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Enhancement of Oxygen Reduction Activities by Pt Nanoclusters Decorated on Ordered Mesoporous Porphyrinic Carbons

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Abstract

The high cost of Pt-based membrane electrode assembly (MEA) is a critical hurdle for the commercialization of polymer electrolyte fuel cells (PEFCs). Recently, non-precious metal-based catalysts (NPMCs) have demonstrated much enhanced activity but their oxygen reduction reaction (ORR) activity is still inferior to that of Pt-based catalyst resulting in much thicker electrode in the MEA. For the reduction of mass transport and ohmic overpotential we adopted a new concept of catalyst that combines ultra-low amount of Pt nanoclusters with metal-nitrogen (M-N_x) doped ordered mesoporous porphyrinic carbon (FeCo-OMPC(L)). The 5 wt% Pt/FeCo-OMPC(L) showed a 2-fold enhancement in activities compared to a higher loading of Pt. Our experimental results supported by first-principal calculations indicate that trace amount of Pt nanoclusters on FeCo-OMPC(L) significantly enhances the ORR

28 activity due to its electronic effect as well as geometric effect from the dual active
29 sites. In terms of fuel cell commercialization, this class of catalyst is a promising
30 candidate due to its limited use of Pt in the MEA.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been recognized as an ideal electrical power system due to its eco-friendly and highly efficient energy conversion characteristics. However, the development of cost effective electrocatalyst by reducing or excluding the platinum in the fuel cell is one of the main challenges for the practical application of PEFCs.¹⁻⁷ After Jasinski's pioneering work about notable oxygen reduction reaction (ORR) activity on Co-phthalocyanine in alkaline medium,⁸ the class of non-precious metal-based catalysts (NPMCs) has been receiving attention, especially the nitrogen coordinated transition metal (Fe and/or Co) doped carbon compounds (M-N_x-C).⁹⁻⁴⁰ The development of NPMCs with remarkable catalytic activity and stability towards the ORR rivaling those of Pt-based catalysts has been a challenging task as it requires fine tuning the composition of transition metal and nitrogen coordination number. The ORR activity of M-N_x-C catalysts strongly depends on the types of nitrogen and transition metal sources, heat treatment temperature, and graphiticity and morphology of carbon support, etc.¹⁷⁻⁴⁰ Even though the ORR activity and durability in alkaline media have been improved via the optimization of the synthetic process,³³⁻³⁴ the ORR activity in acid medium is still inferior to Pt-based electrocatalysts. Recently, Dodelet *et al.*⁴¹ and Joo *et al.*⁴⁰ reported high ORR activity for NPMC, i.e. Fe- and/or Co-N-C catalyst and self-supported ordered mesoporous porphyrinic carbon (OMPC), which shows a commensurate ORR activity with Pt/C in acidic electrolyte using rotating disk electrode (RDE).

In terms of membrane electrode assembly (MEA) fabrication, however, NPMC-based MEA has around ten times thicker catalyst layer than that of conventional Pt/C MEA⁴¹ due to high catalyst loading resulting in increased mass transport resistance as

well as electrical resistance. The high ORR activity observed at a half-cell configuration could not be observed in NPMC-based MEA. Hence, decreasing the catalyst loading in the unit area may be important to obtain consistent performance in MEA, as shown in the RDE evaluation.

In this study, we evaluate a new concept that can enhance the ORR activity via using a low-amount of platinum nanocluster on NPMC (Pt/NPMC hybrid catalyst). The Pt/NPMC hybrid catalyst shows much enhanced ORR activity due to its electronic effect and also due to the geometric effect caused from dual active sites. The density-functional-theory (DFT) calculations suggest the mechanism of Pt cluster formation on the NPMC and also explain its positive effect on ORR that is constrained by its loading.

2. Experimental Section

2.1. Material synthesis

Nitrogen coordinated transition metal based ordered mesoporous carbon was synthesized by a nanocasting method.^{40;42-44} Ordered mesoporous silica (OMS(L)) templates with ca. 20 nm large mesopores were well mixed with 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine iron(III) chloride (Fe-TMPPCl) and 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine cobalt(II) (Co-TMPP) as a metalloporphyrinic precursors, then the mixture was pyrolyzed at 800 °C for 3 h in N₂ atmosphere. The silica templates and metal particles in the composite were removed by washing in 10% HF solution, then the resulting FeCo-OMPC(L) was washed with deionized water for several times, followed by drying at 80 °C overnight. The OMPC(L) without transition metals was also prepared with 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H porphyrin (TMPPH) and OMS(L) template under the same pyrolysis condition as described before.⁴⁰ Pt/FeCo-OMPC(L) electrocatalysts with various Pt loading were prepared by sodium borohydride (NaBH₄) reduction method.⁴⁵⁻⁴⁷ FeCo-OMPC(L) was well dispersed in DI-based H₂PtCl₆ solution, then excess of 0.5 M NaBH₄ solution was added drop by drop into the mixture with vigorous stirring for the complete reduction of the PtCl₆²⁻ ion to Pt metal. The mixture was stirred for 24 h at ambient temperature, and washed with excess deionized water and dried at 80 °C for 24 h. For the direct comparison of ORR activities, catalysts that have the same Pt loading were prepared by using FeCo-OMPC(L), OMPC(L) and Vulcan XC-72 as supports using the same procedures.

2.2. Characterization

The morphology and distribution of Pt nanoclusters in the Pt/FeCo-OMPC(L), Pt/OMPC(L), and Pt/C catalysts were examined by field emission transmission

electron microscope (FE-TEM, Tecnai TF30 ST, FEI). High-angle annular dark field (HAADF) images and EDS-mapping of FeCo-OMPC(L) and Pt/FeCo-OMPC(L) was observed by Titan Double Cs corrected TEM (Titan cubed G2 60-300, FEI). X-ray diffraction (XRD, D/MAX-2500, RIGAKU) patterns of the prepared catalysts were obtained to calculate the Pt particle size using Scherrer's equation. The surface area and the pore size distribution of the catalysts were measured by N₂ adsorption-desorption isotherms (ASAP-2020, Micrometrics). The metal contents of Pt, Fe, and Co were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the composition of C and N elements was examined with elemental analyzer (EA). X-ray photoelectron spectroscopy (XPS) was performed on AXIS NOVA with monochromated Cu K_α X-ray source.

In situ electrochemical cell for X-ray absorption spectroscopy (XAS) analysis was specially designed to operate at potentiostatic mode. Teflon based *in situ* XAS cell was mounted on a goniometer stage passivated implanted planar silicon (PIPS, Canberra Co.) and the fluorescence detector was positioned on top of the electrochemical cell (Fig. S7). XAS signals of Fe k-edge, Co k-edge, and Pt L₃-edge for the catalysts were recorded in fluorescence mode on the BL10C beam line at the Pohang Light Sources (PLS) with a ring current of 200 mA at 3.0 GeV. The monochromatic X-ray beam could be obtained using a liquid nitrogen-cooled Si (111) double crystal monochromator. Working electrode for the *in situ* XAS analysis was prepared by spray coating the Nafion containing catalyst ink onto the Nafion membrane. Precise energy calibration was simultaneously carried out for each measurement with each reference metal foil placed in front of the third ion chamber using partially-bypassed X-ray beam. The data processing of the experimental spectra

to normalized XANES and Fourier-transform (FT) EXAFS were performed through the standard XAFS procedure.⁴⁸⁻⁵¹

2.3. Electrochemical analysis

The ORR kinetics on Pt/FeCo-OMPC(L) catalysts were examined using rotating disk electrode (RDE) method in a typical three-electrodes cell with a Pt counter electrode and hydrogen reference electrode (Gaskatel GmbH, Germany). The catalyst ink was prepared by sonication of 30 mg of Pt/FeCo-OMPC(L) in 1.2 ml of ethanol and DI mixture with 0.02 ml of 5wt% Nafion solution. A catalyst ink was pipetted onto a glassy carbon (GC, 0.196 cm²) disk electrode mounted on the inverted rotator under rotating at 300 rpm to make uniform thin film, then dried under rotation for 20 min at room temperature.⁵² The total amount of catalyst loading was 84 $\mu\text{g}_{\text{catalyst}}/\text{cm}^2$, but the Pt mass loading was dependent on the Pt contents in the Pt/FeCo-OMPC(L). The catalyst film coated on the GC electrode was cleaned and activated in nitrogen saturated 0.1 M HClO₄ electrolyte by cyclic voltammetry between 0 V and 1.2 V vs. RHE with a scan rate of 100 mV/s for 50 cycles until obtaining quasi steady-state I-V characteristic. The ORR kinetics was examined by linear sweep voltammetry (LSV) using anodic sweep from 0.05 V to 1.15 V vs. RHE with a sweep rate of 10 mV/s in oxygen saturated 0.1 M HClO₄ as a function of RDE rotation rates from 400 rpm to 2,500 rpm.

2.4. DFT calculation

Periodic plane-wave DFT calculations were performed using the Vienna ab initio simulation package (VASP)⁵³⁻⁵⁴ with projector augmented wave (PAW) potentials⁵⁵ and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.⁵⁶ The spin-polarization method was used in the calculations to correctly account for magnetic properties. Monkhorst-Pack⁵⁷ mesh **k**-points of (3 × 3 × 3) and (3 × 3 × 1) for bulk

and surface calculations, respectively, were used. The plane-wave cutoff energy was
 optimized at 415 eV. To describe the interaction between Pt cluster and surface,
 adsorption energy is defined as $E_{\text{ads}} = E[\text{Pt}_n/\text{surface}] - E[\text{Pt}_n] - E[\text{surface}]$, where
 $E[\text{Pt}_n/\text{surface}]$, $E[\text{Pt}_n]$, and $E[\text{surface}]$ are the calculated electronic energies of
 adsorbed Pt_n on a surface, pure Pt_n cluster, and a clean surface, respectively. Also, we
 calculated the binding energy of atomic oxygen (BO) as a descriptor for scaling the
 ORR activity.⁵⁸⁻⁶⁰ BO is defined as $\text{BO} = E[\text{O}/\text{surface}] - E[\text{surface}] - E[\text{O}]$, where
 $E[\text{O}/\text{surface}]$ and $E[\text{O}]$, respectively, are the calculated electronic energies of
 adsorbed oxygen atom on a surface and a triplet oxygen atom. Since the topmost
 layer's Co metal center of the surface model of Pt/FeCo-OMPC(L) (Fig. S3) was
 replaced by Pt to support the experimental observation using the EXAFS analysis, we
 compared BO only on the Fe metal center. The vacancy formation energy of the metal
 center⁶¹ is defined as $E_{\text{M-vac}} = E[\text{d-surface}] + E[\text{M}] - E[\text{p-surface}]$, where d-surface
 and p-surface are the surfaces with and without an M vacancy ($\text{M} = \text{Co}$ or Fe). In this
 study, we used gas-phase atomic metals' energies by considering the number of their
 unpaired electrons. Incorporation energy of Pt into the vacancy of the metal centers is
 calculated by $E_{\text{Pt-incorp}} = E[\text{Pt-surface}] - E[\text{Pt}] - E[\text{d-surface}]$, where Pt-surface is the
 surface after incorporation of Pt into the M vacancy. Similar to the previous study,⁴⁰
 the surface calculations on the perfect FeCo-OMPC(L) surface were first carried out
 on a C, N, and M-terminated (0001) plane (120 C, 12 N, 14 O, 2 Fe, 2 Co, and 2 H
 atoms) based on its bulk structure (Fig. S4) with a vacuum space of 10 Å. Only the
 bottom bilayer of the 2-layer FeCo-OMPC(L) surface was fixed, and the top bi-layer
 and the adsorbates were fully relaxed. Then, the M metal center on the topmost layer
 was removed and replaced by Pt to examine the vacancy formation and incorporation
 energies.

3. Results and Discussion

Figure 1(a) shows schematic of the synthetic procedure of Pt/FeCo-OMPC(L) via nanocasting method using large pore OMS(L) hard template (Fig. 1(b)) and NaBH₄ reduction. EDS mapping images for FeCo-OMPC(L) (Fig. 1(e)) show uniformly distributed Fe, Co, and N elements in the mesoporous carbon structures with a 7-8 nm pore size (Fig. 1(c)). The FeCo metallic nanoparticles were removed by the HF washing procedure. The final FeCo-OMPC(L) consisted of 1.63 wt% Fe, 1.47 wt% Co, and 6.8 wt% N, as summarized in Table 1. Pt nanoclusters were well distributed on FeCo-OMPC(L) as shown in Fig. 1(d). EDS mapping images for Pt/FeCo-OMPC(L) catalyst as shown in Fig. 1(f) clearly demonstrates the presence of Fe, Co and N elements along with some Pt clusters. The average Pt particle sizes calculated with Pt (111) diffraction peaks from XRD were 2.1 nm for Pt/FeCo-OMPC(L), 3.5 nm for Pt/OMPC(L), and 6.8 nm for Pt/C, respectively (Table S1). Pt lattice fringe was observed with (111) spacing of 2.27 Å (Pt_{111, bulk}=2.26 Å) that is in good agreement with the 2.26 Å calculated from Pt(111) diffraction peaks. The metal contents in the Pt/FeCo-OMPC(L) catalysts were summarized in Table 1. The Fe, Co, and N elemental composition shows a slight change in weight content before and after Pt loading by NaBH₄ reduction.

Figure 2(a) shows the ORR polarization curves for the as-prepared catalysts measured in 0.1 M HClO₄ using the RDE technique. The half-wave potential on Pt/FeCo-OMPC(L) was 858 mV vs. RHE which was 13 mV and 103 mV higher than that of Pt/OMPC(L) and Pt/C catalysts, respectively. The Pt/FeCo-OMPC(L) showed 1.4 and 8.3-fold enhanced kinetic activity compared to Pt/OMPC(L) and Pt/C at 0.9 V vs. RHE, respectively (Table S1). The specific activity and mass activity for Pt/FeCo-OMPC(L) were also improved by a factor of 2 and 7 relative to those of Pt/OMPC(L)

and Pt/C at 0.9 V, respectively (Fig. 2(b)). This change in ORR activity is clearly due to interaction between Pt nanoclusters and the support. The ORR activity of the support catalysts followed the same order; FeCo-OMPC(L) > OMPC(L) > Vulcan XC-72 (VC) (Fig. S1).

A substantial increase in the ORR activity was observed with the introduction of Pt nanoclusters on the FeCo-OMPC(L) (Fig. 3(a)). The positive shift of half-wave potential ($E_{1/2}$) was an evidence for the enhancement of ORR activity with the different Pt loading on the FeCo-OMPC(L) support. The mass transport resistance corrected ORR kinetics increased by a factor of 9 for 5 wt% Pt/FeCo-OMPC(L) compared to that of FeCo-OMPC(L) at 0.9 V vs. RHE. When the Pt-based mass activity was compared with commercial 40 wt% Pt/C catalyst, 5 wt% Pt/FeCo-OMPC(L) showed ca. 2-fold enhanced mass activity at 0.9 V as shown in Fig. 3(b). Electrochemical surface area (ECSA) of Pt measured by CO stripping increased with Pt metal loading, however, the overall ORR activity was not linearly improved in accordance with the amount of the Pt nanoclusters on the FeCo-OMPC(L).

The above results suggest that the enhancement of the ORR activity on Pt/FeCo-OMPC(L) can be attributed to not only dual active sites but also the electronic effect between Pt nanoparticles and FeCo-OMPC(L). Prior to figuring out the electronic effect, we carefully considered the dual active site effect originating due to the loading of Pt on FeCo-OMPC(L) support. The high surface area of FeCo-OMPC(L) is one of the main factors for the high activity towards the ORR. However, we did observe that a surface area of the Pt/FeCo-OMPC(L) catalysts decreased from 970 to 458 m²/g with an increase in Pt loading, as plotted in Fig. 4. Decrease in the surface area of Pt/FeCo-OMPC(L) can be explained by blocking of the mesopores and micropores in the FeCo-OMPC(L) by 2-3 nm Pt nanoclusters as well as by the

different density of materials. Total pore volume of the catalysts was also decreased from 1.78 to 1.06 cm³/g with an increase in the Pt loading amount. In other words, the activity loss of the 10 wt% Pt/FeCo-OMPC(L) may be caused by the decrease of the absolute number of active site. Therefore, the activity enhancement due to the increase in Pt loading was limited by the loss of FeCo-OMPC(L) active area caused by the increase in the number of Pt nanoclusters.

In order to understand the electronic effect between the Pt nanoclusters and transition metals (Fe and/or Co) or N in FeCo-OMPC(L) we carried out XPS, *in situ* EXAFS analyses and DFT calculations. Figure 5 shows the XPS result for the FeCo-OMPC(L) and Pt/FeCo-OMPC(L) catalysts. The N 1s XPS spectrum for all catalysts indicate three dominant nitrogen species at 398.6, 400.1, and 401.5 eV associated with pyridinic N (N1), pyrrolic N (N2), and graphitic N (N3), respectively.²⁵ Binding energy (BE) shift to lower energy was observed for the graphitic N (N3) for 5 wt% Pt/FeCo-OMPC(L) which is associated with modification of electronic structure of N site binding with Fe or Co. In contrast, no binding energy shift was examined for pyridinic N (N1) and pyrrolic N (N2) peaks for the catalysts. As the Pt loading increased, lower shift of BE for Pt 4f_{7/2} was observed indicating an increase in Pt-Pt interaction. The XPS results showed that the electronic structures of Pt nanoclusters on FeCo-OMPC(L) were modified by N elements connected with transition metals in the FeCo-OMPC(L).

We investigated the effect of Pt nanoclusters on the electronic structure of the FeCo-OMPC(L) with *in situ* XAFS analysis. *In situ* XAFS analysis was performed at constant potential mode (0.3 V vs. RHE) to eliminate the oxygen molecule coordinated with the central Fe and/or Co in the axial direction and the surface of Pt in the Pt/FeCo-OMPC(L). The XANES spectra revealed that the square planar D_{4h}

structure of Co-TMPP and Fe-TMPPCl compounds was broken down or distorted in the FeCo-OMPC(L) catalyst during the pyrolysis process at high temperatures (Fig. S2). The FT EXAFS for Fe k-edge, Co k-edge of FeCo-OMPC(L) indicated no existence of Fe or Co metallic phase in the FeCo-OMPC(L) structure which is in good agreement with the TEM-EDS mapping images (Fig. 6(b) and 6(c)). There is no evident FT peaks related with Pt-TM coordination (TM=Fe, Co), whereas Pt-N coordination was observed at around 1.93 - 2.01 Å from FT EXAFS for Pt L₃-edge, as shown in Fig. 6(a). The peak intensity for Pt-N coordination decreased with an increase in Pt amount in the Pt/FeCo-OMPC(L). This means that the Pt nanoclusters are mainly positioned at near N-site and the interaction between Pt nanoclusters and N becomes weaker with an increase in the Pt loading in the Pt/FeCo-OMPC(L) catalysts. A slight elongation of Fe-N distance was observed, whereas the Co-N distance had no big change with Pt contents.

To support our experimental observations, we carried out DFT calculations using the FeCo-OMPC(L) bulk structure consisting of 152 atoms (120 C, 12 N, 14 O, 2 Fe, 2 Co, and 2 H). As discussed earlier, the EXAFS analysis clearly revealed no interaction between Pt and the metal centers on Pt/FeCo-OMPC(L) catalyst. To propose a plausible model and mechanism for the Pt nanocluster formation on FeCo-OMPC(L), we prepared the FeCo-OMPC(L) bulk structure, similar to the previous study (Fig. S4).⁴⁰ The model using the PBE exchange-correlation functional is in good agreement with the EXAFS and HRTEM results, such as the interlayer distance (Expt.: 4.77 Å and DFT: ~4.5 Å).⁴⁰ To match with the averaged coordination number of M-N (N = 3.3) for FeCo-OMPC(L) in Table 2, we kept N = 3 by removing one coordinated N with each metal center. Also, the M-N distances of the bulk model are in agreement with experiment (Co-N: 1.84 Å versus 1.76 Å and Fe-N: 1.83 Å versus

269 1.74 Å) (Table 2 and S2). Using the bulk structure, the C, N, Fe, and Co-terminated
 270 (0001) surface was generated for the surface calculations (Fig. S3). Then, we
 271 calculated the vacancy formation energies for the metal centers. As summarized in
 272 Table S2, the Co site can be more easily removed than the Fe site (6.09 eV/atom
 273 versus 6.74 eV/atom, respectively). Especially, the strong incorporation strength of Pt
 274 into the vacancy indicates that the first step of the Pt nanocluster formation on FeCo-
 275 OMPC(L) may be the incorporation process on the surface vacancy after leaching out
 276 of unstable surface metal centers. The essential energy can be provided by the
 277 exothermic reduction reaction using NaBH₄ as discussed in the experimental section.
 278 We observed that the Fe-N distance is lengthened by 2.2 % after the addition of Pt
 279 (DFT: 1.84 Å versus 1.87 Å and Expt.: 1.74 Å versus 1.92 - 1.99 Å (Table 2 and S3).
 280 Also, the calculated distances of Pt-N and Pt-Pt for Pt₁₉/FeCo-OMPC(L) support
 281 experiment (DFT: 1.97 Å versus 2.64 Å, respectively, and Expt.: 1.93 – 2.01 Å versus
 282 2.85 – 2.86 Å) (Table 2 and S3). According to the reasonable agreement with the
 283 modeling and experimental results, we propose a mechanism of the growth of Pt
 284 nanoclusters on FeCo-OMPC(L). As shown in Fig. 7 and S5, the first step is the
 285 removal of unstable surface metal centers, preferentially Co, and the incorporation of
 286 Pt into the metal-center vacancy. Then, the subsequent Pt nanocluster growth may
 287 occur via the linkage of the replaced Pt center (Fig. S5). It is desirable to execute
 288 more size-dependent studies, but due to high computational time, we optimized only
 289 two cases of Pt₆ and Pt₁₉ (Fig. S6). It was found that the adsorption energy of Pt
 290 nanoclusters becomes weakened as the nanoclusters grow (Pt₆: -5.21 eV and Pt₁₉: -
 291 4.31 eV). Using the perfect FeCo-OMPC(L) model, we found that the longitudinal M-
 292 M distances range from ~0.8 to 1.5 nm. Thus, if we assume that the Pt nanoclusters of
 293 ~2 nm in diameter is sphere-like, the possibility to link Pt and the metal center is low

within the calculated M-M distance range, supporting the EXAFS's analysis. In addition to the mechanistic study, we calculated BO by placing one oxygen atom only at the Fe metal center on the surface because of the surface (Pt/FeCo-OMPC(L)_{def}) doesn't have the Co metal center. The Pt/FeCo-OMPC(L)_{def} catalyst (−2.86 eV) showed a slight decrease in BO from that of FeCo-OMPC(L)_{def} (−3.10 eV), indicating an enhanced ORR activity by the Pt nanocluster on FeCo-OMPC(L) (Fig. 7(d)).

From the results, we verified that the enhancement of the ORR mass activity on Pt/FeCo-OMPC(L) was attributed to both the electronic effect and the geometric effect caused by dual active sites of Pt nanoclusters and FeCo-OMPC(L). Therefore, the best electrochemical activity towards ORR was exhibited on 5 wt% Pt/FeCo-OMPC(L) considering the complementary effect between the absolute number of the active sites and electronic effect.

4. Conclusions

We reported a new approach for the enhanced ORR activity as well as the reduction of the precious metal utilization for fuel cell commercialization. We have synthesized a new class of electrocatalysts consisting of a trace amount of Pt nanoclusters on M-N doped ordered mesoporous porphyrinic carbon to enhance the intrinsic catalytic activity. The FeCo-OMPC(L) itself exhibits ORR activity due to its nitrogen coordinated metal centers, however, by adding low amount of Pt nanoclusters on FeCo-OMPC(L), much improved ORR activity could be obtained. Both the electronic and geometric effects were observed as the reason of activity enhancement. The 5 wt% Pt/FeCo-OMPC(L) electrocatalyst indicated a factor of two improvement in the ORR mass activity compared to Pt/C. The FeCo-OMPC(L) Pt loaded catalysts greater than 5 wt% showed decreased mass activities because of the

319 reduced electronic effect and the shrunken absolute number of active sites caused by
320 increased Pt particle size and density.
321

322 **Associated content**

323 Supporting information

324

325 **Author information**

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Cover Image

Figure Legends

Figure 1. (a) Synthetic process of Pt/FeCo-OMPC(L). TEM image of (b) OMS(L), (c) FeCo-OMPC(L), and (d) Pt/FeCo-OMPC(L), and EDS mapping images of (e) FeCo-OMPC(L) and (f) 5 wt% Pt/FeCo-OMPC(L).

Figure 2. (a) Polarization curves for the ORR on prepared 5% Pt/FeCo-OMPC(L) ($4.49 \mu\text{g}_{\text{Pt}}/\text{cm}^2$), 5% Pt/OMPC(L) ($6.22 \mu\text{g}_{\text{Pt}}/\text{cm}^2$), and 5% Pt/C ($3.88 \mu\text{g}_{\text{Pt}}/\text{cm}^2$) catalysts in O_2 -saturated 0.1 M HClO_4 with a sweep rate of 10 mV/s at 1600 rpm (total catalyst loading is $84 \mu\text{g}_{\text{catalyst}}/\text{cm}^2$) and (b) comparison of mass and specific activities at 0.9 V vs. RHE.

Figure 3. (a) Polarization curves for the ORR on FeCo-OMPC(L), 5% Pt/FeCo-OMPC(L) ($4.49 \mu\text{g}_{\text{Pt}}/\text{cm}^2$), and 10% Pt/FeCo-OMPC(L) ($6.63 \mu\text{g}_{\text{Pt}}/\text{cm}^2$) electrocatalysts in O_2 -saturated 0.1 M HClO_4 with a sweep rate of 10 mV/s at 1600 rpm (total catalyst loading is $84 \mu\text{g}_{\text{catalyst}}/\text{cm}^2$) and (b) comparison of mass activities at 0.9 V vs. RHE for 3%, 5%, and 10% Pt/FeCo-OMPC(L) and commercial 40 wt% Pt/C.

Figure 4. Trends of surface area and total pore volume of Pt/FeCo-OMPC(L) obtained from N_2 adsorption/desorption isotherms.

Figure 5. XPS spectrums of N1s, Pt4f_{7/2} for FeCo-OMPC(L), 5% Pt/FeCo-OMPC(L), and 10% Pt/FeCo-OMPC(L).

Figure 6. Fourier-transform (FT) EXAFS of Fe k-edge, Co k-edge, and Pt L_{III}-edge from in-situ XAFS analysis under potentiostatic condition at 0.3 V vs. RHE for FeCo-OMPC(L), 5% Pt/FeCo-OMPC(L), and 10% Pt/FeCo-OMPC(L) catalyst.

Figure 7. Schematic illustration of FeCo-OMPC(L) surfaces (a) before and (b) after the replacement of Co to Pt and (c) after the Pt nanocluster formation. For clarity, only the topmost layer is shown, and (d) DFT results of specific activities versus

calculated binding energy of atomic oxygen on the Fe center without and with the Pt nanocatalyst.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1. Composition of prepared FeCo-OMPC(L), 5% Pt/FeCo-OMPC(L), and 10% Pt/FeCo-OMPC(L) catalysts

	<i>FeCo-OMPC(L)</i> (wt.% / at.%)	<i>5% Pt/FeCo-OMPC(L)</i> (wt.% / at.%)	<i>10% Pt/FeCo-OMPC(L)</i> (wt.% / at.%)
Pt	-	5.31 / 0.36	7.85 / 0.54
Fe	1.63 / 0.36	1.63 / 0.38	1.49 / 0.36
Co	1.47 / 0.31	1.33 / 0.30	1.10 / 0.25
N	6.80 / 6.04	5.90 / 5.51	5.10 / 4.87
C	90.10 / 93.29	85.83 / 93.46	84.46 / 93.99

Table 2. The structural parameters obtained from FT EXAFS curve-fitting process for the Fe, Co K-edge k^2 -weighted in-situ EXAFS spectra of the FeCo-OMPC(L), 5% Pt/FeCo-OMPC(L), and 10% Pt/FeCo-OMPC(L) catalysts

<i>Edge</i>	<i>Path</i>	<i>Catalysts</i>	<i>R (Å)^a</i>	<i>N^b</i>
Co K-edge	Co-N	FeCo-OMPC(L)	1.76	2.4
		5% Pt/FeCo-OMPC(L)	1.72	1.6
		10% Pt/FeCo-OMPC(L)	1.72	1.7
Fe K-edge	Fe-N	FeCo-OMPC(L)	1.74	4.2
		5% Pt/FeCo-OMPC(L)	1.92	3.7
		10% Pt/FeCo-OMPC(L)	1.99	3.2
Pt L ₃ -edge	Pt-N	5% Pt/FeCo-OMPC(L)	1.93	1.4
		10% Pt/FeCo-OMPC(L)	2.01	0.6
	Pt-Pt	5% Pt/FeCo-OMPC(L)	2.85	7.6
		10% Pt/FeCo-OMPC(L)	2.86	7.4

(a: bond distance, b: coordination number)

Supporting Information (SI)

Figure S1. Polarization curves for the ORR on FeCo-OMPC(L), OMPC(L), and Vulcan XC-72 (VC) in O₂-saturated 0.1 M HClO₄ with a sweep rate of 10 mV/s at 1600 rpm.

Figure S2. Normalized (a) Fe k-edge and (b) Co k-edge XANES spectra for FeCo-OMPC(L), 5% Pt/FeCo-OMPC(L), and 10% Pt/FeCo-OMPC(L) catalysts.

Figure S3. (a) The surface model with the (0001) surface plane consisting of 152 atoms (120 C, 12 N, 14 O, 2 Fe, 2 Co, and 2 H). The Co metal on the topmost layer was replaced by Pt to explain the Pt nanocluster growth. and (b) schematic side view of the FeCo-OMPC(L) surface without the M defect.

Figure S4. The bulk structure of FeCo-OMPC(L) consisting of 152 atoms (120 C, 12 N, 14 O, 2 Fe, 2 Co, and 2 H).

Figure S5. Schematic of the growth of Pt nanocluster on FeCo-OMPC(L). M and V are a metal center and its vacancy, respectively.

Figure S6. Schematic illustration of the growth of Pt nanocluster on FeCo-OMPC(L) with (a) Pt₁, (b) Pt₆, and (c) Pt₁₉.

Figure S7. Specially designed *in situ* electrochemical cell for X-ray absorption spectroscopy (XAS) analysis.

Figure S1

Figure S2

Figure S3

Figure S4

Figure S5

Figure S6

Figure S7

Table S1. Comparison of Pt particle size (d_{Pt}) calculated from XRD, and half-wave potentials ($E_{1/2}$), kinetic currents (i_k), specific activity (i_s), and mass activity (i_m) at 0.9 V vs. RHE, and ECSA measured by CO stripping of the prepared catalysts

<i>Catalysts</i>	d_{Pt} (nm)	$E_{1/2}$ (mV)	i_k (mA/cm ²)	i_s (μ A/cm ²)	i_m (A/mg _{Pt})	<i>ECSA</i> (m ² /g _{Pt})
FeCo-OMPC(L)	-	723	0.15	-	-	-
5% Pt/FeCo-OMPC(L)	2.10	858	1.33	350	0.30	84.81
10% Pt/FeCo-OMPC(L)	2.28	866	1.65	258	0.25	96.45
5% Pt/OMPC(L)	3.50	845	0.94	157	0.15	96.58
5% Pt/C	6.80	755	0.16	50	0.04	80.50

Table S2. The vacancy formation energies for the metal centers and incorporation energies of Pt

	$E_{M-vac} \text{ (eV/atom)}^a$	$E_{Pt-incorp} \text{ (eV/atom)}^b$
Co	6.09	−5.03
Co, Fe	6.34	−4.73
Fe	6.74	−4.80

a. Vacancy formation energy of M.

b. Incorporation energy of Pt atom into a metal vacancy.

Table S3. Coordination number and geometrical parameters calculated using DFT^a

<i>Surface</i>	<i>N</i>	$r_{(Co-N)} (\text{\AA})$	$r_{(Fe-N)} (\text{\AA})$	$r_{(Pt-N)} (\text{\AA})$	$r_{(Pt-Pt)} (\text{\AA})$
Bulk OMPC(L)	3	1.83	1.84	-	-
Pt ₁ /FeCo-OMPC(L) _{def}	3	1.83	1.87	1.93	-
Pt ₆ /FeCo-OMPC(L) _{def}	3	1.83	1.87	1.95	2.58
Pt ₁₉ /FeCo-OMPC(L) _{def}	3	1.83	1.87	1.97	2.64

a. FeCo-OMPC(L)_{def} is the surface with a Co vacancy on the topmost surface.