Highly Dispersed Nonprecious Metal Catalyst for Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cells

Yunfeng Zhan, Fangyan Xie, Hao Zhang, Yanshuo Jin, Hui Meng,* Jian Chen,* and Xueliang Sun*



ABSTRACT: This study reports a high-performing nonprecious metal catalyst for the oxygen reduction reaction that is composed of highly dispersed Fe centered active sites on bamboolike carbon nanotubes. NH_2 -MIL-88B is used as the iron source and ZIF-8 as the carbon source. The precursors are uniformly mixed by ball milling, which destroys their crystal structures. A bamboolike carbon nanotube network results from the pyrolysis of the mixed precursors. The morphology is controlled by the proportion of the precursors and the pyrolysis temperature. The catalyst shows excellent oxygen reduction activity in both half-cell and full-cell tests. The onset potential and half-wave potential are 0.96 and 0.78 V vs RHE, respectively. In the fuel cell test, the current density reaches 0.85 A cm⁻² at 0.7 V and 1.24 A cm⁻² at 0.6 V (*iR*-corrected). The novel synthesis approach of the highly dispersed catalyst provides new strategy in the design of high effective nonprecious metal catalysts for fuel cell.

KEYWORDS: fuel cell, highly dispersed catalyst, nonprecious metal catalyst, membrane electrode assembly, carbon nanotubes, oxygen reduction

1. INTRODUCTION

With high energy-conversion efficiency and negligible pollutant emissions, the polymer electrolyte membrane fuel cells (PEMFCs) are seen as one of the most attractive power technologies for the applications of electric vehicles and backup power. As a competitor to lithium-ion battery-powered electric vehicles, the fuel cell electric vehicle (FCVH) has been demonstrated by many traditional vehicle manufacturers and new electric vehicle manufacturers. Among the many problems impeding the large-scale commercial application of PEMFCs, the high cost is an inescapable problem because of the use of Pt-based catalysts. Compared to the hydrogen oxidation reaction (HOR) at the anode, the sluggish oxygen reduction reaction (ORR) at the cathode requires more Pt, which further increases the usage of Pt. To date, extensive research has focused on finding alternatives to Pt-based catalysts, such as transition metal oxides, nonprecious metal alloys, and metalfree heteroatom-doped carbon.¹⁻⁶ Among the potential electrocatalysts, transition metal-nitrogen-carbon catalysts, including metal-nitrogen-doped graphene, carbon nanotubes, and porous carbon are regarded as the most promising

materials.^{7–10} In Dodelet's work, a current density of 99 A cm⁻³ (0.8 V) in the PEMFC test was achieved with Fe/N/C catalyst.¹¹ The Zelenay group prepared M/N/C catalysts from polypyrrole, cyanamide, and polyaniline in the presence of transition metal salts (Fe and Co) with current density of 0.6 A cm⁻² at 0.7 V.^{3,12}

Metal–organic framework (MOF) have found applications in various fields. Recently, MOFs have been identified as a suitable precursor for carbon-based ORR catalysts after hightemperature pyrolysis. The resulting material has a high porosity, large surface area, well-defined microstructures, and uniform heteroatoms decoration.^{13–15} Fe or Co is introduced to work as the active site component in MOF-derived

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Figure 1. Schematic illustration of the preparation of the nonprecious metal catalyst.



Figure 2. SEM images of (a) ZIF-8, (b) NH2-MIL-88B, and (c) BM-Z-M; and (d) XRD patterns of ZIF-8, NH2-MIL-88B and BM-Z-M.

catalysts.^{16,17} For example, Dodelet impregnated ZIF-8 with 1,10-phenanthroline and FeAc, and a current density of 0.8 A cm⁻² at 0.7 V was reached.¹⁸ To improve the electrode structure, Liu et al. prepared a nanofibrous Fe/N/C catalyst with a current density of 0.75 A cm⁻² at 0.7 V.¹⁷

This work reports a controlled synthesis of MOF-based highly dispersed nonprecious metal catalysts for ORR. An Fecontaining MOF (NH₂-MIL-88B) is used to replace the inorganic iron source. ZIF-8 is used to obtain a high-surfacearea carbon. The dual-MOF precursor is mixed by ball milling. The advantage of ball milling was clarified by Dodelet^{18,19} and Mukerjee.^{20,21} The ball-milling process guarantees a homogeneous distribution of Fe in the precursor, leading to the formation of highly dispersed active sites. In the preparation of M/N/C catalysts, the uncontrolled morphology and metal aggregates usually result in a low density of active sites and poor stability.²²⁻²⁴ The as-prepared catalyst shows a structure of bamboolike carbon nanotubes with abundant highly dispersed Fe active sites. The catalytic activity is evaluated in fuel cells instead of only by rotating-disk electrodes, which shows the possible application of the catalyst in fuel cell.^{3,25} The fuel cell test shows a high current density of 0.85 A cm⁻² at 0.7 V (iR-corrected).

2. RESULTS AND DISCUSSION

The key strategy of the material preparation in this work is the introduction of an iron source from an iron-containing MOF instead of an inorganic iron precursor. To realize the uniform mixing of the iron precursor and carbon precursor, we designed a unique process: crystal formation, crystal destruction, and pyrolysis. As illustrated in Figure 1, ZIF-8 and NH₂-MIL-88B are formed first and then mixed by a ball-milling process during which the crystals are smashed into small particles. The MOF fragments of ZIF-8 and NH₂-MIL-88B are mixed uniformly, which is the direct reason for the formation of bamboolike carbon nanotubes and highly dispersed Fe-centered active sites.

As shown in Figure 2, the as-prepared NH₂-MIL-88B and ZIF-8 show the typical morphology of the corresponding group of MOFs. The SEM image of ZIF-8 (Figure 2a) displays a well-shaped rhombic dodecahedral crystal with a uniform size of ~200 nm. In Figure 2b, NH₂-MIL-88 shows a rodlike morphology with a diameter of approximately 500 nm and a length of approximately 1.75 μ m, which is consistent with previous reports.²⁶ The above morphologies are destroyed by the ball-milling process, as shown in Figure 2c, and the agglomerated particles are observed instead of the ordered shapes of these MOF particles. From the XRD patterns in

Figure 2d, both ZIF-8 and NH₂-MIL-88B show typical diffraction peaks of their pure phases. After ball milling, all the diffraction peaks disappear. These XRD results are direct proof of the formation/destruction of MOF crystals. This process is important in the catalyst preparation, which guarantees a uniform mix of ZIF-8 and NH₂-MIL-88B and provides efficient contact between the iron and the carbon source.

Following the ball milling of the MOF mixture that destroyed the MOF crystals and mixed the destructed MOFs uniformly, the mixture was pyrolyzed at 950 °C to obtain the catalyst labeled Fe–N-C-10/1-950. It is interesting to find from the TEM images in Figure 3 that pyrolysis resulted in



Figure 3. (a) TEM images, (b) high-resolution TEM image, (c) EDS mapping images, and (d) HAADF-STEM image of Fe-N-C-10/1-950.

bamboolike carbon nanotubes (BLCNTs). In Figure 3a, b, the BLCNTs are quite long and intertwined, forming a loose 3D network architecture that is favorable for electron transport and mass transfer. The BLCNTs exhibit typical outer diameters ranging from 15 to 20 nm and inner diameters of

~10 nm. The HRTEM image in Figure 3b shows the multiwalled structure of the BLCNTs. The lattice distance between the crystalline plane of the wall is 0.37 nm, corresponding to the (002) basal plane of GC. The elemental composition and dispersion of BLCNTs are recorded by EDX mapping, as shown in Figure 3c. The mapping of carbon replicates the dark-field TEM image of the BLCNTs. In terms of the catalytic activity of the as-prepared catalyst, the amount and dispersion of the iron and nitrogen elements are crucial parameters. It is found from the EDX mapping that both the iron and nitrogen are distributed homogeneously on the whole BLCNTs. There are several dark particles in Figure 3a, corresponding to the bright particles in Figure 3c. These particles should be iron carbide or nitride, which are not active for the ORR.¹ The distribution of iron is observed by HAADF-STEM, because iron is the center of the active sites. As shown in Figure 3d, highly dispersed Fe centered active sites can be found all over the BLCNTs, especially on the walls and intervals, and the active sites disperse uniformly on the walls without aggregation. This finding directly proves the abundance of active sites. And the highly dispersed Fecentered active sites will lead to higher performance because there is no aggregation or coverage of the active sites.

The evolution of the BLCNTs from the destructed MOF mixtures should be clarified. Control experiments are conducted by pyrolyzing the ball-milled NH2-MIL-88B or ZIF-8 alone. Figure S1a, b shows the pyrolysis product of the ball-milled NH2-MIL-88B (denoted as GC). Clear sheet structures with obvious edges are found, on which clear lattice fringes with a lattice distance of 0.35 nm is indexed, suggesting that the GC is well graphitized. This finding is explained by the graphitization of MIL in the presence of iron, which works as a graphitization catalyst.^{27,28} This finding is also proven by the pyrolysis result of ZIF-8, which is amorphous carbon (denoted as NC), as displayed in Figure S1c, d: without the presence of an iron catalyst, ZIF-8 is carbonized instead of graphitized. The BLCNTs can only be formed by the pyrolysis of the ball-milled mixture of NH2-MIL-88B and ZIF-8; otherwise, only carbon sheets (GC) or amorphous carbon (NC) can be formed.

The parameters of the preparation are changed to obtain information about the evolution of the BLCNTs. The ratio of



Figure 4. TEM images of (a) Fe-N-C-20/1-950, (b) Fe-N-C-5/1-950, (c) Fe-N-C-10/1-750, (d) Fe-N-C10/1-850, and (e) Fe-N-C-10/1-1050.



Figure 5. (a) XRD patterns, (b) Raman spectra, (c) N_2 adsorption/desorption isotherms, and (d) pore size distributions of GC, NC, and Fe-N-C-10/1-950.

ZIF-8 to NH₂-MIL-88B and the pyrolysis temperature are changed to determine their influence on the morphology of the resultant catalysts. From the results in Figure 4, it is found that at a fixed temperature of 950 °C, the ratio between ZIF and MIL greatly influences the catalyst morphology. No carbon nanotubes are found at a high ratio of 20/1; instead, carbon rings are formed. The formation of nanotubes can be proposed to be the growth of carbon rings in the normal direction. It is interesting to find the force to trigger such growth. Deceasing the ratio to 10/1, carbon nanotubes are formed, as shown in Figure 3. After the ratio was further decreased to 5/1, carbon nanotubes can still be formed except there is irregularity in the diameters. From the above experiments, it is concluded that the content of MIL is a determining factor in the formation of carbon nanotubes. Returning to Figure S1, without MIL, the product of ZIF is amorphous carbon. At a ratio of 20/1, the product is graphitized, and carbon rings are formed, the graphitization is catalyzed by the iron in the MIL. Further increasing the content of iron leads to the formation of carbon nanotubes, which is well evidenced by Figure 4c, in which a black particle is clearly found at the top of each carbon nanotube. In the TEM images, black particles mean metal particles or the accumulation of small metal particles. In this work, the particles can only be iron-containing particles, which catalyze the formation of carbon nanotubes in the same way as the production of carbon nanotubes in the chemical vapor deposition method. Iron catalyzes the rearrangement of carbon atoms into crystals at high temperature. With the accumulation of carbon atoms, a carbon ring is formed at the bottom of the iron particles. With more and more carbon atoms accumulating, the carbon rings grow into carbon nanotubes.

The ratio of 10/1 is found to be a proper value for the formation of carbon nanotubes. At this ratio, four pyrolysis

temperatures are compared. As shown in Figure 4c, d, carbon nanotubes are formed at all four temperatures. The difference is that at lower temperatures, such as 750 and 850 $^{\circ}\text{C},$ the walls of the carbon nanotubes are much thicker, and little bamboo structure is formed. At higher temperatures of 950 and 1050 °C, bamboolike structures with very thin walls are formed. The thicker walls can be explained by the growth speed of the carbon nanotubes: at low temperatures, the growth speed is low, leading to much accumulation of carbon at the growth step, resulting in thick walls. At higher temperatures, fast growth leads to thinner walls. The bamboo joint is formed because of the relaxation effect of fast growth. In the growth of carbon nanotube, a fast growth is followed by a relaxation, then begins another fast growth. During the fast growth process, the carbon nanotube grows along the axial direction. This growth is slowed during the relaxation, leading to growth in the vertical direction, forming a bamboo joint.

The uniform distribution of the iron-containing species by the ball milling of the precursor determines the formation of bamboolike carbon nanotubes. Graphitic carbon nanotubes are formed at high temperature with iron species as catalyst.^{27,28} The direct pyrolysis of the mixture of Zn-ZIF and iron salts such as $FeSO_4^{28}$ and ferrous acetate/1,10-phenanthroline¹¹ did not result in carbon nanotubes. However, carbon nanotubes are found in the heat treatment of the product of Fe-doped ZIF-8 by Su's²⁸ and Wu's groups,²⁹ who concluded that the homogeneous distribution of Fe is the key factor for the formation of carbon nanotubes. In this work, NH₂-MIL-88B serves as an Fe source that is uniformly mixed with ZIF-8 by a ball-milling process. This process guarantees the homogeneous distribution of Fe in the precursor.

Figure 5a shows the XRD patterns of the catalysts. GC and NC are the products of the direct pyrolysis of ball-milled NH₂-

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Figure 6. (a) XPS survey spectra and high-resolution XPS spectra of (b) C 1s, (c) N 1s, and (d) Fe 2p for GC, NC, and Fe-N-C-10/1-950. (e) X-ray absorption near edge structure (XANES) spectra of Fe-N-C-10/1-950 and Fe foil. (f) Fourier-transformed module of EXAFS signals for Fe-N-C-10/1-950 and Fe foil.

MIL-88B or ZIF-8 alone, respectively. In agreement with the TEM results (Figure S1), GC is graphitized carbon, as proven by a strong peak at approximately 26.8°, which is assigned to the (002) plane of graphitic carbon. The amorphous nature of the NC is also proven by the broad peak at $\sim 25^{\circ}$. In the case of Fe-N-C-10/1-950, a much lower graphitization degree is proven by the broadening of the diffraction peaks at 26.5 and 43.0°. Raman spectra are acquired to obtain information about the degree of structural defects of the as-prepared carbon materials. In Figure 5b, two distinct peaks of the D band $(\sim 1330 \text{ cm}^{-1})$ and G band $(\sim 1590 \text{ cm}^{-1})$ are detected in all three samples. The D and G band are attributed to the defects and the sp²-hybridized graphitic structure of carbon, respectively. The intensity ratio of the D and G bands reflects the degree of structure disorder in the carbon lattice. The I_D/I_G ratio of the GC (0.71) is significantly small, proving small structural defects. The higher I_D/I_G ratio of the NC (1.05) is in consistent with the results of TEM (Figure S1) and XRD, and the defect degree is high for the amorphous NC. It is interesting to find an even higher I_D/I_G ratio for Fe-N-C-10/1-950 (1.14) than that of NC (1.05). This finding conflicts with

the XRD result, which proves the presence of graphitic carbon in Fe-N-C-10/1-950. This result can be explained by the structure and doping species in Fe-N-C-10/1-950 compared to those of NC. The TEM results (Figure 3) show that Fe-N-C-10/1-950 is composed of a bamboo structure with thin walls, which are graphitized as proven by the clear lattice fringe of carbon in the HRTEM image. However, the thin walls have a low graphitic degree, which can be proven by the much wider (002) peak in the XRD pattern than that of the GC. The HRTEM image also shows that the thin walls of the carbon nanotubes are composed of less than six layers of carbon atoms, the lattice fringe is not well established, and many structural defects exist.

In Figure 5c, d, the BET surface area of Fe-N-C-10/1-950 is 1556 m² g⁻¹, which is larger than that of GC (53 m² g⁻¹) and NC (1136 m² g⁻¹). The Horvath–Kawazoe (HK) method and Barrett–Joyner–Halenda (BJH) method are employed to analyze the pore size distributions of micropores and mesopores, respectively. In Figure 5d, the pores are generally dominated by micropores (pore width <2.0 nm) in Fe-N-C-10/1-950. It is proposed that the micropores host the most



Figure 7. (a) CVs of NC, Fe-N-C-10/1-950, Fe-N-C-5/1-950 and Fe-N-C-20/1-950 in O₂-saturated (solid line) and Ar-saturated (dashed line) 0.1 M HClO₄. (b) LSV curves of GC, NC, Fe-N-C-10/1-950, Fe-N-C-5/1-950, Fe-N-C-20/1-950, and Pt/C with a rotation speed of 1600 rpm in O₂-saturated 0.1 M HClO₄. (c)Tafel plots. (d) Electron-transfer number and H₂O₂ yield of NC, Fe-N-C-10/1-950, Fe-N-C-20/1-950 and Pt/C. (e) LSV curves of Fe-N-C@BLCNT at different rotating speeds (400–2500 rpm) in O₂-saturated 0.1 M HClO₄, the insets are the corresponding K-L plots. (f) LSV curves of Fe-N-C-10/1-750, Fe-N-C-10/1-850, Fe-N-C@BLCNT, and Fe-N-C-10/1-1050 at a rotation speed of 1600 rpm in O2-saturated 0.1 M HClO₄.

active sites.³² The abundance of micropores is beneficial for a high activity. In addition, the abundance of mesopores in Fe-N-C-10/1-950 facilitates mass transfer, especially in real fuel cell conditions.³

The elemental compositions of the catalysts are investigated by XPS. In Figure 6a, the XPS survey spectra show the presence of C 1s (~284.8 eV), N 1s (~400.0 eV), O 1s (~531.0 eV), and Fe 2p (~710.0 eV) peaks, among which Fe, N, and C form the active sites of the catalyst. It is noted that Fe-N-C-10/1-950 shows a high nitrogen content of 4.08 at. %, and Fe 2p is detected in Fe-N-C-10/1-950. The highresolution C 1s spectra are shown Figure 6b. The strong peak at 284.8 eV and three weak peaks at ~286.0, ~289.5, and ~291.3 eV are ascribed to C–C/C=C species, the C–N/C–O bond, O–C=O groups, and the C 1s plasmon, respectively. Nitrogen is the key element for the active sites of the ORR. As shown in Figure 6c, the N 1s high-resolution peaks of Fe-N-C-10/1-950 are deconvoluted into five split peaks. The ORR active sites of Fe/N/C catalyst are proven to be FeN₄ or FeN₂₊₂ by XAFS and HRTEM.^{14,30} According to the works of Artyushkova, the XPS peak at ~399.8 eV is ascribed to the nitrogen in Fe-Nx, where x = 4 or 2.³⁰ This explanation

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Figure 8. a) LSV curves of Fe-N-C-10/1-950 before and after multiple cycling (0.6-1.0 V vs RHE) in O₂-saturated 0.1 M HClO₄. (b) Current-time chronoamperometric response of Fe-N-C-10/1-850, Fe-N-C-10/1-950, and Pt/C at 0.7 V vs RHE with a rotating speed of 900 rpm in O₂-saturated 0.1 M HClO₄.

connects the results of XAFS and XPS in the explanation of the active sites of the ORR. Accordingly, the Fe in Fe-Nx can also be indexed in XPS. The Fe 2p high-resolution peaks in Figure6d show a Fe 2p3/2 peak at 708.3 eV and a Fe 2p1/2 peak at 721.0 eV. The positions of these double peaks are different from those of the typical peaks of Fe, for example, 707.2 eV/720.0 eV for Fe⁰ or Fe carbide, 709.6 eV/722.5 eV for Fe²⁺, 714.2 eV for the Fe²⁺ shakeup satellite peak, 711.5 eV/724.6 eV for Fe³⁺, and 717.4 eV for the Fe³⁺ shakeup satellite peak. The evolution of the peak at 708.3 eV is direct proof of the formation of Fe-Nx in Fe-N-C-10/1-950.

The XANES curves of Fe-N-C-10/1-950 in Figure 6e shows near-edge absorption energy above that of Fe foil, suggesting a higher oxidation state of iron ion in Fe-N-C-10/1-950. This is accordant with the XPS results. In Figure 6f, FT-EXAFS curve for Fe-N-C-10/1-950 showed a main peak at about 2 A which was very close to that of Fe–Fe peak of Fe foil at about 2.2 A. This is direct proof that Fe in Fe-N-C-10/1-950 is not single atomic dispersed, because the signal of Fe–N of single atomic Fe scattering paths should appear at about 1.5 A.³¹ For Fe-N-C-10/1–950 there is a small peak at 1.5 A, which proves the coordination of Fe with N in the active site.

The XPS results confirm the formation of Fe-Nx in Fe-N-C-10/1-950. Parallel experiments are performed to study the variations in the precursor ratio and annealing temperatures and their influence on the content and species of Fe and N in the resultant Fe-N-C catalysts. The results in Figure S2a prove the formation of Fe-Nx in the three precursor ratios for pyrolysis at 950 °C. For these three ratios at 950 °C, the total nitrogen content and relative contents of pyridinic-N and Fe-Nx are listed in Tables S1 and S2, which are related to the catalytic performance and are discussed later. Among all three ratios, the 10/1 ratio exhibits the highest atomic content of Fe-Nx and pyridinic-N. Then, at a fixed ratio of 10/1, the pyrolysis temperature is varied to study its influence. Figure S2a compares the XPS results of the four temperatures. Together with the data in Tables S1 and S2, the total nitrogen content decreases with increasing temperature. At 1050 °C, almost no Fe-Nx can be indexed. Therefore, 950 °C is the optimized temperature. The parallel experiments fix the optimized precursor ratio and pyrolysis temperatures.

The evolution of the cathodic reduction peak in the oxygen saturated solution compared with that of the argon saturated

solution proves the ORR activity, as shown in Figure 7a. Among all catalysts, Fe-N-C-10/1-950 shows the most positive onset potential. From the polarization curves in Figure 7b, a large difference between GC and NC are observed. GC is the product of pyrolysis of MIL, while NC is the product of ZIF-8. GC shows no ORR activity, whereas NC shows much improved activity with E_{onset} of 0.88 V and $E_{1/2}$ of 0.7 V vs RHE. Returning to the XPS results in Figure 6, there is no detectable Fe in both the GC and NC, the difference is pyridinic-N. Because graphitic-N and $N-O_2$ have no contribution to the ORR activity in acidic media,³² the ORR activity can only come from pyridinic-N. Tables S1 and S2 show a much higher atomic concentration of pyridinic-N in NC than GC. This finding is direct proof of the activity of pyridinic-N in the ORR in acidic media. Compared to the ZIF-8-derived NC, Figure 7b shows the much-enhanced ORR activity of the dual-MOF-derived catalysts. With an E_{onset} of 0.96 V and an $E_{1/2}$ of 0.78 V, Fe-N-C-10/1-950 shows the best ORR activity, which is better than most of the reported results (Table S3).

The Tafel plots are employed to compare the ORR kinetics of the catalysts. In Figure 7c, two slopes are found for Pt/C, which are 57 mV/dec at low overpotential and 140 mV/dec at high overpotential, which is affected by the intermediates during ORR.⁹ Fe-N-C-10/1–950 shows a Tafel slope of 77 mV/dec which means slower kinetics of the first electron transfer compared with that of Pt/C, whereas no deviation in the Tafel slope proves faster kinetics in the following electron transfer process.

The RRDE results show the H_2O_2 yield of all catalysts, which are less than 1% in 0–0.8 V (Figure 7d). NC shows more H_2O_2 than the other catalysts, but the maximum content is less than 2%. The XPS results show almost no Fe-Nx detected in NC because it is the product of ZIF-8 pyrolysis without any Fe added. The origin of the ORR activity of the NC can only be explained by two factors: the first is pyridinic-N, which is abundant in NC, and the second is the undetectable trace Fe introduced by the chemical reagents according to Dodelet's explanations.³³ The number of electrons transferred in the ORR process is calculated to be nearly 4 for the Fe/N/C catalysts, showing good kinetics. This result is confirmed by the Kouteckye-Levich (K-L) equation. In Figure 7e and Figure S4, the results of K-L plots validate the

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Figure 9. (a, b) Polarization power density plots of a H_2-O_2 PEMFC with NC, Fe-N-C-10/1-950, Fe-N-C-5/1-950, Fe-N-C-20/1-950, Fe-N-C-10/1-850, Fe-N-C-10/1-950, and Fe-N-C-10/1-1050 as cathode catalysts. Back pressure, 1 bar; flow rate, 0.25 L min⁻¹ for H_2 and 0.3 L min⁻¹ for O_2 ; cathode catalyst loading, 4.0 mg cm⁻²; cell temperature, 70 °C.



Figure 10. Relation of the atomic concentrations of Fe-Nx and pyridinic-N with the activities (a) in half-cell and (b) in full-cell.

four-electron-dominated ORR pathway of the Fe/N/C catalysts. The influence of the heating temperatures on the ORR activity is investigated (Figure 7f). The E_{onset} increases from 750 to 950 °C and then decreases at 1050 °C, showing a maximum value at 950 °C. Therefore, 950 °C is chosen as the optimized pyrolysis temperature.

The durability of Fe-N-C-10/1-950 is studied by two strategies with a half-cell method. The first is the accelerating experiment, which cycles the electrode potential between 0.6 and 1.0 V for 4000 cycles, and the second is the chronoamperometric experiment, which holds the electrode potential at 0.7 V to detect the change in current. In Figure 8, after 1000 potential cycles, nearly no decrease in $E_{1/2}$ is observed, and a decrease of 26 and 32 mV in $E_{1/2}$ is found after 3000 and 4000 cycles, respectively. The chronoamperometric experiment shows a 30% loss in the current density for Fe-N-C-10/1-950 after a 24 h aging test. As a comparison, the chronoamperometric result for Fe-N-C-10/1-850 is also plotted in Figure 8b. Fe-N-C-10/1-850 is chosen for comparison because it shows the same E_0 and an even higher diffusion-limited current density than Fe-N-C-10/1-950, as shown in Figure 6f. Fe-N-C-10/1-850 shows a 41% decrease in current density, proving the high stability of Fe-N-C-10/1-950.

The catalysts are prepared into MEA and tested in a fuel cell. Fe-N-C-10/1-950 shows a striking open circuit voltage (OCV) of 1.07 V, but discharging starts at 0.9 V. As a criterion of the activity of a catalyst in fuel cell, the current density at 0.7 V is

compared. In Figure 9a, b, a high value of 0.85 A cm⁻² at 0.7 V (*iR*-corrected) is found for Fe-N-C-10/1-950, which is much higher than other catalysts. The current density at 0.6 V (*iR*-corrected) is as high as 1.24 A cm⁻². The peak power density of Fe-N-C-10/1-950 reaches 0.77 W cm⁻², which is also the highest among all the catalysts. The Fe-N-C-10/1-950 catalyst obtained in this work is one of the most active nonprecious metal catalysts for a PEMFC reported to date (Table S4). Notably, this activity exceeds those values of the latest reported single-atom catalysts (Table S4).

The fuel-cell performance increases in the order NC, Fe-N-C-5/1-950, Fe-N-C-20/1-950, and Fe-N-C-10/1-950, which is agreement with the results of half-cell RDE test shown in Figure 7b. Figure 10 clearly shows that the half-cell (Figure 10a) and full-cell (Figure 10b) activities are related to the atomic concentrations of Fe-Nx and pyridinic-N. The value of $J_{\rm k}$ (kinetic current density) at 0.8 V shows a vertex, following the same trend as pyridinic-N. As discussed above, pyridinic-N contributes to the ORR activity, but the activity is greatly improved by introducing Fe. This result proves that Fe-Nx contributes more to the activity. However, the activity does not exactly follow the trend of Fe-Nx. Fe-N-C-10/1-750 has higher Fe-Nx proportion than the best catalyst (Fe-N-C-10/1-950), but shows inferior ORR activity. The same is with Fe-N-C-20/ 1-950. This proves the Fe-Nx content is not the only factor to determine the ORR activity. The performance increases with metal content, reaching a vertex, then begins to decrease.

Among all the catalysts studied, one group follows this trend: Fe-N-C-5/1-950, Fe-N-C-10/1-950 and Fe-N-C-20/1-950. The metal content increases but the activity vertex appears in the middle one. But another group Fe-N-C-10/1-750, Fe-N-C-10/1-850, Fe-N-C-10/1-950, and Fe-N-C-10/1-1050 does not follow the trend. This result means that both pyridinic-N and Fe-Nx contribute to the ORR activity.

3. CONCLUSIONS

In summary, we report highly dispersed Fe-centered active sites on bamboolike carbon nanotubes as Fe/N/C catalyst via pyrolysis of ball-milled binary MOFs. The key strategy of the material preparation in this work is the novel introduction of an iron source, which is MIL instead of an inorganic iron precursor. Ball milling is used to realize the uniform mixing of the iron precursor and carbon precursor. The preparation process includes crystal formation, crystal destruction and mixing by ball milling, and pyrolysis, which results in bamboolike carbon nanotubes. Both the precursor ratio and the temperature of the heat treatment play a crucial role in the morphology and surface properties of the resultant catalysts, which in turn influence the ORR activities. The optimized catalyst exhibits high ORR activity both in the RDE and PEMFC tests. The high performance is explained by the uniform dispersion of the Fe-centered active sites on the bamboolike carbon nanotube networks with enhanced electron conductivity and mass/charge transfer properties as well as high surface areas.

4. EXPERIMENTAL SECTION

4.1. Synthesis. 4.1.1. Synthesis of ZIF-8 and NH₂-MIL-88B. ZIF-8 and NH₂-MIL-88B were prepared by a similar method with reported work.³⁴ To prepare ZIF-8, we dissolved 2-methylimidazole (4 g) in methanol (MeOH, 60 mL) to form solution A. Zn(NO₃)₂·6H₂O (1.68g) was dissolved in MeOH(20 mL) to form solution B. Solution B was quickly added into solution A with continuous stirring for 1 h. The mixture was kept under thermo neutral condition for 24 h without stirring. After collecting by centrifugation and washing with pure water and MeOH, the precipitate was dried overnight (T = 70°C). For preparing NH₂-MIL-88B, 160 g of F127 surfactant and 179 mg of FeCl₃·6H₂O was added into deionized water (14 mL). After stirring for 1 h, 0.3 mL of acetic acid was added to the above solution. After string for another 1 h, 60 mg of 2-aminoterephthalic acid (NH₂-BDC) was added and kept stirring for 2 h. The resulting product was transferred to autoclave and kept at 110 °C for 24 h. The collected precipitates were washed and dried (T = 70 °C).

4.1.2. Synthesis of Fe–N–C Catalyst. The ball-milled powder (denoted as BM-Z-M) was pyrolyzed for 2 h at 950 °C under a N₂ atmosphere. The powder was then leached with 0.5 M H₂SO₄ for 10 h. Finally, the product was washed to pH 7 with pure water and dried overnight (T = 70 °C). The pyrolysis was repeated at 950 °C in NH₃ for 0.5 h.

The catalysts named Fe-N-C-20/1-950 and Fe-N-C-5/1-950 are prepared under similar conditions with Fe-N-C-10/1-950 except for changing the mass ratio of ZIF-8 and NH₂-MIL-88B to 20:1 and 5:1, respectively. The catalysts named as Fe-N-C-10/1-750, Fe-N-C-10/1-850 and Fe-N-C-10/1-1050 are synthesized under the same conditions except for changing the pyrolysis temperatures to 750, 850, and 1050 °C, respectively.

4.1.3. Synthesis of \overline{NC} and \overline{GC} . NC and GC were synthesized in a similar manner as Fe-N-C-10/1-950 but without NH₂-MIL-88B (NC) and ZIF-8 (GC) during the ball-milling process, respectively.

4.2. Material Characterizations. XRD patterns were recorded on a Rigaku-D/Max-IIIA ($2\theta = 5-70^\circ$, 5° /min). TEM images were obtained using a JEM-2100HR microscope. Aberration-corrected scanning transmission electron microscopy (STEM) was conducted

on a Titan Cubed Themis G2 300 (FEI) at 200 kV with the mode of STEM. SEM images were measured by a Gemini FE-SEM. The Raman spectra were obtained by a Renishaw-laser micro-Raman spectrometer (laser wavelength = 633 nm). The BET surface area was conducted with a Kubo-X1000. XPS was recorded on a Thermo-ESCA-Lab 250 instrument. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were performed in the soft X-ray microcharacteriztion beamline (SXRMB) at the Canadian Light Source.

4.3. Electrochemical Characterizations. The ORR performance was studied with PINE bipotentiostat. A glassy carbon electrode, Ag/AgCl (saturated KCl) and platinum foil $(1.0 \times 1.0 \text{ cm}^2)$ were used as the working electrode, reference electrode and counter electrode, respectively. The catalyst ink was prepared by mixing catalyst (10 mg) in a 510 μ L solution mixture of 5 wt % Nafion solution (10 μ L, DuPont Co. Ltd.) and ethanol (500 μ L). Then, the catalyst ink was ultrasonic dispersaled for 0.5 h and dropped onto the electrode and dried naturally. For comparison a Johnson Matthey Pt/C catalyst (46.6 wt %, JM) was tested. The electrolyte was 0.1 M HClO₄. The stability was studied by potential cycling (0.6–1.0 V, 50 mV s⁻¹) and by holding at a constant potential (0.7 V).

The electron-transfer number (n) was obtained from Koutecky–Levich (K-L) equation:

$$\frac{1}{J} = \frac{1}{JL} + \frac{1}{JK} = \frac{1}{B\omega^{1/2}} + \frac{1}{JK}$$
(1)

$$B = 0.2nC_0 F(D_0)^{2/3} \nu^{-1/6}$$
(2)

J, measured current density, $J_{\rm L}$, diffusion-limited current density; $J_{\rm K}$, kinetic current density; ω , rotation speed; *n*, number of electron transfer; *F*, Faraday constant (96485 C mol⁻¹), D_0 , oxygen diffusion coefficient, C_0 , oxygen concentration; ν , kinetic viscosity.

The percentage of H_2O_2 released during the ORR ($H_2O_2\%$) and *n* were calculated from following equations:

$$H_2 O_2 \% = 200 \frac{I_R / N}{I_D + (I_R / N)}$$
(3)

$$n = \frac{4I_{\rm D}}{I_{\rm D} + (I_{\rm R}/N)} \tag{4}$$

 $I_{\rm RP}$ ring current; $I_{\rm D}$, disk current; N (0.37), current collection efficiency. The ring potential was hold at 1.2 V vs RHE.

4.4. Fuel Cell Measurements. The catalyst ink was ultrasonically mixied catalyst (10 mg), 5 wt % Nafion solution (217 μ L), and ethanol (283 μ L) for 0.5 h. The Nafion-to-catalyst ratio (NCR) was 1:1. The catalyst ink was coated on a gas diffusion electrode with a loading of 4 mg cm⁻². A commercially available Pt anode (0.5 mgPt cm⁻², NCR = 1:2) was purchased from Shanghai HESEN. The cathode, anode and DuPont Nafion 211 membrane were sandwiched by hot pressing at 135 °C for 240 s at 10 psi. Fuel cell was tested on a KIKUSUI PLZ164WA electronic. The flow rates of O₂ and H₂ were 0.25 and 0.30 L min⁻¹ with 1 bar back pressure. The cell temperature was 70 °C, humidification temperatures of O₂ and H₂ were 85 and 80 °C, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c00126.

TEM images of GC and NC; high-resolution XPS spectra of N 1s for catalysts derived from different precursor ratio and carbonization temperatures; LSVs and the corresponding K-L plots of NC, Fe-N-C-5/1-950, Fe-N-C-20/1-950, and Pt/C; summary of element content and fitting results for N 1s XPS spectra of various catalysts; performance comparison of ORR activities for nonprecious catalysts in acidic medium;

performance comparison of H_2/O_2 fuel cell for non precious catalysts as the cathode (PDF)

AUTHOR INFORMATION

Corresponding Authors

Hui Meng – Siyuan Laboratory, Guangzhou Key Laboratory of Vacuum Coating Technologies and New Energy Materials, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Guangdong Provincial Key Laboratory of Optical Fiber Sensing and Communications, Department of Physics, Jinan University, Guangzhou, Guangdong 510632, China; ☉ orcid.org/0000-0003-0400-5485; Email: tmh@jnu.edu.cn

Jian Chen – Instrumental Analysis & Research Center, Sun Yatsen University, Guangzhou, Guangdong 510275, China; orcid.org/0000-0001-5725-4368; Email: puscj@ mail.sysu.edu.cn

Xueliang Sun – Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada; ⊚ orcid.org/0000-0003-0374-1245; Email: xsun9@uwo.ca

Authors

Yunfeng Zhan – Siyuan Laboratory, Guangzhou Key Laboratory of Vacuum Coating Technologies and New Energy Materials, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Guangdong Provincial Key Laboratory of Optical Fiber Sensing and Communications, Department of Physics, Jinan University, Guangzhou, Guangdong 510632, China

Fangyan Xie – Instrumental Analysis & Research Center, Sun Yat-sen University, Guangzhou, Guangdong 510275, China

Hao Zhang – Instrumental Analysis & Research Center, Sun Yat-sen University, Guangzhou, Guangdong 510275, China

Yanshuo Jin – Siyuan Laboratory, Guangzhou Key Laboratory of Vacuum Coating Technologies and New Energy Materials, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Guangdong Provincial Key Laboratory of Optical Fiber Sensing and Communications, Department of Physics, Jinan University, Guangzhou, Guangdong 510632, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c00126

Notes

The authors declare no competing financial interest.

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