y. Wang, H. Sun, P. An, W. Chen, Z. Guo, C. Lee, D. Chen, I. Shakir, M. Liu, T. Hu, Y. Li, A. I. Kirkland, X. Duan, Y. Huang, *Nat. Catal.* **2018**, *1*, 63–72.
- [8] J. Wang, F. Ciucci, Small 2017, 13, 1604103.
- [9] S. Ibraheem, S. Chen, J. Li, Q. Wang, Z. Wei, J. Mater. Chem. A 2019, 7, 9497–9502.
- [10] J. Maruyama, J. Okamura, K. Miyazaki, Y. Uchimoto, I. Abe, J. Phys. Chem. C 2008, 112, 2784–2790.
- [11] C. Domínguez, F. J. Pérez-Alonso, M. A. Salam, S. A. Al-Thabaiti, M. A. Peña, F. J. García-García, L. Barrioa, S. Rojas, *Appl. Catal. B* **2016**, *183*, 185–196.
- [12] J. Maruyama, S. Maruyama, T. Fukuhara, K. Hanafusa, J. Phys. Chem. C 2017, 121, 24425–24433.
- [13] M. Lefèvre, J. P. Dodelet, P. Bertrand, J. Phys. Chem. B 2002, 106, 8705– 8713.
- [14] Y. Wang, D. Adekoya, J. Sun, T. Tang, H. Qiu, L. Xu, S. Zhang, Y. Hou, Adv. Funct. Mater. 2019, 29, 1807485.

- [15] Y. Miyahara, K. Miyazaki, T. Fukutsuka, T. Abe, J. Electrochem. Soc. 2014, 161, F694–F697.
- [16] J. Maruyama, M. Yamamoto, T. Hasegawa, S. Iwasaki, Z. Siroma, A. Mineshige, *Electrochim. Acta* 2013, 90, 366–374.
- [17] M. M. Najafpour, G. Renger, M. Hołyńska, A. N. Moghaddam, E.-M. Aro, R. Carpentier, H. Nishihara, J. J. Eaton-Rye, J.-R. Shen, S. I. Allakhverdiev, *Chem. Rev.* 2016, 116, 2886–2936.
- [18] Y. Gorlin, B. Lassalle-Kaiser, J. D. Benck, S. Gul, S. M. Webb, V. K. Yachandra, J. Yano, T. F. Jaramillo, J. Am. Chem. Soc. 2013, 135, 8525–8534.
- [19] Y. Gorlin, T. F. Jaramillo, J. Am. Chem. Soc. 2010, 132, 13612-13614.
- [20] J. T. Mefford, X. Rong, A. M. Abakumov, W. G. Hardin, S. Dai, A. M. Kolpak, K. P. Johnston, K. J. Stevenson, *Nat. Commun.* **2016**, *7*, 11053.
- [21] T. Takeguchi, T. Yamanaka, H. Takahashi, H. Watanabe, T. Kuroki, H. Nakanishi, Y. Orikasa, Y. Uchimoto, H. Takano, N. Ohguri, M. Matsuda, T. Murota, K. Uosaki, W. Ueda, J. Am. Chem. Soc. 2013, 135, 11125–11130.
- [22] J. Zhang, Z. Zhao, Z. Xia, L. Dai, Nat. Nanotechnol. 2015, 10, 444–452.
- [23] W. Wang, J. Luo, S. Chen, Chem. Commun. 2017, 53, 11556-11559.
- [24] J. Maruyama, T. Amano, S. Inoue, Y. Muramatsu, N. Yoshizawa, E. M. Gullikson, Chem. Commun. 2018, 54, 8995–8998.

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