Enhancement of Oxygen Reduction Performance of Biomass-Derived Carbon through Co-Doping with Early Transition Metal

Yuanyuan Dong, Long Zheng, Yijie Deng, Lina Liu, Jianhuang Zeng, Xiuhua Li, and Shijun Liao

The Key Laboratory of Fuel Cell Technology of Guangdong Province & The Key Laboratory of New Energy of Guangdong Universities, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, People’s Republic of China

We report an early transition metal co-doped carbon catalyst prepared by pyrolyzing a 3D chitosan hydrogel precursor mixed with Zr and Fe species. The catalyst exhibits high activity and pronounced long-term stability for the oxygen reduction reaction (ORR) in both acidic and alkaline media. We find that co-doping with Zr can greatly enhance the catalyst’s performance, whereas doping with only Zr results in no improvement. For our optimal sample ZFNC-3-800, its current density at 0.9 V (vs. RHE) could be reach 0.64 mA/cm², which is 1.7 times that of FNC-800. Through TEM, XRD and XPS analyses, we find that co-doping with Zr can change the microstructure of the catalyst, immobilize its iron and nitrogen components and modify the distribution of N species in the final catalyst. Importantly, co-doping with Zr leads to the creation of Zr₂FeOₓ species, contributing to the possible structure of N₄-x-Fe-Oₓ in our ZFNC-3-800 catalyst and enhance its performance. Fe atoms are much more electron-deficient in this structure than in FeₙNₓ species and thus favor the adsorption and activation of oxygen molecules. This work is the first to explore co-doping with early transition metals and to reveal their important role in a specific catalyst.

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For fuel cell and various rechargeable metal-air batteries, the electrochemical oxygen reduction reaction (ORR) is still the main technical issue because of its sluggish kinetics. Pt-based nanomaterials have so far been regarded as the most efficient ORR catalysts. However, the scarcity and consequent high price of Pt as well as its susceptibility to CO poisoning and fuel crossover are barriers to the large-scale application of fuel cells and metal-air batteries. To solve this problem, a series of alternative materials have been designed as ORR electrocatalysts, including carbon nanostructures, transition metals and their oxides, and carbides. Among these, non-precious-metal doped carbon materials (NPM/C), especially Fe-N-C electrocatalysts, exhibit considerable ORR activity and thus have been regarded as one of the most promising alternatives. However, their electrochemical activity and stability are still far below what is required for practical applications, especially in acidic medium. Thus, great efforts have been made in recent years to explore and design new types of doped carbon catalyst, including by doping with one or more elements, designing special pore structures and special morphologies, confining nanocrystals inside carbon nanomaterials, and developing hybrid materials. Although ORR performance can be somewhat enhanced by structural and morphological design factors, finding low-cost, easily prepared, efficient, and durable catalysts for the ORR in both alkaline and acidic media remains a challenge.

Biomass-derived carbon-based catalysts usually inherit a particular structure from their biomass precursors. Biomass is the most promising category of precursors for doped carbon catalysts because biomass sources are rich, have porous structures and provide high specific surface areas. Various biomass-derived carbon catalysts have been extensively investigated in recent years. Doping with transition metals such as Fe, Co, Ni, and Mo is usually done to improve their ORR performance. Although their performance can be enhanced to some extent by doping with single or binary group VIII elements, their ORR activity, especially in acid medium, and their stability remain serious issues.

Early transition metal nitrides, or oxynitrides, have been extensively investigated as ORR catalysts, owing to their high chemical stability under cathode conditions. However, doping or co-doping carbon-based catalysts with early transition metal has rarely reported. Therefore, we tried to synthesize zirconium, co-doped carbon catalysts by pyrolyzing the well-designed chitosan hydrosol precursor mixed with iron and zincium species. This precursor endows catalysts with a particular 3D porous structure and a large specific surface area. As expected, co-doping with Zr greatly enhanced catalytic activity and stability in both acid and alkaline media, whereas doping with Zr alone resulted in almost no enhancement. This is the first report on the co-doping of an early transition metal with group VIII metals and our work may provide a new strategy to develop efficient ORR electrocatalysts through co-doping with early transition metals.

Experimental

Chemicals.—Chitosan (≥99.0%) and polyvinyl pyrrolidone (PVP) were purchased from Shanghai Boao Biological Technology Co., Ltd. Potassium ferricyanide (K₃[Fe(CN)₆]), (≥99.5%) and zirconium nitrate (Zr(NO₃)₄.5H₂O (≥99.4%) were supplied by Tianjin Kemiu Chemical Reagent Co., Ltd. Hydrochloric acid (HCl, 37%) was obtained from the Guangzhou Chemical Reagent Factory.

Catalyst preparation.—A typical synthesis process for our Fe, Zr co-doped carbon catalysts is as follows (Scheme 1). First, 0.1 g PVP is uniformly dissolved in 50 ml HCl solution (0.5 wt%), followed by the addition of 0.5 g chitosan to yield a homogeneous and transparent hydrosol A. K₃[Fe(CN)₆] (0.082 g) and Zr(NO₃)₄ (0.036 g) are added to the HCl solution with magnetic stirring for 4 h to form solution B. Then, solution B is added dropwise into the as-obtained hydrosol A. After 4 h of stirring, the mixture is freeze-dried in a bulk tray dryer at a pressure of 0.1 mbar and at ~40°C for 2 hours, to yield the precursor powder. Finally, the dried fluorescein precursor powder is placed in a tubular furnace and heated to 800°C at a rate of 2°C/min under an Ar flow of 50 sccm and is kept at this temperature for 2 h for pyrolysis. After that, the sample is immersed in 5 M HF solution for 1 h to remove excess Fe and Zr ions, and then washed with deionized water.

*E-mail: chsjiao@scut.edu.cn

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water until its pH reached neutral. It is then dried at 80°C and finally heat-treated at 800°C under an Ar flow again for further pyrolysis and graphitization.

We denote our prepared catalysts as ZFNC-r-T, where r indicates the molar ratio of Fe to Zr and T indicates the pyrolysis temperature.

For comparison, we prepared FNC-800 catalyst (without the addition of zirconium salt in the precursor) and ZNC-800 catalyst (without the addition of iron salt in the precursor) following procedures similar to those described above.

**Characterization.**—Scanning electron microscopy (SEM) was conducted on a Nova Nano 430 field emission scanning electron microscope (FEI, USA). X-ray powder diffraction (XRD) was conducted on a TD-3500 powder diffractometer (Tongda, China) with Cu-Kα radiation sources operated at 40 kV and 30 mA. Transmission electron microscopy (TEM) was performed with a JEM-2100 HR transmission electron microscope (JEOL, Japan). Specific surface areas were recorded by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption on a Tristar II 3020 gas adsorption analyzer (Micromeritics, USA). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo-VG Scientific, USA).

**Electrochemical measurements.**—Electrochemical measurements were conducted on an electrochemical workstation (Ivium Technologies, The Netherlands) with a typical three-electrode system in 0.1 M KOH and 0.1 M HClO4 solutions. A catalyst layer-covered glassy carbon electrode (GCE, diameter 5 mm) was used as the working electrode, which was prepared by the following procedures. Initially, 5 mg catalyst was dispersed in 1 mL Nafion ethanol solution (0.25 wt%) and sonicated for 30 min to yield a catalyst ink. The clean GCE was evenly coated with 20 μL of the as-obtained catalyst ink and then dried by an infrared lamp. The as-prepared working electrode, which was prepared by the following procedures, was conducted on a Nova Nano 430 field emission scanning electron microscope (FEI, USA).

**Results and Discussion**

Figure 1 depicts the morphologies of the chitosan-derived carbon-based electrocatalysts. We found that the morphologies are significantly affected by the dopants. Sample CS-800, obtained by direct pyrolysis of chitosan, is bulky, while the morphologies and microstructures of the transition metals-doped samples clearly depend on the dopant transition metal ions. FNC-800 catalyst exhibits a very good thin nanosheet structure, whereas the ZNC-800 shows a sponge-like amorphous structure (Figure 1c). However, once Fe and Zr are co-doped, the catalyst (ZFNC-3-800) shows a dendritic, coral-like structure, quite different from that of the other two catalysts. TEM image (Figure 1b) further reveals the graphene-like thin coral structure of ZFNC-3-800, confirming that the morphology and microstructure of the catalyst simultaneously doped with Zr and Fe species significantly differs from the ones doped with a single metal. In other words, co-doping with Zr changes the morphology of the chitosan-derived catalysts.

The catalysts doped with metal ions possess the different microstructures, which leads to differences in the specific surface area and the pore distribution. Figure 2a clearly shows that I and IV type N2 adsorption-desorption isotherms characterize the microporous structure of CS-800 and the mesoporous structure of the doped catalysts, respectively. The pore distribution profiles further prove this. The odd curve in Figure 2d indicates the existence of macropores in ZNC-800, which likely are the results of the lumpy accumulations. ZFNC-3-800 catalyst with a dendritic, coral-like structure possesses the largest specific surface area (1225.4 m²/g), closely followed by the FNC-800 (1023.7 m²/g), while the ZNC-800 has the lowest (435.3 m²/g). Clearly, co-doping with Zr caused a significantly increase in the surface area and pore volume of the materials. It is well recognized that a larger specific surface area and a larger pore volume in the doped carbon catalysts favor the exposure of active sites and mass transfer during the reaction process, resulting in excellent ORR activity.

The number of electrons transferred (n) at different potentials was determined by Koutecky-Levich (K-L) plots:39

\[
\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_L} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_k}
\]

where \( J, J_k \), and \( J_L \) are the measured current density, limiting current density, and kinetic diffusion-limited current density, respectively; \( n \) is the number of electrons transferred; \( \omega \) is the angular velocity of the electrode (rad/s); \( C_0 \) (1.2 × 10⁻³ mol/L) is the saturated concentration of oxygen; \( D^0 \) (1.9 × 10⁻³ cm²/s) is the oxygen diffusion coefficient; \( v \) (0.01 cm²/s) is the kinetic viscosity of the electrolyte; and \( F \) is the Faraday constant.
that the co-doping of Zr into chitosan results in the formation of new species (Zr$_2$FeO$_x$ and Zr$_7$O$_8$N$_4$) during the pyrolysis of ZFNC-3-800.

To further verify the presence of new species on the ZFNC-3-800 catalyst surface, the as-prepared ZFNC-3-800 catalyst was characterized by XRD and the results are shown in Figure 3b. The clear characteristic diffraction peaks of Zr$_7$O$_8$N$_4$ and Zr$_2$FeO$_x$ are marked with red and blue lines. Additionally, the characteristic peaks intensity in Figure 3b is stronger than in Figure 3a, which is due to the absence of acid leaching. Considering the XRD patterns of ZFNC-3-800 catalyst before and after acid leaching, it is concluded that the Zr$_7$O$_8$N$_4$ and Zr$_2$FeO$_x$ species are indeed present on the catalyst surface. The ZrO$_2$ diffraction peak intensity is very low in the XRD pattern of the as-prepared ZFNC-3-800 catalyst, indicating that the amount of ZrO$_2$ on the catalyst surface is very small. This observation also is a clue that Zr species are present in other forms (e.g., Zr$_7$O$_8$N$_4$ and Zr$_2$FeO$_x$), which can be proven to contribute to the materials’ enhanced performance.

Figure 4 presents the HAADF and corresponding elemental mapping images of ZFNC-3-800 catalyst. Clearly, C, N and Fe were uniformly dispersed on the surface of the sample, while Zr and O species were partially agglomerated. The composographs of Zr, O and N (Figure 4h) throws light on the existence of Zr$_7$O$_8$N$_4$, while the composite image of Fe, Zr and O (Figure 4g) provides some clues about the formation of Zr$_2$FeO$_x$ species in ZFNC-3-800 catalyst. The characteristic diffraction peaks of Zr$_2$FeO$_x$ and Zr$_7$O$_8$N$_4$ are marked in Figure 3b. The clear characteristic peaks intensity is stronger in Figure 3b than in Figure 3a, which is due to the absence of acid leaching. Considering the XRD patterns of ZFNC-3-800 catalyst before and after acid leaching, it is concluded that the Zr$_7$O$_8$N$_4$ and Zr$_2$FeO$_x$ species are indeed present on the catalyst surface. The ZrO$_2$ diffraction peak intensity is very low in the XRD pattern of the as-prepared ZFNC-3-800 catalyst, indicating that the amount of ZrO$_2$ on the catalyst surface is very small. This observation also is a clue that Zr species are present in other forms (e.g., Zr$_7$O$_8$N$_4$ and Zr$_2$FeO$_x$), which can be proven to contribute to the materials’ enhanced performance.

Figure 5 shows the ORR performances of the catalysts in alkaline medium (0.1 M KOH solution). In N$_2$-saturated electrolyte, no obvious redox features can be observed for any of the three catalysts; the highest capacity of ZFNC-3-800 may indicate that it has the highest surface area of the three. By contrast, in the O$_2$-saturated electrolyte, all three catalysts exhibit obvious oxygen reduction peaks, and the Zr-Fe co-doped sample, ZFNC-3-800, exhibits the highest peak potential (0.858 V) and the highest onset potential (0.984 V), compared with 0.823 V and 0.946 V for FNC-800, and 0.746 V and 0.891 V for ZNC-800 (Fig. 5b), revealing the significant enhancement achieved with Zr co-doping.

Figure 5c shows the LSV curves of the catalysts in 0.1 M KOH solution at a rotation rate of 1600 rpm. ZNC-800 catalyst, doped solely with Zr, exhibits very poor ORR performance, showing an ORR activity slightly lower than that of the CS catalyst, derived from chitosan without any dopants. This indicates that Zr is an inert dopant; as expected, doping with Fe results in tremendous enhancement of ORR performance. It is interesting that co-doping with Fe and Zr led to further improvement of the catalyst’s ORR performance, given that doping with sole Zr was confirmed to have no positive effect. The current density (0.64 mA/cm$^2$) at 0.9 V vs. RHE of our optimal sample ZFNC-3-800 was 1.7 times that of FNC-800 (0.38 mA/cm$^2$), surpassing state-of-art commercial Pt/C (0.58 mA/cm$^2$). Figure 5d presents the normalized results for all four catalysts. Their performances follow the trend: ZFNC-3-800 > FNC-800 > CS > ZNC-800.

To investigate the effects of new species on ORR activities of catalysts, we prepared a series of ZFNCR-r-800 catalysts with different Fe/Zr molar ratios based on the optimal loading of Fe dopant and the optimal pyrolysis temperature. In alkaline medium (Figures 6a and 6b), the ORR activities of this series of catalysts are affected by the Fe/Zr molar ratio. Specifically, the peak potential gradually increases with a decrease in Fe/Zr molar ratio, peaks at Fe/Zr ≈ 3:1, and then decreases when the ratio drops further. The onset potential and half-wave potential follow the same trend. Moreover, our optimal

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**Figure 1.** SEM images of (a) CS-800, (b) FNC-800, (c) ZNC-800 and (d) ZFNC-3-800 catalysts; the scale bar represents 200 nm. TEM images of (e) CS-800, (f) FNC-800, (g) ZNC-800 and (h) ZFNC-3-800 catalysts; the scale bar represents 100 nm.
catalyst ZFNC-3-800 is clearly superior to the state-of-art NPM-based catalysts reported in the literature.\textsuperscript{36,34,37,40,42-44}

In acidic medium (Figures 6c and 6d), the effects of the Fe/Zr ratio on ORR performance show the same trend as that in alkaline medium. The ZFNC-3-800 catalyst with Fe/Zr molar ratio of 3:1 performs best. A positive shift (27 mV) in the onset potential is sufficient to account for the positive effect resulting from co-doping with Zr. Although the ORR activity of ZFNC-3-800 is not as good as that of catalysts previously reported,\textsuperscript{26,29,38,45-49} the positive effect caused by the co-doping with the early transition metal Zr is very interesting.

Additionally, the limiting current density obviously changes as the Fe/Zr molar ratio in both alkaline and acidic electrolytes, which is assigned to variations in active sites and specific surface areas of catalysts. The active sites are influenced by the amount of Zr, resulting in different yields of \( \text{H}_2\text{O}_2 \). In addition, \( \text{ZrO}_2 \) will be formed by excessively adding Zr, which agglomerate to reduce the specific surface area of catalysts. To explore the origin of the influences that Fe/Zr co-doping had on ORR activity, XRD, SEM and TEM are carried out to identify the changes in crystal phase and microstructure caused by differences in the Zr co-doping amount.

As shown in Figure 7a, when small amount of Zr are used (such as Fe/Zr molar ratios of 5:1 and 3:1), the catalyst is dominated by \( \text{Zr}_2\text{FeO}_x \) species (marked with triangle). Notably, the peak intensity of \( \text{Zr}_2\text{FeO}_x \) species is gradually enhanced with an increment of co-doped Zr. Combined these findings with the activity data and the results of TEM and XRD, we can easily infer that the formation of \( \text{Zr}_2\text{FeO}_x \) species is responsible for the enhanced ORR activity of ZFNC-3-800 catalyst. It is noteworthy that \( \text{Zr}_2\text{O}_x\text{N}_y \) species are not considered as active moieties although they are clearly found in XRD pattern of ZFNC-3-800 catalyst, which is dominated by the \( \text{Zr}_2\text{O}_x\text{N}_y \) species, is much poor than that of the chitosan pyrolysis sample. Further increasing the amount of Zr (Fe/Zr = 1:1 and 1:5) introduces excessive Zr species, resulting in large amount of \( \text{Zr}_2\text{O}_x\text{N}_y \) and \( \text{ZrO}_2 \), as is clearly shown in Figure 7a. The plentiful \( \text{Zr}_2\text{O}_x\text{N}_y \) and \( \text{ZrO}_2 \) nanoparticles (Figures 7b-7e) block the pores of the ZFNC-r-800 catalysts, as indicated by the reduction in specific surface area and pore volume, which finally leads to difficulties in the transport of intermediate. The change in conductivity caused by \( \text{ZrO}_2 \) is also an important reason for the decline in ORR activity shown by the ZFNC-r-800 catalysts (r = 1 and 0.2).

Figure 2. (a) The \( \text{N}_2 \) adsorption-desorption isotherms and (b-e) pore size distribution profiles of chitosan-derived catalysts.
To further illustrate the positive effects of co-doping with Zr, XPS is employed to determine the electronic structure and composition of ZFNC-3-800 catalyst. Table I lists the atomic compositions of FNC-800 and ZFNC-3-800. Obviously, the co-doping with Zr affected the catalyst’s elemental composition. The N, O and Fe content of ZFNC-3-800 catalyst is significantly higher than that of the catalyst doped only with Fe; in particular, the iron content increases almost six-fold. This should be attributed to the formation of new species (Zr$_7$O$_8$N$_4$ and Zr$_2$FeO$_x$) on the catalyst’s surface (Figure 3). The greater of N and Fe content means that the co-doping with Zr can effectively reduce the loss of iron and nitrogen during the pyrolysis process, thus enhancing the ORR activity (Figure 5 and Figure 6).

The survey XPS spectra of FNC-800 and ZFNC-3-800 are shown in Figure 8a, clearly revealing that Zr and Fe are well doped into the catalysts. Figure 8b presents the high-resolution N 1s XPS spectra of FNC-800 and ZFNC-3-800, respectively. The characteristic peaks at 398.8, 400.6, 410.9 and 406.0 eV can be assigned to pyridinic-N (N$_1$), pyrrolic-N (N$_2$), graphitic-N (N$_3$) and oxidized-N (N$_4$), respectively.\(^50\)
We conducted deconvolution for the N 1s spectra. The binding energies of N₁ and N₃ species are evidently affected by co-doping with Zr. The changes in the binding energy of N species signify that the Zr co-doping modifies the chemical environment of N. It should be attributed to the formation of ZrO₂N₄ species in ZFNC-3-800 catalyst. Zr co-doping also modulates the distribution of N species (Table II). The proportion of N₃ species is significantly increased, accompanied by decreases in the amount of N₁ and N₂ species. In addition, the total percentage of N₁ and N₃ species is improved by 10.74% in ZFNC-3-800. The N₁ and N₃ species, which can be transformed into each other during calcination, are considered to be active species in oxygen reduction reaction. Therefore, the enhanced fraction of active species caused by the co-doping of Zr also contributes to the improvement in ORR activity.

Figure 8c shows the high-resolution C 1s XPS spectra of ZFNC-3-800 and FNC-800. The peaks at ~284.8, 285.9 and 289.7 eV represent the C-C (sp² carbon), C-N and C-O species, respectively. After the co-doping Zr into the catalyst, the binding energy of C-N species shifted positively (~0.3 eV), implying that the electronic density of elemental C was modified. We suggested it should be caused by the coordination of O of Zr-O structure due to the doping of Zr.

Figure 8d shows the high-resolution Fe 2p spectra of FNC-800 and ZFNC-3-800. The peaks located at 711.3, 726.1 and 720.1 eV represent Fe and Zr species, respectively.

| Element | C   | N   | O   | Fe  | Zr  |
|---------|-----|-----|-----|-----|-----|
| FNC-800 | 90.95 | 2.7 | 6.24 | 0.11 | —   |
| ZFNC-3-800 | 87.15 | 2.89 | 8.61 | 0.6  | 0.75 |

Figure 7. (a) XRD patterns of ZFNC-r-800 catalysts with different Fe/Zr molar ratios; SEM (b) and TEM (c) images of ZFNC-1-800; SEM (d) and TEM (e) images of ZFNC-0.2-800.
Figure 8. The survey XPS spectra (a) and high-resolution N 1s XPS spectra (b) of FNC-800 and ZFNC-3-800; N1, N2, N3 and N4 represent pyridinic-N, pyrrolic-N, graphitic-N and oxidized-N, respectively; high-resolution C1s (c) and Fe 2p (d) spectra of Fe-NC and ZFNC-3-800.

are assigned to Fe 2p$_{3/2}$, Fe 2p$_{1/2}$ and satellite peaks, respectively.$^{44,51}$ The binding energy of Fe shifts positively after co-doping with Zr. It is resulted from a decrease in the electron density of Fe in ZFNC-3-800 catalyst, which should be attributed to the interaction between Fe and some elements with larger electronegativity. FeN$_x$ species have been widely reported as active species of Fe-N-C catalysts for ORR.$^{52-54}$ Therefore, we presume that the structure of N$_{4-x}$-Fe-O$_x$-Zr may be formed in ZFNC-3-800 catalyst owing to the co-doping of Zr, in other words, the doped Zr affected the electron density of Fe through the formation of –O– bridge bond. In comparison with FeN$_4$ species, the Fe atoms in this structure are much more electron deficient, which facilitates the adsorption and activation of oxygen molecules and finally promotes ORR activity.

To gain further insights into the reaction kinetics, RDE measurements were conducted with rotation speeds ranging from 900 to 2500 rpm. K-L equation was employed to calculate the electron transfer numbers. As shown in the inset of Figures 9a and 9b, the K-L plots determined with different potentials in the mixed kinetic-diffusion controlled area exhibit good linearity and similar slopes. The calculated electron transfer numbers are 4.07 and 4.02, indicating that ZFNC-3-800 catalyst follows a four-electron route in both alkaline and acidic media.

To detect the stability of ZFNC-3-800 catalyst, the current–time (i–t) chronoamperometric response analysis (Figure 10a) is conducted in O$_2$-saturated alkaline and acidic solutions, respectively. After 50000s, the half-wave potential exhibited a small negative shift of only 12 mV for the alkaline electrolyte and 5 mV for the acidic electrolyte. These results indicate the high durability of ZFNC-3-800. Additionally, the resistance of ZFNC-3-800 toward methanol crossover is also investigated. As shown in Figure 10b, slight changes are observed in the ORR current for ZFNC-3-800 after the introduction of 3 M methanol in both alkaline and acidic electrolytes, which confirms that the ZFNC-3-800 catalyst exhibits strong tolerance against methanol crossover.

Conclusions

In summary, we successfully developed a novel early transition metal co-doped carbon catalyst ZFNC-3-800 by pyrolyzing the chitosan hydrosol containing iron and zirconium species. The catalyst exhibits excellent ORR activities in both alkaline and acidic media. According to the characterization results, co-doping with Zr changes the microstructure of catalyst, modifies the distribution of N species Table II. The proportions of N species in FNC-800 and ZFNC-3-800 catalysts.

| Catalysts | Pyridinic-N | Pyrrolic-N | Graphitic-N | Oxidized-N |
|-----------|-------------|------------|-------------|------------|
| FNC-800   | 27.95%      | 34.48%     | 25.86%      | 11.71%     |
| ZFNC-3-800| 22.76%      | 16.88%     | 41.79%      | 18.57%     |
and causes the production of Zr$_2$FeO$_x$ species. Our catalyst’s dendritic, coral-like porous structure and enhanced amount of active N species are likely responsible for the improvement in ORR activity. Moreover, the appearance of Zr$_2$FeO$_x$ species may promote the formation of N$_{4-x}$-Fe-O$_x$ structure, in which the Fe atoms are much more electron-deficient than that in FeN$_4$ species and facilitate the adsorption and activation of oxygen molecules, and ultimately spurs the enhancement in ORR activity and stability.

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ORCID
Shijun Liao https://orcid.org/0000-0003-2481-0377

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