An Iron-Based Catalyst with Multiple Active Components Synergetically Improved Electrochemical Performance for Oxygen Reduction Reaction

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Abstract: Lack of highly active and stable non-precious metal catalysts (NPMCs) as an alternative to Pt for oxygen reduction reaction (ORR) in the application of zinc-air batteries and proton-exchange membrane fuel cells (PEMFCs) significantly hinders the commercialization of these energy devices. Herein, we synthesize a new type of catalyst composed of nitrogen-coordinated and carbon-embedded metal ($Fe-N/Fe_3C/Fe/C$) by pyrolyzing a precursor at 800 °C under argon atmosphere, and the precursor is obtained by heating a mixture of the tri (dipyrido [3,2-*a*:2′,3′-*c*] phenazinyl) phenylene and $FeSO_4$ at 160 °C in a Teflon-lined stainless autoclave. The resultant $Fe-N/Fe_3C/Fe/C$-800 exhibits the highest activity for the ORR with onset and half-wave potentials of 1.00 and 0.82 V in 0.1 M KOH, respectively. Furthermore, it also shows a potential ORR activity in 0.1 M $HClO_4$, which is promising for the application in commercial PEMFCs. Most importantly, $Fe-N/Fe_3C/Fe/C$-800 exhibits a comparable electrochemical performance to Pt/C for the application in zinc-air battery. The specific capacity approaches 700 mAh·g^{-1}, and the maximum power density is also comparable to that of Pt/C at the current density of 200 mA·cm^{-2}. The work opens up a simple strategy to prepare ORR electrocatalyts for zinc-air battery and PEMFCs.

Keywords: electrocatalysts; oxygen reduction reaction; iron–nitrogen coordination; iron nanoparticles

1. Introduction

Exploring highly active and stable non-precious metal catalysts (NPMCs) as an alternative to Pt for oxygen reduction reaction (ORR) is crucial to battery devices, such as zinc-air batteries and proton exchange membrane fuel cells (PEMFCs) [1–6]. At present, the Fe-N/C catalysts have been widely considered as the most potential candidates among NPMCs because of their high activity and durability [7–9]. They are mainly prepared by pyrolysis from the mixture of iron salt and nitrogen-containing carbon species [2,10]. In general, the $Fe-N_x$ are assumed to be catalytically active sites in these catalysts [11]. However, some argued that Fe species only promotes the formation of N-doped carbon, and these nitrogen-doped nanomaterials are catalytically active [12–17]. In addition, iron particles and/or iron carbides are often formed in preparing the $Fe-N_x$ catalysts during the

pyrolyzing process at high temperatures, which can hardly be completely removed by the pickling [18]. Their role in Fe-N/C catalysts for ORR is quite difficult to be ruled out without the support of in situ techniques. Recently, Deng et al. reported that carbon nanotube-embedded (CNT-embedded) iron nanoparticles were highly active for ORR in acidic media [19]. Yang et al. synthesized CNT/Fe_3C nanoparticle hybrids that exhibited high performances in both alkaline and acidic environments [20]. Although the active sites of Fe-N/C catalysts remain debate, a large number of researches have indicated that Fe species, nitrogen-containing carbon materials and pyrolysis temperatures are critical parameters influencing the performance of Fe-N/C catalysts [21]. Nevertheless, the mentioned synthetic method often leads to uncontrollable agglomeration and inhomogeneous microstructures of metal nanoparticles in these catalysts [22]. To address the bottleneck, template [23,24] and template-free [25,26] synthesis of NPMCs have been developed. In particular, Müllen and Dai's groups synthesized high-performance electrocatalysts by pyrolysis of self-supporting porphyrin-based polymer frameworks [27,28]. In these catalysts, metal nanoparticles are uniformly distributed and embedded in nitrogen-rich carbon.

Herein, we prepared a highly effective ORR electrocatalyst formed by nitrogen-coordinated and carbon-embedded metal (Fe-N/Fe_3C/Fe/C) via the template-free pyrolysis of tri (dipyrido [3,2-*a*:2′,3′-*c*] phenazinyl) phenylene-based metal organic framework (MOF). Fe-N/Fe_3C/Fe/C-800 exhibited the excellent activity and durability for ORR, evidenced by a very similar onset potential to Pt/C in acidic and alkali corrosive media, as well as a comparable half-wave potential of 0.82 V to Pt/C in a 0.1 M KOH solution. Meanwhile, Fe-N/Fe_3C/Fe/C-800 showed a good stability and excellent methanol tolerance in both alkaline and acidic environments. The half-wave potentials were only negatively shifted by 23.3 and 20.2 mV after 3000 cycles in alkaline and acidic electrolytes, respectively, while there were insignificant changes observed between the cyclic voltammetry (CV) curves taken in methanol and without methanol in both electrolytes.

2. Results and Discussion

We synthesized Fe-N/Fe_3C/Fe/C-800 by the pyrolysis of the metal organic framework at 800 °C under the argon for 1.5 h (Scheme 1). The synthesis details were provided in the experimental section. Figure 1a shows an SEM image of Fe-N/Fe_3C/Fe/C-800 with a disordered carbon morphological feature. The HRTEM images of Fe-N/Fe_3C/Fe/C-800 were mainly amorphous. Metal nanoparticles with a diameter of ~30 nm were decorated on carbon and covered with graphitic carbon shells (~5 nm) (Figure 1b). The elemental composition of the catalyst was analyzed by using HAADF-STEM-EDS STEM images (Figure 1c–h). The metal nanoparticles were identified as Fe or Fe_3C embedded in graphitic carbon, instead of FeS. However, the TEM images showed an unclear crystal lattice, which was difficult to distinguish carbon-embedded Fe from Fe_3C nanoparticles. HAADF-STEM-EDS images indicated that Fe, N and S were uniformly distributed on the carbon matrix except Fe and Fe_3C sections. The elemental S was from the starting reactant, $FeSO_4$. Figure 2a compares the XRD patterns of Fe-N/Fe_3C/Fe/C-800, Ligand-800 and S-ligand-800. A broad diffraction peak at 25.4 assigned to the (002) planes of graphitic carbon and a peak observed at 44.8° in Fe-N/Fe_3C/Fe/C-800 indicated the presence of α-Fe (JCPDS, 87–0722) [29]. The peaks at 43.6° and 50.5° were assigned to the crystalline planes of Fe_3C species (JCPDS, 89–2867) [30]. The results of XRD indicated that the catalyst contained both Fe and Fe_3C nanoparticles. To further provide insight into the structure of Fe-N/Fe_3C/Fe/C-800, its surface compositions were further examined by XPS, XANES and EXAFS. The full XPS spectra of the catalyst were recorded in Figure 2b. All elements, including C, O, N, S and Fe, were detected. The percentages of the elemental C, N, O, S and Fe were approximately 85.05, 6.65, 5.59, 2.21 and 0.51% in weight, respectively. Four dominant nitrogen peaks at 398.2, 399.4, 400.9, and 402.1 eV corresponded to pyridinic (25.10%), pyrrolic (24.93%), graphitic (25.19%) and quarternary (24.78%), respectively (Figure 2c). The pyridinic and pyrrolic N were regarded as ORR active reagents because they are capable of coordinating with transition metal by lone-pair electrons [31,32]. Graphitic nitrogen was also reported to be important for ORR. Recently, density functional theory (DFT) calculation announced

that existence of quaternary N in graphene structures significantly enhanced the catalytic activity of carbon, because of a non-uniform electron distribution. These forms of nitrogen with high content were beneficial to create the highly active catalysts. In the Fe2p spectrum, the peaks at 710.1 and 713.6 eV were assigned to the binding energies of the $2p_{3/2}$ orbitals of Fe^{2+} and Fe^{3+} species, respectively (Figure 2d) [33]. The peaks at 722.9 and 727.5 eV were attributed to the binding energies of the $2p_{1/2}$ orbitals of Fe^{2+} and Fe^{3+} species. The satellite peak was also observed at 717.2 eV. The XANES and EXAFS for Fe K-edge of Fe-N/Fe$_3$C/Fe/C-800 and references are shown in Figure 2e,f. The reference Fe phthalocyanine had a pre-edge peak at 7118 eV that was assigned to a 1s → 4pz shakedown transition characteristic for a square-planar D4h symmetry. The pre-edge feature was not observed in Fe-N/Fe$_3$C/Fe/C-800 that revealed a different local environment of Fe-N$_x$, such as a distorted square planer (D2h). The shoulder at 7112 eV in the spectrum of Fe-N/Fe$_3$C/Fe/C-800 was the feature of metallic Fe species (Figure 2e). There were two dominant peaks for Fe-N/Fe$_3$C/Fe/C-800 in EXAFS. The characteristic peak at 1.6 Å indicated an Fe-N interaction, and the peak at 2.2 Å coincided with Fe-Fe scattering of metallic Fe and Fe$_3$C standards (Figure 2f) [34]. We also compared the EXAFS of Fe-N/Fe$_3$C/Fe/C-800 with Fe phthalocyanine and metallic Fe. The characteristic peaks of the Fe-N and Fe-Fe interactions in these references were slightly different from Fe-N/Fe$_3$C/Fe/C-800. This is because Fe and Fe$_3$C in Fe-N/Fe$_3$C/Fe/C-800 were embedded in carbon, and the Fe-N bonding symmetry in the catalyst was not square-planar (D4h)-like in the Fe phthalocyanine. Thus, taking all of these analysis, including SEM, TEM, XRD, XPS, XANES and EXAFS data together, Fe-N, carbon embedded Fe$_3$C and Fe nanoparticles were identified as the components of the catalyst that were distributed in the N, S co-doped amorphous carbon.
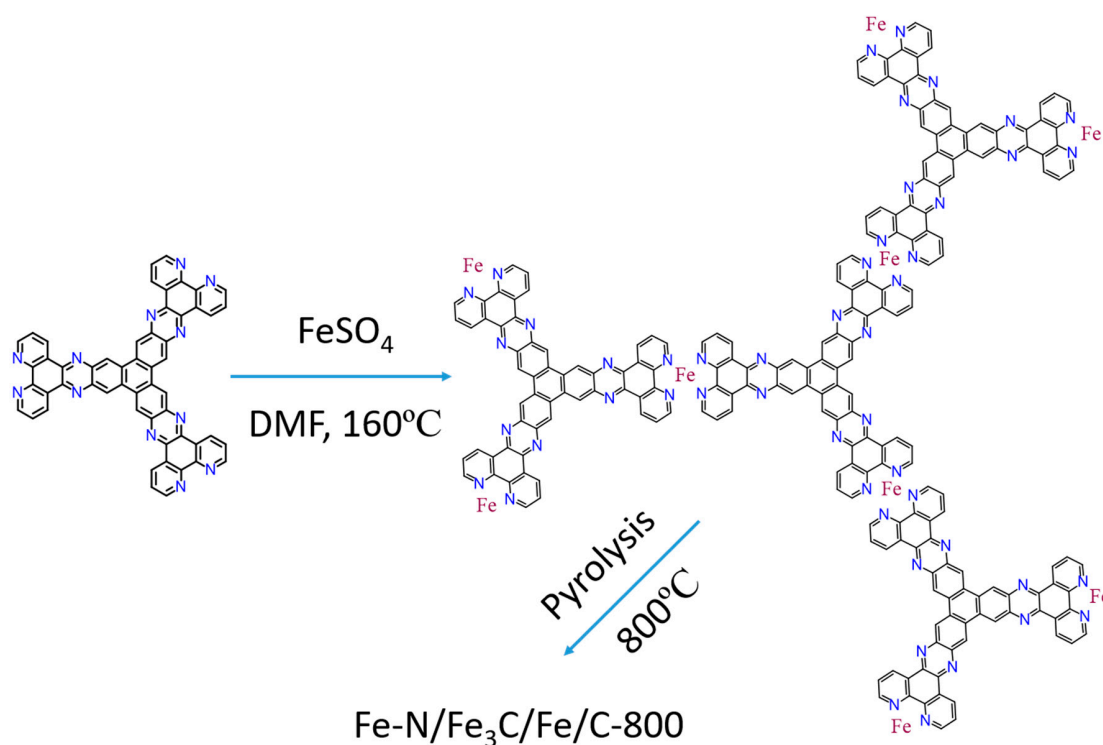
Scheme 1. The illustration of the synthesis for Fe-N/Fe$_3$C/Fe/C-800.
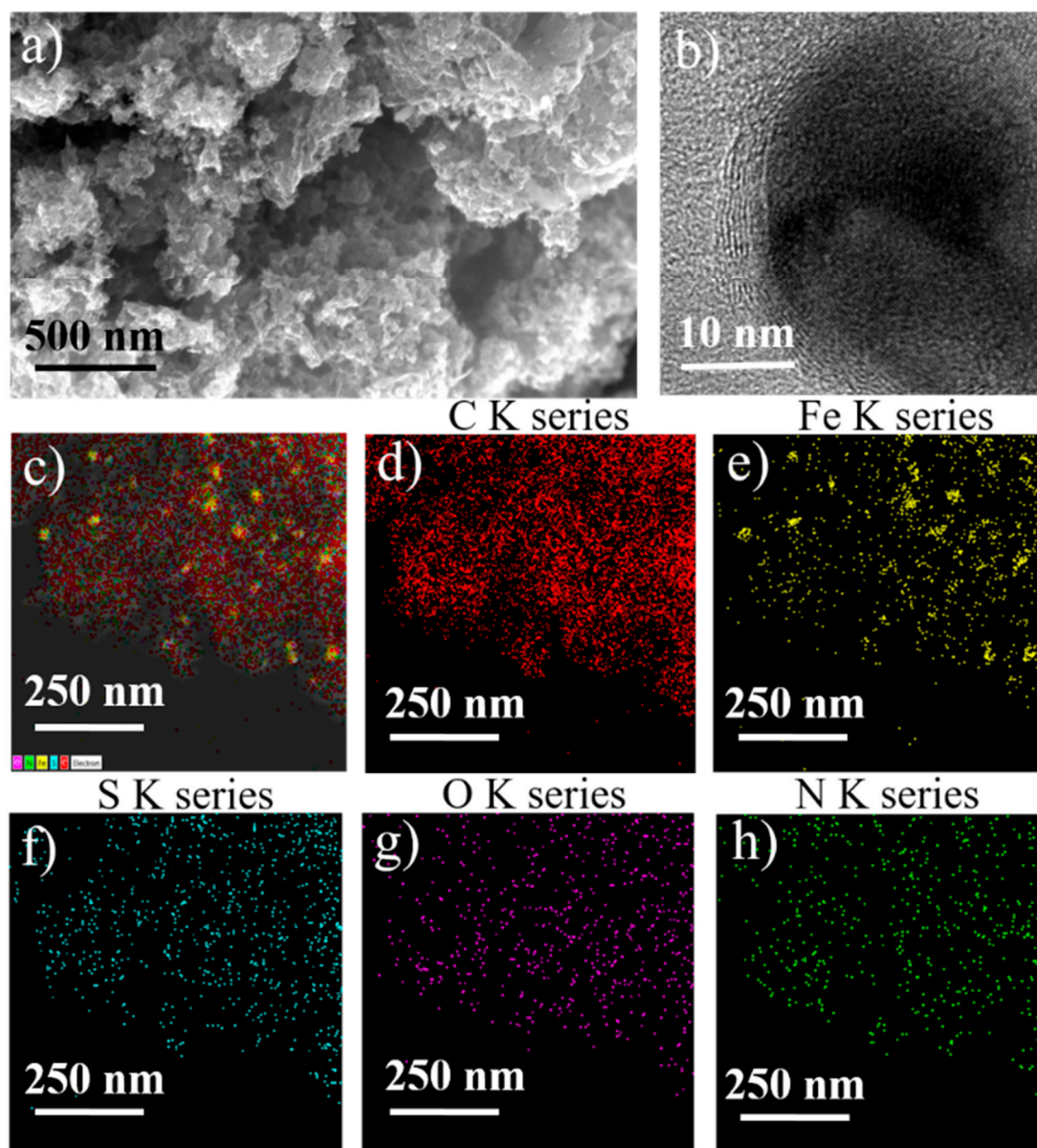
Figure 1. (**a**) Scanning electron microscopy image of Fe-N/Fe$_3$C/Fe/C-800; (**b**) high-magnification TEM images of Fe-N/Fe$_3$C/Fe/C-800; (**c–h**) HAADF-STEM-EDS images of Fe-N/Fe$_3$C/Fe/C-800.
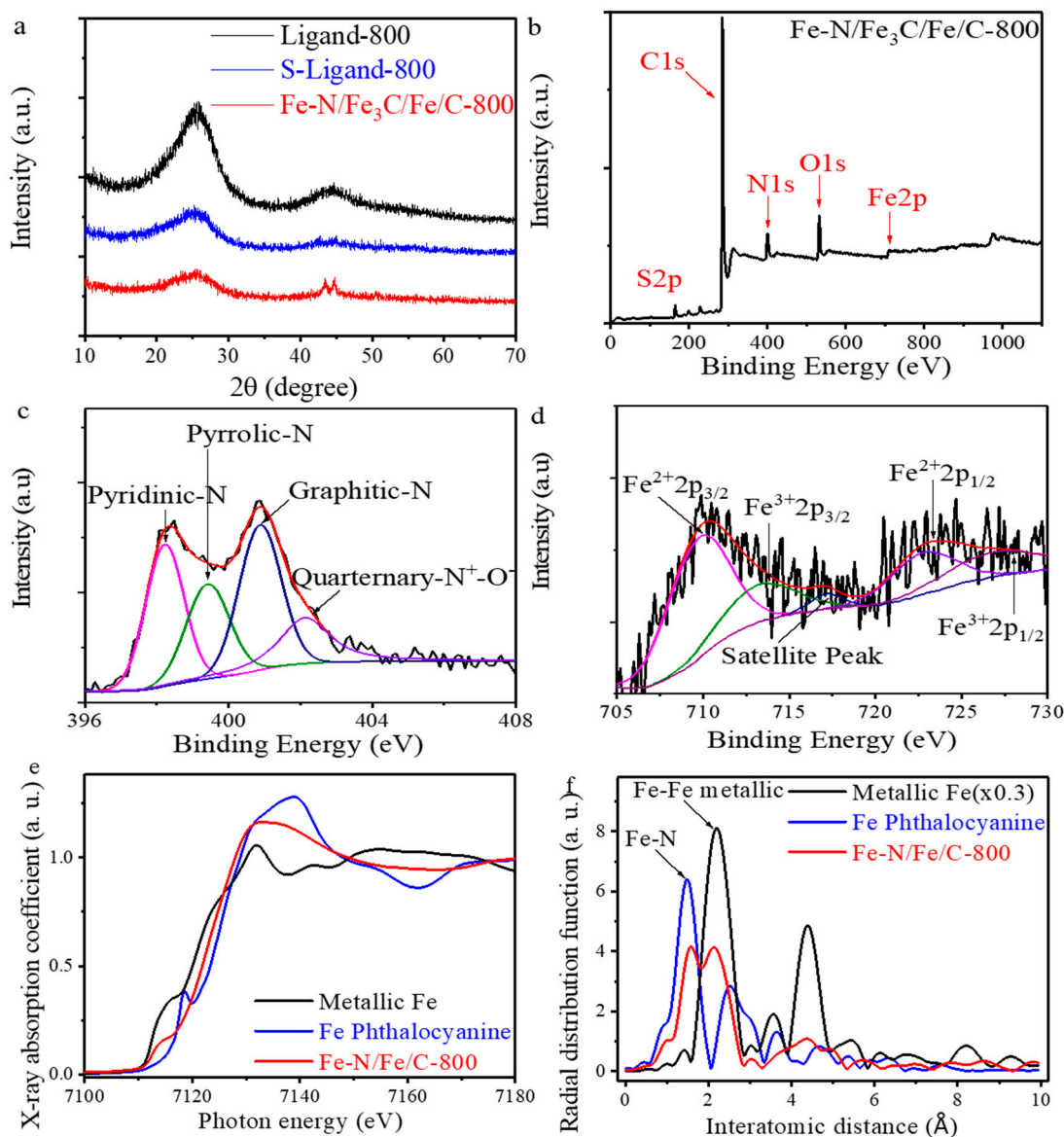
Figure 2. (**a**) XRD spectra of Ligand-800, S-Ligand-800 and Fe-N/Fe$_3$C/Fe/C-800; (**b**) full XPS spectrum of Fe-N/Fe$_3$C/Fe/C-800; (**c**) XPS spectra of Fe2p for Fe-N/Fe$_3$C/Fe/C-800 in the range of 705 to 730 eV; (**d**) XPS spectra of N1s for Fe-N/Fe$_3$C/Fe/C-800; (**e**) XANES spectra for Fe K-edge of Fe-N/Fe$_3$C/Fe/C-800 and references; and (**f**) EXAFS spectra for Fe K-edge of Fe-N/Fe$_3$C/Fe/C-800 and references.

The catalytic activities of Fe-N/Fe$_3$C/Fe/C-800 and Pt/C catalysts for ORR were investigated by cyclic voltammetry (CV) and LSV measurements in O$_2$- or N$_2$-saturated 0.1 M KOH and 0.1 M HClO$_4$ ((Figure 3). Fe-N/Fe$_3$C/Fe/C-800 exhibited a quasi-rectangular double-layer capacity current in N$_2$ saturated 0.1 M KOH solution (Figure 3a). Its ORR peak potential was located at 0.79 V in O$_2$ saturated 0.1 M KOH solution, which was negatively shifted by 0.07 V relative to Pt/C. However, its peak current (106.5 μA) was much higher than that of Pt/C (75.6 μA) (Figure 3a). In the case of the acidic medium, Fe-N/Fe$_3$C/Fe/C-800 also showed a larger peak current of 151.0 μA than that of Pt/C (115.2 μA) (Figure 3c). The higher capacitance currents of Fe-N/Fe$_3$C/Fe/C-800 in both alkaline and acidic media may be caused by a favorable O$_2$ transport within the layer of the catalyst [35]. The catalytic activities for ORR of Fe-N/Fe$_3$C/Fe/C-800 and Pt/C catalysts were also studied by rotating disk electrode (RDE) in Figure 3b,d. The onset potential for the Fe-N/Fe$_3$C/Fe/C-800 in alkaline conditions (1.00 V)

was very similar to that for Pt/C. The half-wave potentials ($E_{1/2}$) for Fe-N/Fe$_3$C/Fe/C-800 and Pt/C were 0.82 and 0.85 V, respectively (Figure 3b). Although $E_{1/2}$ (0.62 V) of Fe-N/Fe$_3$C/Fe/C-800 was more negatively shifted relative to Pt/C in acidic media, there were insignificant differences observed from their onset potentials (Figure 3d). In addition, the diffusion limited current densities (j_L) of Fe-N/Fe$_3$C/Fe/C-800 were 6.23 and 5.48 mA cm^{-2} at a rotating speed of 1600 rpm in 0.1 M KOH and 0.1 M HClO$_4$, respectively, which were close to the theoretical limiting current density of 6.0 mA cm^{-2}. Figure 4a exhibits the Tafel plots of Fe-N/Fe$_3$C/Fe/C-800 and Pt/C catalysts in 0.1 M KOH, derived from Figure 3b. Fe-N/Fe$_3$C/Fe/C-800 showed a Tafel slope of 45 mV/dec that was similar to that of Pt/C (40 mV/dec), indicating a good kinetic process for ORR. The Tafel plots of Fe-N/Fe$_3$C/Fe/C-800 and Pt/C catalysts in 0.1 M HClO$_4$ are shown in Figure 4b, deduced from Figure 3d. The former had a Tafel slope of 152 mV/dec and the later owned a Tafel slope of 81 mV/dec.
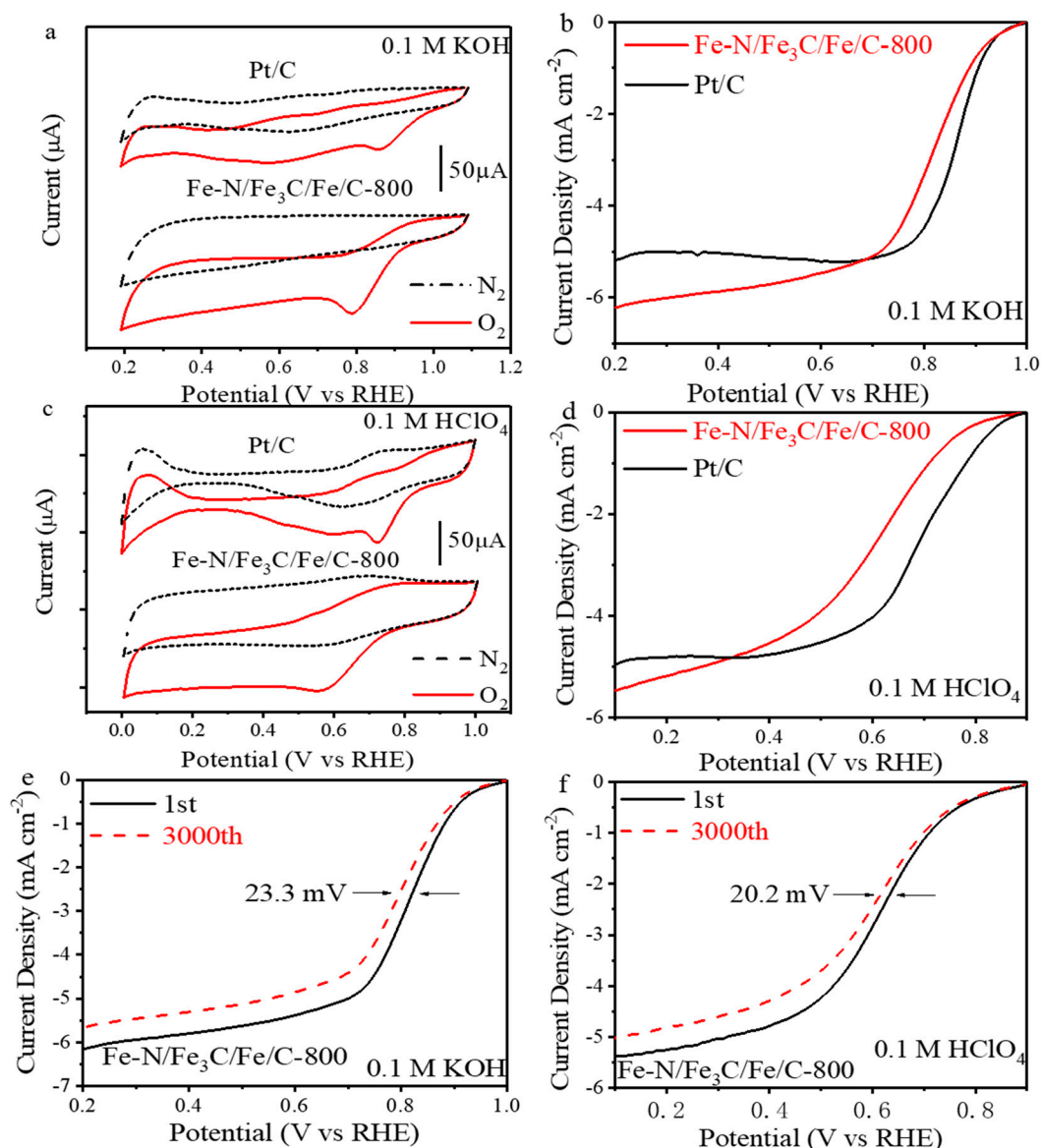

Figure 3. (**a**) Cyclic voltammograms of Pt/C and Fe-N/Fe$_3$C/Fe/C-800 in 0.1 M KOH; (**b**) Oxygen reduction reaction (ORR) polarization curves of Pt/C and Fe-N/Fe$_3$C/Fe/C-800 in 0.1 M KOH; (**c**) cyclic voltammograms of Pt/C and Fe-N/Fe$_3$C/Fe/C-800 in 0.1 M HClO$_4$; (**d**) ORR polarization curves of Pt/C and Fe-N/Fe$_3$C/Fe/C-800 in 0.1 M HClO$_4$; (**e,f**) endurance test of Fe-N/Fe$_3$C/Fe/C-800 for 3000 cycles in O$_2$-saturated KOH and HClO$_4$ (0.1 M) (Scanning rate: 10 mV/s, rotating).
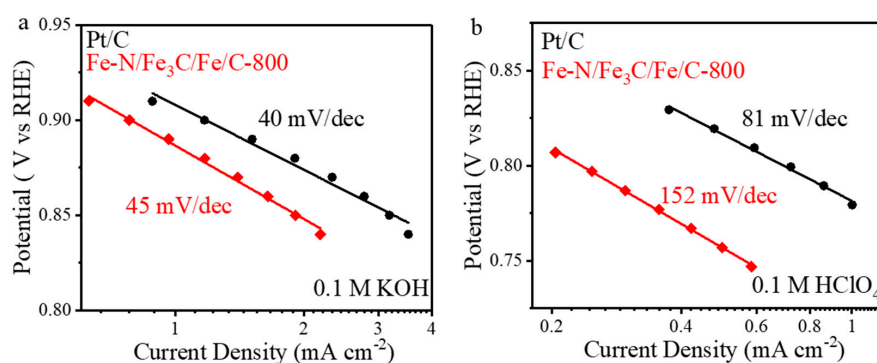
Figure 4. The Tafel plots of Fe-N/Fe$_3$C/Fe/C-800 and Pt/C catalysts (**a**) in 0.1 M KOH and (**b**) in 0.1 M HClO$_4$.

Because of the complicated structure of Fe-N/Fe$_3$C/Fe/C-800, it is difficult to tell what kinds of iron species (Fe-N$_x$, Fe$_3$C and Fe particles) serve as the major active sites. N-doped carbon was previously proposed as the major active sites in some publications [36–38]. To explore the role of N-doped carbon, we carried out a control experiment which was researched on the pure tri (dipyrido [3,2-a:2′,3′-c] phenazinyl) phenylene without FeSO$_4$. The resulting product was labelled as Ligand-800, which exhibited a worse ORR catalytic performance than that of Fe-N/Fe$_3$C/Fe/C-800, especially in acidic conditions (Figure S2b). The role of S-doping was also studied by the S-doped ligand (S-ligand-800), which was prepared by pyrolyzing the tri (dipyrido [3,2-a:2′,3′-c] phenazinyl) phenylene and ZnSO$_4$. The S-ligand-800 showed a better activity than Ligand-800 in both alkaline and acidic media, indicating S-doping improved the catalytic activity of Ligand-800. It might be because the addition of N into carbon support could increase the electronic density near the Fermi level, facilitate the transfer of electrons between the electronic bands of C and O$_2$ σ* antibonding orbitals, and further improve the electrocatalytic efficiency. In particular, S with the approximate electronegativity to carbon has also been introduced into carbon materials as a dopant [39–41]. The two control experiments indicate that addition of Fe species into the ligand significantly enhances the catalytic activity, and pristine N-doping and S-doping are insignificant for improving ORR activities. Although Fe$_3$C and Fe nanoparticles are unstable in acidic media, carbon embedded Fe$_3$C and Fe nanoparticles for ORR were recently reported to be catalytically active and durable in an acidic electrolyte [42,43]. On a basis of these analyses, we concluded that all of Fe species (Fe$_3$C, Fe nanoparticles and Fe-N$_x$) may be capable of making major contributions to catalytic activities, independently or synergistically. The ORR polarization curves at different pyrolyzing temperatures were shown in Figures S2c,d. The best catalyst was obtained at the optimized temperature (800 °C). The LSV measurements proceeded after 3000 cycles exhibited a negative shift of $E_{1/2}$ of 23.3 and 20.2 mV in alkaline and acidic media (Figure 3e,f), respectively, which indicated an excellent stability. The decreases in $E_{1/2}$ and j_L of Fe-N/Fe$_3$C/Fe/C-800 were caused by the oxidation of carbon support and active sites.

The LSV curves of Fe-N/Fe$_3$C/Fe/C-800 at different rotating rates were recorded in Figure 5a,b. The corresponding Koutecky-Levich (K-L) plots were shown in insets of Figure 5a,b. It was reported that relationship can typically be expressed as a function between the inverse current and the inverse square root of the rotation rate with the change of potentials [44–47]. The average electron-transfer numbers (n) were calculated to be 3.94 and 3.92 for the acidic and alkaline electrolytes, respectively, indicating the ORRs for Fe-N/Fe$_3$C/Fe/C-800 were four-electron process in both electrolytes. The disk and ring current measurements at 1600 rpm in 0.1 M KOH and 0.1 M HClO$_4$ were shown in Figure S2a,b, respectively. Figure S2c shows that the peroxide species yield was less than 12%, and the average electron transfer number was approximately 3.93 in an alkaline solution. For an acidic electrolyte, the peroxide species yield was less than 2%, and the average electron transfer number was

calculated to be 3.92. These results were consistent with the electron-transfer number, according to the Koutecky–Levich plots.
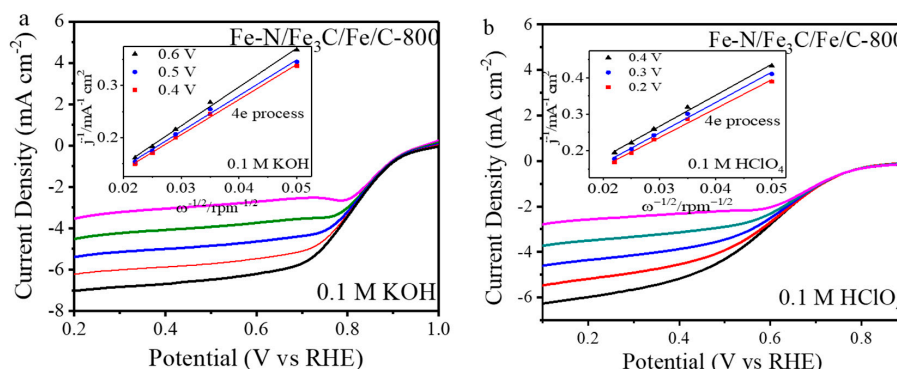

Figure 5. (**a**) ORR polarization curves of Fe-N/Fe₃C/Fe/C-800 at different rotating rates and K–L plots (inset) in 0.1 M KOH; (**b**) ORR polarization curves of Fe-N/Fe₃C/Fe/C-800 at different rotating rates and K–L plots (inset) in 0.1 M HClO₄.

Notably, our catalyst exhibited excellent tolerance toward methanol relative to Pt/C in both alkaline and acidic media. The CV curves for Fe-N/Fe₃C/Fe/C-800 had no insignificant changes taken in methanol and without methanol (Figure 6a,b). In the case of Pt/C, the methanol electro-oxidation hinders the ORR process; the obvious methanol oxidation peaks were observed (Figure 6c,d). These results suggest that our catalyst is a better choice relative to Pt/C for ORR in the application of direct methanol fuel cells.
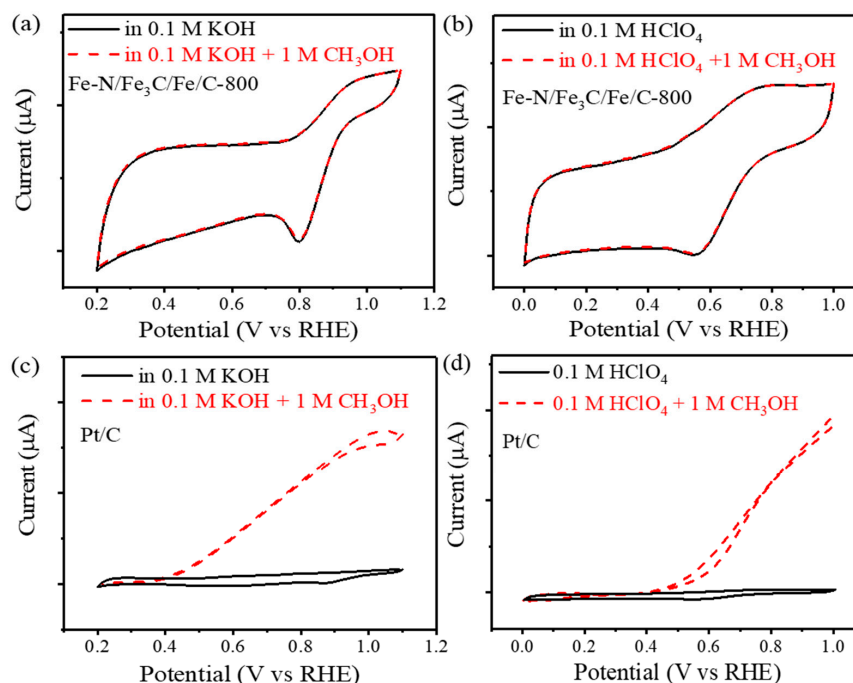

Figure 6. (**a**) Cyclic voltammograms of Fe-N/Fe₃C/Fe/C-800 before and after adding 1 M CH₃OH in O₂-saturated 0.1 M KOH; (**b**) cyclic voltammograms of Fe-N/Fe₃C/Fe/C-800 before and after adding 1 M CH₃OH in O₂-saturated 0.1 M HClO₄; (**c**) cyclic voltammograms of Pt/C before and after adding 1 M CH₃OH in O₂-saturated 0.1 M KOH; (**d**) cyclic voltammograms of Pt/C before and after adding 1 M CH₃OH in O₂-saturated 0.1 M HClO₄.

We also evaluated the performance of zinc-air batteries using Fe-N/Fe$_3$C/Fe/C-800-based air cathodes. The specific capacity of zinc-air batteries was obtained in a 6 M KOH electrolyte under ambient air at a current density of 20 mA·cm^{-2} (Figure 7a). The Fe-N/Fe$_3$C/Fe/C-800 showed a specific capacity of 700 mAh·g^{-1} that is comparable to Pt/C-based battery. Figure 7b shows voltages and power density as a function of current density for Fe-N/Fe$_3$C/Fe/C-800 and Pt/C. The maximum power density was approximately 110 mW cm^{-2}. Both of them exhibited very similar electrochemical performance. The scarcity and high cost of Pt-based materials limited their scale application for zinc batteries, based on this consideration. Fe-N/Fe$_3$C/Fe/C-800 could be regarded as the promising replacement of noble-metal-based catalysts for zinc batteries.
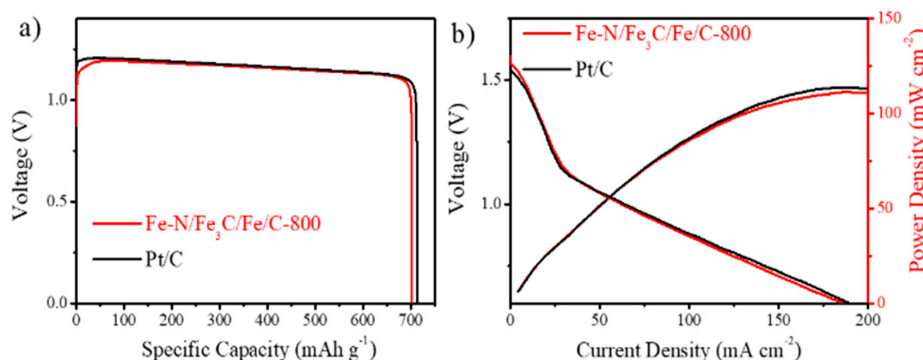

Figure 7. Zinc-air batteries performance. (**a**) Specific capacity under constant discharge current density (20 mA cm^{-2}) using the Fe-N/Fe$_3$C/Fe/C-800 and Pt/C-based air cathodes. (**b**) Voltage-current curves and power density of two-electrode zinc-air batteries of the Fe-N/Fe$_3$C/Fe/C-800 and Pt/C-based air cathodes in 6 M KOH.

3. Materials and Methods

3.1. Chemicals

The 2, 3, 6, 7, 10, 11-hexabromo-triphenylene was purchased from TCI (98%, Japan). Tris (dibenzylideneacetone) dipalladium (0) (97%), rac-BINAP (97%), benzophenone imine (95%) and 1, 10-Phenanthroline-5, 6-dione (97%) were purchased from Aldrich (USA).

3.2. Synthesis of Tri (dipyrido[3,2-a:2′,3′-c] phenazinyl) Phenylene

Triphenylene-cored hexamine was prepared by following a previously reported procedure [48]. In a typical synthesis, a suspension of triphenylene-cored hexamine (0.134 g, 0.24 mmol) in ethanol (6.0 mL) was added into Et3N (0.218 g, 2.16 mmol). The solution was stirred with a magnetic heated stirrer for 10 min. Then, 1, 10-Phenanthroline-5, 6-dione (0.230 g, 1.08 mmol) in ethanol (6.0 mL) was added into the mentioned solution. The mixture was stirred at a reflux temperature for 12 h. The product was sonicated and centrifuged for several times. The resulted precipitate was dried at 80 °C overnight under vacuum to give 0.2 g nitrogen-rich carbon ligand tri (dipyrido[3,2-a:2′,3′-c] phenazinyl) phenylene. The calculated C, H and N elemental analysis showed 77.13% C, 2.88% H and 19.99% N, while the experimental elemental analysis exhibited 75.84% C, 3.12% H and 18.83% N.

3.3. Synthesis of Catalysts

Tri (dipyrido[3,2-a:2′,3′-c] phenazinyl) phenylene (0.2 g) was added into 40 mL DMF, and a homogenous solution was formed after sonication. Then, FeSO$_4$·7H$_2$O (0.38 g, 1.08 mmol) was added into the mentioned solution under vigorous stirring conditions. The resulted solution was heated at 110 °C overnight. Finally, the mixture was transferred to a 50 mL Teflon-lined stainless autoclave and heated at 160 °C for 12 h. The brown solid was collected via centrifugation, washed with DMF and

ethanol more than once and dried overnight under vacuum at 80 °C. Finally, the dried precursor was heated to 700, 750, 800, and 850 °C for 1.5 h at a heating rate of 5 °C/min. The pyrolyzed product was ultrasonically leached in 6 M hydrochloride acid (HCl) for 8 h. The leached sample was washed to be neutralized with deionized water, and dried overnight in a vacuum drying oven at 80 °C.

3.4. Characterization of Catalysts

X-ray diffraction (XRD, D/Max2000, Rigaku, Japan) was tested with Cu-Kα radiation. An Escalab instrument (Escalab 250 xi, Thermo Scientific, Loughborough, UK) was used to measure X-ray photoelectron spectroscopy (XPS), and provided a base pressure of 5×10^{-9} Torr by a monochromatic Al Kα radiation (1486.6 eV). The scanning electron microscope (S-4800, Hitachi, Tokyo, Japan) was used to characterize morphology with an operating voltage of 10 kV, and HRTEM (JEM-2100F, JEOL, Tokyo, Japan) was characterized at a voltage of 200 kV. Co K-edge X-ray absorption spectra, X-ray absorption near edge structure (XANES) spectra and extended X-ray absorption fine structure (EXAFS) spectra were analyzed on the BL10C beam line at the Pohang Light Source (PLS-II) in Korea with a ring current of 200 mA at 3.0 G eV.

3.5. Electrochemical Measurement

CV measurements of the catalysts were determined using a glassy carbon (4 mm in diameter) electrode. The measurements were tested with a standard three-electrode electrochemical system filled with 0.1 M KOH or 0.1 M HClO$_4$ electrolytes. A Pt wire was served as a counter electrode. The Hg/HgO and Ag/AgCl were used as reference electrodes in alkaline and acidic media, respectively. Before the electrochemical measurements, high-purity O$_2$ gas was filled with the solution for approximately 20 min and kept for the whole testing process. Sixty microliter of Nafion solution (5.0 wt %) containing a 3.0 mg catalyst was adequately dispersed into the solution of ethanol (0.35 mL) and deionized water (0.15 mL). Then, the solution was ultrasonicated to form homogeneous ink. Afterwards, 5.0 μL of the obtained catalyst ink (0.21 mg cm^{-2}) was dropped onto the electrode surface for ORR. The loading of Pt/C (20% Pt on Vulcan XC-72, Premetek Co) was 1.5 times the catalysts' loading (0.32 mg cm^{-2}). Measurements were also proceeded in N$_2$ flowing through the electrochemical cell as the control experiments. Linear sweep voltammetry (LSV) measurements of the samples were characterized by using a rotating disk electrode (RDE). The scan rate of the working electrode was 10 mV·s^{-1} and varying rotating speeds from 400 to 2000 rpm after 10 cycles were performed.

Zinc-air batteries: The air cathodes were made by coating a mixture of the activated charcoal and PTFE (the weight ratio = 7:3) on the nickel foam, and each air cathode was fixed to be ~500 μm by an electrode pressing machine. Sixty microliter of Nafion solution (5.0 wt %) containing 3.0 mg catalyst were dispersed in 0.35 mL of ethanol and 0.15 mL of deionized water to form homogeneous ink. The 250 μL ink was carefully dropped onto the above air cathode and kept it in a vacuum container for 30 min, followed by a mildly pressing procedure. The prepared-catalyst–air cathodes were used to assemble primary and rechargeable zinc-air batteries. A zinc plate was used as the anode that was separated by a nylon polymer membrane with the cathode, and 6 M KOH electrolyte was filled between the cathode and anode. The nickel foam was used as a current collector [49].

4. Conclusions

In summary, we synthesized an electrocatalyst composed of Fe-N/Fe$_3$C/Fe/C-800 by template-free pyrolysis of a tri (dipyrido [3,2-a:2′,3′-c] phenazinyl) phenylene-based metal organic framework. The catalyst demonstrated high activity and good durability for ORR in both alkaline and acidic media. The catalyst also exhibited strong methanol tolerance that makes it potential in practical PEMFCs. Notably, Fe-N/Fe$_3$C/Fe/C-800 showed as a potential alternative to Pt/C in zinc-air batteries. Such a template-free approach toward porous carbons-supported nanocomposites of nitrogen-coordinated and carbon-embedded metal opens up a new avenue for preparing non-precious metal catalysts for applications in energy conversion and storage devices.

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